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STABILITÉ ET CINÉTIQUE DES DÉFAUTS PONCTUELS DANS SiO2 ET SiC

par

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Service de Recherches de Métallurgie Physique

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Guido ROMA

- Novembre 2012 -

RAPPORT CEA-R-6307 – Guido ROMA

«Stabilité et cinétique des défauts ponctuels dans SiO_2 et SiC»

Résumé -Ce document est conçu comme une vue d'ensemble des travaux de recherche de Guido Roma sur la stabilité et la cinétique des défauts ponctuels dans le dioxyde de silicium et le carbure de silicium, deux matériaux d'intérêt pour le nucléaire ainsi que dans de nombreux autres domaines. Un résumé étendu en français est suivi par le document principal, en anglais. Le premier chapitre décrit le contexte, introduit l'approche utilisée et explique le choix des matériaux. Le chapitre suivant discute les approximations et les aspects spécifiques de l'application de la Théorie de la Fonctionnelle de la Densité (DFT) aux défauts ponctuels dans les matériaux non-métalliques, en particulier en ce qui concerne l'étude de leur stabilité et cinétique. Le chapitre 3 est dédié aux défauts intrinsèques dans le dioxyde de silicium et la compréhension de l'auto-diffusion dans le quartz et la silice. Le chapitre 4 résume et discute les travaux sur les défauts intrinsèques et les impuretés de palladium dans le carbure de silicium. Un chapitre de conclusions résume les résultats principaux et suggère des développements et nouveaux sujets à aborder.

2012– Commissariat à l'Énergie Atomique – France

RAPPORT CEA-R-6307 – Guido ROMA

«Stability and kinetics of point defects in SiO_2 and in SiC »

Abstract -This document is conceived as an overview of Guido Roma's research achievements on defects stability and kinetics in two materials of interest in nuclear science and for many other application domains : silicon dioxide and silicon carbide. An extended summary in french is followed by the main document, in english. Chapter 1 describes the context, introduces the approach and explains the choice of silicon dioxide and silicon carbide. Chapter 2 discusses several approximations and specific issues of the application of Density Functional Theory to point defects in non-metallic materials for the study of defects energetics and diffusion. Chapter3 is devoted to native defects in silicon dioxide and the understanding of self-diffusion in crystalline and amorphous SiO_2. Chapter 4 summarises the results on native defects and palladium impurities in silicon carbide. A conclusion, including suggestions for future developments, closes the main part of the document.

2012– Commissariat à l'Énergie Atomique – France

Commissariat à l'Énergie Atomique et aux Énergies Alternatives
Service de Recherches de Métallurgie Physique

Mémoire

présenté pour obtenir le diplôme de

HABILITATION À DIRIGER DES RECHERCHES

Spécialité « Physique — Science des Matèriaux »

par

Guido Roma

Stabilité et cinétique des défauts ponctuels dans SiO_2 et SiC

Présenté le 29 mai 2012 devant le jury composé de :

Mme	Marie-France Barthe	CNRS Orléans	(Examinatrice)
M.	Hartmut Bracht	Université de Münster	(Rapporteur)
M.	Thierry Deutsch	CEA Grenoble	(Examinateur)
M.	Paolo Giannozzi	Université de Udine	(Rapporteur)
M.	Francesco Mauri	Université Paris VI	(Président du Jury)
M.	Laurent Pizzagalli	CNRS Poitiers	(Rapporteur)

Avant-propos

Ce document est écrit en franglais. Mais ne vous inquiétez pas ! Je ne dis pas cela au sens d'Étiemble [1], je partage sa critique du mélange de langues à l'échelle du mot. J'entends ici sur une échelle plus grande, celle des chapitres ; un peu comme pour l'alternance entre *solo* et *tutti* dans un concerto baroque, où il y a toujours une cadence pour marquer le passage entre l'un et l'autre.

La raison est éminemment pratique et il n'est pas nécessaire d'en donner ici plus de détails. J'espère que le lecteur, plus à l'aise dans l'une ou l'autre langue, ou dans une autre encore, ne m'en voudra pas, ni pour l'hétérogénéité qui en découle, ni pour mon incompétence dans l'une et l'autre langue.

Dieses Schriftstück ist auf Frenglisch geschrieben. Aber keine Angst, was ich meine, ist keine Mischung von Französisch und Englisch auf der Skala der Wörter, die Étiemble zu Recht kritisierte [1], sondern eine Zusammenstellung von französischen und englischen Kapiteln, ein bisschen wie *solo* und *tutti* in einem Concerto Grosso.

Die Ursache dessen im Detail zu erklären ist nicht notwendig, es hat praktische Gründe. Ich hoffe, dass der geneigte Leser mir meine Schwächen in beiden Sprachen nicht übel nehmen wird.

This document is written in Frenglish. But please don't worry ! I do not intend a mix of French and English on the scale of words, the one that Étiemble has thoughtfully criticised [1]. I mean on the scale of chapters ; a bit like *solo* and *tutti* follow each other in a Concerto Grosso.

The reason is a practical one and I don't need to go into details. I hope that the reader will excuse this heterogeneity, as well as my weaknesses in both English and French, whatever is the language he is most acquainted with.

1. Étiemble, *Parlez-vous Franglais ?*, Gallimard, 1964.

Résumé Ce document est conçu comme une vue d'ensemble de mes travaux de recherche sur la stabilité et la cinétique des défauts ponctuels dans le dioxyde de silicium et le carbure de silicium, deux matériaux d'intérêt pour le nucléaire ainsi que dans de nombreux autres domaines. Le chapitre préliminaire (page ix) est essentiellement un résumé détaillé, en français, des chapitres 1,2,3,4, suivi d'un projet à quatre ans qui fait office de conclusions. La partie centrale du document, en anglais, est constituée de quatre chapitres, dont le premier (1) décrit le contexte, introduit l'approche utilisée et explique le choix des matériaux. Le chapitre suivant (2) discute les approximation et les aspects spécifiques de l'application de la Théorie de la Fonctionnelle de la Densité (DFT) aux défauts ponctuels dans les matériaux non-métalliques, en particulier en ce qui concerne l'étude de leur stabilité et cinétique. Le chapitre 3 est dédié aux défauts intrinsèques dans le dioxyde de silicium et la compréhension de l'autodiffusion dans le quartz et la silice. Les succès et les échecs de la DFT dans ses approximations semi-locales y sont discutés en liaison avec l'interprétation de quelques résultats expérimentaux importants. Le chapitre 4 résume et discute les travaux sur les défauts intrinsèques et les impuretés de palladium dans le carbure de silicium. L'accent est mis sur la cinétique de ces défauts, ce qui permet de discuter le recuit de certains défauts de stœchiométrie, des paires de Frenkel, des lacunes de silicium, ainsi que la diffusion du palladium. Un chapitre de conclusion résume les résultats pricipaux et suggère des développements et nouveaux sujets à aborder. Les appendices contiennent une compilation de données pour les défauts dans le carbure de silicium (A.1), un curriculum vitæ (B, en français) et un choix d'articles (C).

Abstract This document is conceived as an overview of my research work on defects stability and kinetics in two materials of interest in nuclear science and for many other application domains : silicon dioxide and silicon carbide. The preliminary chapter (page ix) is an extended summary in french of chapters 1,2,3,4, followed by a four years project playing the role of a conclusion. Chapter 1 describes the context, introduces the approach and explains the choice of silicon dioxide and silicon carbide. Chapter 2 discusses several approximations and specific issues of the application of Density Functional Theory to point defects in non-metallic materials for the study of defects energetics and diffusion. Chapter 3 is devoted to native defects in silicon dioxide and the understanding of self-diffusion in crystalline and amorphous SiO_2. It discusses achievements and failures of DFT in semilocal approximations in connection with the interpretation of some notable experimental results. Chapter 4 summarises the work that I have done on native defects and palladium impurities in silicon carbide, with a focus on kinetic properties controlling the annealing of stoichiometric defects, Frenkel pairs, and silicon vacancies, as well as the diffusion of Pd impurities. A conclusion 5 closes the main part of the document, written in english. Appendixes include a compilation of defect data for silicon carbide (A.1), a Curriculum Vitæ (B, in french) and a selection of articles (C).

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Introduction, quasi un résumé

0

0.1 Vers une métallurgie des isolants

La recherche sur les matériaux à la Direction de l'Énergie Nucléaire du CEA a comme but principal celui de contrôler les performances des matériaux utilisés dans tout le cycle du nucléaire industriel ; ces matériaux travaillent en conditions extrèmes, en particulier du fait de l'irradiation, mais souvent, aussi, des températures d'exercice. Ces matériaux sont hors équilibre thermodynamique, contenant des concentrations élevées de défauts ponctuels et étendus, des impuretés, et sont souvent soumis à des formes de corrosion d'origines variées. Leurs propriétés sont le résultat d'un compromis entre structure électronique, structure crystalline et microstructure, qui est déterminé largement par les cinétiques à l'état solide, en particulier par les phénomènes de diffusion, qui jouent souvent un rôle clé. Ces caractéristiques, par ailleurs, ne sont pas propres au matériaux du nucléaire, mais se retrouvent dans toutes les situations, très fréquentes en milieu industriel comme dans la vie courante, où les matériaux se trouvent loin de l'équilibre thermodynamique.

Ce constat a guidé, pendant des décennies, la métallurgie physique et les études pour les matériaux du nucléaire, aussi bien du point de vue expérimental que de celui de la "modélisation atomique classique" (hamiltoniens empiriques) ; la maîtrise de ces outils par le SRMP était déjà reconnue au moment de mon arrivée.

Pour les isolants et semi-conducteurs, malgré un essor spectaculaire des méthodes de structure éléctronique depuis la fin des années '70, l'étude théorique des défauts a été plutôt dirigée vers la compréhension de caractéristiques optiques ou électroniques spécifiques de tel ou tel défaut, identifié par quelque technique spectroscopique. L'effet global de la présence et de la cinétique des défauts sur les propriétés macroscopiques des matériaux a été, pour l'essentiel, passé sous silence. Cela, sans doute, à cause du fait que l'utilisation des semi-conducteurs et isolants comme matériaux fonctionnels a lieu, la plupart du temps, à des températures auxquelles les concentrations d'équilibre des défauts sont moindres.

Il n'en est pas ainsi quand ces matériaux sont utilisés dans un réacteur nucléaire ou comme matériaux de confinement des déchets nucléaires ; il s'agit alors de transposer certaines démarches, acquises pour les métaux, à ces matériaux. Dans ce sens on peut parler d'une *métallurgie des isolants*. La mécanique quantique est ici indispensable pour décrire quantitativement

la liaison chimique et pouvoir donc établir une hierarchie entre les différents mécanismes élémentaires à l'échelle nanométrique ; la présence de charges localisées et de l'interaction coulombienne à longue portée entre les défauts complique considérablement la tâche.

Des nombreux problèmes restent ouverts dans ce domaine, comme par exemple la compréhension des phénomènes de diffusion accélérée par excitations électroniques, de l'équilibration des charges sous irradiation ou de l'influence, parfois spectaculaire, des champs électriques sur la plasticité.

Les thématiques décrites par la suite témoignent d'un souci constant de conjuguer l'étude de matériaux d'intérêt pour le nucléaire avec les défis posés à la science des matériaux non-métalliques, de chercher un compromis entre la nécessité de donner des réponses à des problèmes technologiques réels et la volonté de comprendre des phénomènes généraux pour des matériaux prototypiques, tels un oxyde isolant amorphe ou un sémiconducteur binaire à large bande interdite.

0.2 Défauts et diffusion : pourquoi la structure électronique ?

L'étude des défauts ponctuels dans les solides implique la description de systèmes contenant au moins quelques dizaines voire une centaine d'atomes. Malgré cette difficulté, les défauts sont si importants dans les matériaux que l'on n'a pas hésité à utiliser les calculs de structure électronique, entre autre dans le formalisme de la Théorie de la Fonctionnelle de la Densité (DFT), pour les décrire. En effet, tout matériau présente une concentration d'équilibre de lacunes, interstitiels et autres défauts natifs du fait de la compétition entre abaissement de l'entropie configurationnelle et augmentation de l'énergie associée aux défauts [1, 2]. Par ailleurs, l'entropie configurationnelle n'est pas la seule qu'il faudrait considérer, bien que la plupart des études se limitent à cette contribution.

L'influence des défaut ponctuels sur les propriétés des matériaux est multiple, via leur structure électronique, sur les propriétés optiques ou électriques, mais aussi sur le transport de la chaleur et la plasticité. Pour tous les matériaux les défauts ponctuels contrôlent presque toujours le transport de masse, donc la diffusion et, en conséquence, les chemins cinétiques qui déterminent comment un matériau hors équilibre atteint l'équilibre ou un état stationnaire hors équilibre, s'il s'agit d'un "matériau forcé" [3].

Une spécificité importante des défauts dans les matériaux non-métalliques est la capacité de piéger les charges ; cela implique que les défauts ponctuels jouent un rôle fondamental dans le positionnement du niveau de Fermi. À cela il faut rajouter le transport de charge pour les matériaux où la conductivité est essentiellement ionique.

Les propriétés spécifiques, et en particulier les propriétés énergétiques, d'un défaut ponctuel ne peuvent être reliées directement à une propriété ou un comportement macroscopique. C'est en général l'effet combiné de tous les défauts présents dans un matériau qui doit être pris en considération.

Pour cela existent différentes méthodes de simulation à des échelles supérieures de temps et d'espace ; le couplage avec les propriétés élémentaires des défauts calculées en ab initio résulte une hiérarchie d'approches multi-échelle.

Le Monte Carlo atomique (AKMC) est la plus détaillée, qui décrit les mouvements de saut de tous les atomes d'un solide sur un réseau rigide ; si l'on se limite à certains objets, défauts ou solutés par exemple, on peut utiliser leur probabilité de se déplacer, apparaître, disparaître, par exemple en se combinant entre eux, pour faire alors du Monte Carlo sur objets/évènements, ou EKMC. Ces deux approches gardent une description spatiale du matériaux. En simplifiant ultérieurement, les populations de défauts et leurs modifications dans le temps peuvent être décrites par des moyennes spatiales obéissant à des équations d'évolution, du type de l'équation maîtresse. Les paramètres de ces équations sont déterminés, en particulier, par les coefficients de diffusion et les taux de réaction entre défauts (Cinétique Chimique Homogène, CCH, appelée aussi dynamique d'amas).

Selon le niveau de description, ces méthodes permettent de simuler des systèmes de grande taille et sur des temps très longs [4, 5]. Les briques de base restent, dans les trois cas, les énergies de formation et migration des défauts. Pourtant, l'accent de la plupart des études DFT de défauts dans les isolants est mis plutôt sur l'influence des défauts sur les propriétés optiques et électroniques, en négligeant leur stabilité et leur cinétique. Il est vrai que l'utilisation de ces matériaux se fait généralement à des températures relativement basses, mais cette explication n'est que partielle.

Deux questions qui viennent naturellement à l'esprit sont les suivantes : peut-on mesurer expérimentalement les énergies de formation et migration des défauts ? Et d'un point de vue théorique, quelle est l'approche la plus adaptée pour les prédire ?

Les réponses à ces questions ne sont pas simples. Expérimentalement on peut mesurer des énergies d'activation qui, dans certains cas, peuvent être attribuées à un défaut en particulier. Mais souvent les défauts sont nombreux et sans un modèle théorique fiable il n'est pas possible de relier les quantités mesurées à un interstitiel ou à une lacune, et encore plus difficilement peut-on remonter à la charge du défaut. À cela il faut ajouter qu'il est aussi difficile de faire la part de l'énergie de formation et de celle de migration, dont on mesure dans la plupart des cas seulement la somme. Pour attribuer une énergie de migration il faut associer l'identification d'un défaut, typiquement par une méthode spectroscopique, à la détection d'un processus cinétique, par exemple grâce à une trempe ou un recuit. D'autres techniques qui permettent de mesurer une énergie de migration, séparément de la formation, sont les méthodes de frottement interne et de relaxation diélectrique [6, 7].

D'autres difficultés du point de vue expérimental sont liées au contrôle des potentiels chimiques atomiques (par exemple la pression partielle d'oxygène pour un oxyde) et électronique (même en contrôlant la concentration de dopant dans un semi-conducteur on ne sait pas forcément où se place le niveau de Fermi). Le couplage entre défauts natifs et impuretés peut parfois permettre de determiner un mécanisme [8, 9], mais les effets

de correlation qui peuvent en découler sont souvent difficiles à évaluer, comme le montre l'étude sur le Pd dans SiC résumé par la suite [10].

En ce qui concerne les approches théoriques, les potentiels empiriques à charges fixes présentent des limites évidentes, à la fois pour la transférabilité [11, 12], très limitée, ensuite parce qu'ils sont incapables de décrire les différents états de charge d'un défaut. Les potentiels à charges variables, bien que proposés déjà il y a depuis une vingtaine d'années, n'ont pas donné satisfaction jusqu'à présent quant à la description des défauts dans les oxides [13, 14].

Si l'on exclut aussi les méthodes de type liaisons fortes (qui dans certains cas sont, par ailleurs, utilisables avec un certains succès pour traiter des systèmes relativement gros [15]) il est clair que l'approche DFT se présente comme un très bon candidat pour la tâche assignée, étant aussi un bon compromis entre robustesse, rapidité et précision. Nous verrons, toutefois, que la limite intrinsèque des fonctionnelles d'échange et correlation couramment utilisées se manifeste, pour les défauts, même dans des matériaux dont la description du cristal parfait est plus qu'acceptable.

C'est armé de cet outil que j'ai essayé de répondre à un certain nombre de questions fondamentales pour à la compréhension des phénomènes de diffusion et, plus en général, à la cinétique des défauts dans le quartz, la silice et dans le carbure de silicium.

0.3 Des matériaux du nucléaire à SiO_2 et SiC

Les matériaux du nucléaire sont soumis à un très grand nombre de constraintes. Ils sont utilisés, presque toujours, à haute température, il sont dans un environnement chimique souvent varié et parfois hostile (phénomènes de corrosion) et, point spécifique notable, ils sont maintenus hors équilibre par une création continue de défauts sous l'effet d'irradiations de différents types (neutrons, électrons, particules α et rayons Γ). Cela produit des modifications de la microstructure et même des transitions de phase. Les conséquences vont du gonflement, aux modifications des propriétés mécaniques, électriques et thermiques. Si les métaux ont été le champs d'action privilégié pour les chercheurs du domaine, les isolants ne sont pas pour autant absents dans les réacteurs nucléaires (UO_2, PuO_2, hydrures métalliques et autres produits de corrosion non voulus, matrices de stockage céramiques ou vitreuses). Bien que les études expérimentales sur ces matériaux ne manquent pas [16, 17, 18], la compréhension théorique a avancé plus lentement.

Les matériaux cités et les conditions dans lesquelles ils sont utilisés ou se forment sont trop complexes pour qu'on puisse en envisager une étude "directe" à l'échelle atomique. Il est clair que pour avancer dans la compréhension des matériaux isolants du nucléaire il faut passer d'abord par une étude de matériaux plus simples, en quelque sorte des matériaux modèle pour les matériaux du nucléaire, tout en étant étudiés comme matériaux réels dans d'autres domaines.

C'est dans cet esprit que mes activités de recherches se sont focalisées sur SiO_2 et SiC.

Le premier est le composant principal des verres de stockage des déchets nucléaires. Mais c'est aussi un matériau d'importance énorme pour

la microélectronique, un oxide iono-covalent, cristallin et amorphe, qui ne présente pas des problèmes particuliers en terme de description par la DFT (au moins pour les phases tétrahédriques).

Le deuxième, le carbure de silicium, est aussi un matériau étudié depuis longtemps pour ses applications comme matériau fonctionnel (semiconducteur à large bande interdite, adapté pour les hautes fréquences et hautes puissances). Il a été utilisé, et est toujours envisagé, comme matériau de gainage dans des réacteurs à caloporteur gazeux, dans les particules de combustible dites "Triso" [1], comme barrière de confinement pour les produits de fission et comme matériau de structure. Le carbure de silicium est aussi considéré, en tant que matériau haute température, comme matériau de structure dans les réacteurs pour la fusion nucléaire.

0.4 Résumé des chapitres 2, 3 et 4

0.4.1 Défauts et calcul ab initio

Le chapitre 2 traite de l'approche ab initio utilisée pour décrire les défauts.

Quelques principes de base

La première section rappelle brièvement les bases de la théorie atomique de la diffusion [19], s'appuyant sur la théorie de l'état de transition (TST) et l'équation de Eyring [20]. L'accent est mis sur le traitement grand canonique, nécessaire pour les matériaux non élémentaires [21] et discute les implications de l'omission de termes entropiques, approximation très courante et parfois oubliée.

On rappelle également la connection entre potentiels chimiques et conditions expérimentales. En montrant, en figure 2.1 page 10, les contributions entropiques du solide et de la molécule de O_2 (calculées pour ref. [22]), on met en évidence l'importance de l'entropie translationnelle dans le cas de réactions de formation des défauts pour un oxide dans une atmosphère d'oxygène. Dans cette section est également rappelée l'importance de contrôler l'erreur commise non seulement sur les énergies que l'on calcule pour les supercellules contenant le défaut, mais également pour le potentiel chimique de référence.

Charges et énergie de Fermi

La section suivante discute de la concentration d'équilibre des défauts chargés et de la dépendance du potentiel chimique électronique, c .à d. du niveau de Fermi. La liaison entre minimisation de l'énthalpie libre du solide et l'expression de l'énergie de formation des défauts chargés est esquissée. On discute comment les porteurs de charge, les impuretés et les défauts intrinsèques (ou natifs) déterminent, tous ensemble, la position du niveau de Fermi par le biais de la contrainte de neutralité. C'est en résolvant cette équation avec les données calculées en ab initio que nous avons pu évaluer l'auto-dopage dans SiO_2 [23]. Les caractéristiques générales

1. Tri-structural isotropic

des mécanismes possibles de compensation de charge selon les matériaux sont discutés et le cas spécifique des halogénures alcalins est mentionné comme exemple notable.

Interaction des images périodiques

Un point auquel a dû se confronter quiconque a effectué des calculs DFT de défauts en conditions périodiques est celui de l'interaction coulombienne entre les images périodiques des ces mêmes défauts. Ce sujet est traité en section 2.3. Les principales difficultés ainsi que les solutions les plus courantes y sont résumées [24, 25], en discutant les choix faits pour nos calculs. En particulier, on y discute de l'alignement de potentiel et de sa connection avec les corrections électrostatiques, encore très récemment objet de débat [26, 27, 28, 29]. Quelques remarques sur la prise en compte de l'auto-interaction, la part de l'interaction élastique et électrostatique, ainsi que quelques rappels sur des aspects techniques souvent passés sous silence, complètent la discussion.

Quelle structure électronique ?

La section 2.4 considère l'approximation fondamentale de la DFT, c. à d. le choix de la fonctionnelle d'échange et correlation, pour la description des défauts. À ce propos, il est nécessaire de rappeler que la structure électronique des défauts, et notamment la position des niveaux électroniques localisés dans la bande interdite d'un solide isolant ou semiconducteur, non seulement est importante pour déterminer les propriétés optiques du défaut, mais influent indirectement sur ses propriétés thermodynamiques. Dans cette section on discute, en effet, de l'étroite connexion entre les niveaux de transition de charge, optiques et thermodynamiques, et la stabilité des différents états de charge des défauts, ainsi que des conséquences de la sousestimation de la bande interdite par les approximations les plus courantes (LDA/GGA) sur le positionnement des niveaux de défauts que l'on vient de citer. Les méthodes actuellement considérées pour pallier ces limites des fonctionnelles semi-locales [30] sont citées et très brièvement discutées. Une sous-section en encadré discute du choix de l'approximation LDA (par rapport à GGA) pour les défauts dans SiC et SiO_2.

Exploration des paysages énergétiques

La modélisation des mécanismes de diffusion ne peut se faire sans la détermination de chemins de migration des atomes et des points de selle correspondants du paysage énergétique vu par les défauts. Avantages et désavantages des méthodes que nous avons utilisées constituent le sujet de la section 2.5. Une de ces méthodes se base sur des relaxations contraintes, en utilisant une contrainte particulière, que nous avons décrite dans un article sur les recombinaisons de paires de Frenkel dans le carbure de silicium [31]. L'autre méthode que nous avons utilisée, aujourd'hui jouissant d'une grande popularité, est la méthode de la bande élastique (NEB), dont nous rappelons quelques limites.

0.4.2 Défauts et diffusion dans le quartz et la silice

Le chapitre 3 est dédié aux défauts natifs et à la diffusion dans le dioxide de silicium. Après quelques lignes d'introduction, la première section (3.1) propose un rappel de l'état de l'art, tant du point de vue théorique qu'expérimental, à la fin des années 90, quand j'ai pour la première fois abordé le sujet. Les questions qui ont guidé et accompagné, en filigrane, le travail sur SiO_2 y sont exposées.

Auto-diffusion de l'oxygène

La section 3.2 résume les résultats obtenus au cours des années pour les énergies de formation et de migration des défauts natifs dans le quartz [22, 23] et la silice [32, 33, 34, 35] et discute les prédictions concernant l'auto-diffusion de l'oxygène [22, 36, 37, 38].

Défauts neutres La première sous-section 3.2.1 esquisse le cadre obtenu sur la base des seuls défauts neutres [22], qui ont permis de comprendre quantitativement l'effet de la pression partielle d'oxygène et de classifier, au moins partiellement, les résultats expérimentaux selon ce paramètre. Ils ont aussi montré un accord très satisfaisant avec le seul coefficient d'auto-diffusion de l'oxygène obtenu en conditions fermées [39].

Défauts chargés Les résultats obtenus pour les défauts chargés sont décrits dans la sous-section suivante (3.2.2) ; ils ont permis d'évaluer l'influence de la position du niveau de Fermi sur les propriétés de diffusion. Ce point a entraîné à une étude de l'auto-dopage dans SiO_2 [23] dont les principaux résultats peuvent être cernés par un coup d'œuil sur la figure 3.3, dont les trois tableaux résument les énergies de formation des défauts natifs dans le quartz et la silice, leur dépendance du niveau de Fermi et des potentiels chimiques atomiques.

Toutefois, les résultats que l'on vient de mentionner ont ouvert un certain nombre de questions liées au rôle des défauts chargés dans la diffusion (notamment des interstitiels d'oxygène chargés négativement), à la compensation de charge dans SiO_2, au rôle éventuel des impuretés. Ces questions sont exposées sous-section 3.2.3.

SiO_2 amorphe Avant de répondre à une partie de ces questions, une section sur les différences et similitudes entre défauts dans le quartz et dans silice était nécessaire [32, 33, 34]. Quelques éléments de cette comparaison sont exposés sous-section 3.2.4, où l'on montre également que les questions posées dans la section précédente sont valables aussi bien pour le quartz que pour la silice, et peut-être de façon encore plus pressante pour cette dernière [40].

L'encadré sur la visualisation de la structure des défauts à l'aide des Fonctions de Wannier à Localisation Maximale (MLWF) est inséré ici en guise d'intermède. Nous l'avons utilisée dans l'article sur les défauts de coordinence dans SiO_2 [35], également mentionné dans cette section.

La correction GW et la solution d'un dilemme La dernière sous-section (3.2.5) de cette section dédiée à l'autodiffusion de l'oxygène permet de donner une réponse satisfaisante à la plupart des questions soulevées précédemment. En effet, l'utilisation de la méthode GW pour corriger les énergies de formation des interstitiels d'oxygène de charge négative a bouleversé le panorama en ce qui concerne les niveaux de transitions de charge pour ces défauts et leur contribution à la diffusion en conditions fermées [38]. Il reste toutefois encore à établir dans quelles conditions les approximations utilisées peuvent être transposées à d'autres cas de figure, ce que nous discutons également dans cette sous-section, en nous appuyant sur quelques détails de la structure électronique des défauts étudiés.

Auto-diffusion du silicium

Bien que les limites des fonctionnelles semi-locales doivent être évaluées aussi pour les défauts de silicium, on ne pouvait omettre une discussion de l'auto-diffusion du silicium sur la base des résultats que nous avons obtenus pour les énergies de formation et de migration des défauts de silicium. Les régimes prédits par la théorie (interstitiel en équilibre avec le silicium massif, antiSchottky en mode fermé, lacunaire en équilibre avec un gaz d'oxygène), ainsi que la comparaison à l'expérience, sont donc l'objet de la dernière section du chapitre (section 3.3), qui reprend et complète la discussion de ref. [37]. Quelques remarques sur l'atteinte de l'équilibre dans les échantillons expérimentaux terminent la section et le chapitre.

0.4.3 Défauts ponctuels et cinétique dans le carbure de silicium

Le chapitre 4 est dédié aux travaux sur les défauts natifs, les impuretés de palladium et leur cinétique dans le carbure de silicium. Peut-être encore plus que pour SiO_2 le travail sur le carbure de silicium a été conçu pour comprendre les effets d'irradiation. La perspective de mettre en place une simulation de cinétique chimique homogène (CCH) des effets d'irradiation dans le carbure de silicium, a fourni l'occasion de colliger les données que j'ai obtenues depuis que j'ai commencé à faire des simulations sur le SiC, complétée par des résultats de la littérature. L'ensemble comprend les énergies de formation et de migration de défauts ponctuels, ainsi qu'énergies de liaison d'agrégats et barrières d'énergie pour des réactions entre défauts dans le polytype cubique de ce matériau. La première section du chapitre (4.1) résume en forme graphique (figure 4.1) toutes ces données, qui sont disponibles dans l'annexe A.1.

Diffusion et rôle des contributions entropiques

La sous-section suivante, 4.1.1, en traitant du calcul des entropies de formation et migration des défauts [41], permet de discuter brièvement l'auto-diffusion du silicium et du carbone dans le carbure de silicium. Quelques remarques spécifiques sur la migration de certains défauts et leur description en DFT trouvent ici leur place la plus naturelle, avant de passer à las discussion des aspects liées aux contributions entropiques.

À ce propos sont ici rappelés les résultats de ref. [41] au sujet de la validité de la formule empirique de Zener [42, 43] en suggérant une extension possible aux défauts chargés. Il est question, ensuite, du respect de la règle de Meyer-Neldel [44] (ou règle de compensation entre énergie et entropie de migration). La même procédure que nous avons utilisée en ref. [41] est ici appliquée aux entropies de saut que nous avons calculées pour ref. [45]. Cela est résumé figure 4.2, où la règle de Meyer-Neldel est respectée dans la même mesure que pour le groupe de défauts constitué par les interstitiels de silicium et de carbone.

Recuit des défauts et effets irradiation

La section 4.2 regroupe la description des études visant à la compréhension de mécanismes cinétiques pouvant influencer l'évolution des concentrations de défauts pendant et après l'irradiation dans le carbure de silicium.

Recombinaison de paires de Frenkel La première sous-section (4.2.1) rappelle les motivations et les résultats obtenus pour la recombinaison des paires de Frenkel homogènes et hétérogènes [31]. Ces dernières produisent des antisites ; la possibilité, qui en découle, d'une décomposition à une échelle nanométrique pilotée par un biais cinétique n'avait pas été explorée auparavant. La complexité des chemins de recombinaison et l'utilisation des données obtenues dans un modèle à un'échelle supérieure (de type CCH) sont deux points ultérieurs à souligner. L'étude montre l'importance de la structure des lacunes de silicium produites par l'irradiation pour l'évolution des populations de défauts.

Défauts de coordinence Les paires de Frenkel sont un exemple de défaut stœchiométrique, mais d'autres existent, comme les paires d'antisites. Ces derniers, ainsi que leur chemin de recombinaison, ont fait l'objet d'une étude [45] qui est brièvement décrite sous-section 4.2.2. Ces défauts, qui sont, selon les résultats obtenus, virtuellement absent avant et après irradiation, pourraient jouer un rôle pendant l'irradiation vis-à-vis de l'amorphisation du matériau.

Métastabilité de la lacune de silicium et corrections GW Comme mentionné au sujet de la recombinaison des paires de Frenkel, la structure de la lacune de silicium est très importante pour déterminer les chemins cinétiques empruntés par le carbure de silicium sous irradiation. C'est pour cette raison que le travail effectué sur la métastabilité de la lacune de silicium [46] a toute sa place dans ce programme de compréhension des effets d'irradiation. De surcroît, l'application de la correction GW non seulement aux énergies de formation, mais aussi à une position de col, est une première à notre connaissance. La sous-section 4.2.3 résume les résultats principaux de ce travail en ce qui concerne l'interprétation d'expériences de photoluminescence et la contribution des différents états de charge au chemin de conversion d'une lacune en complexe $V_C C_{Si}$.

Agrégats dans le carbure de silicium Avant de terminer cette section, dédiée aux transformations cinétiques dans SiC intrinsèque, nous avons voulu ajouter quelques commentaires sur la formations d'agrégats qui dans le carbure de silicium présentent des énergies de liaison considérables [47, 48, 49, 50]. Les résultats principaux d'une étude que nous avons menée sur les agrégats de silicium [51] sont ici résumés. Cela fourni l'occasion de mentionner les limites de l'approche DFT pour les interstitiels de silicium, que nous avons mises en évidence dans une autre publication [52].

Impuretés de palladium dans le carbure de silicium

La dernière section (4.3) du chapitre sur le carbure de silicium résume les principaux résultats obtenus sur la stabilité et la mobilité du palladium dans le carbure de silicium cubique [10]. Le moteur de cette étude a été une problématique éminemment appliquée, ce qui illustre très bien comment l'échange entre études fondamentales et appliquées a lieu véritablement dans les deux sens. En effet, l'étude des mécanismes de diffusion du Pd assistés par les défauts intrinsèques a mis en évidence des aspects fondamentaux de la diffusion. D'une part, on a montré que les énergies d'activation effectives pour l'impureté peuvent être bien inférieures aux énergies de migration des défauts intrinsèques qui participent à la migration [10]. D'autre part, il est maintenant clair [53] que l'énergie de migration effective du défaut intrinsèque peut, elle même, être considérablement abaissée simplement à cause d'effets de correlation ; ces derniers sont déterminés par les spécificités du mécanisme de couplage entres les mouvements de l'impureté et du défaut intrinsèque. L'accent sur les aspects cinétiques du Pd dans SiC a été mis dès que les calculs d'énergie de mise en solution ont confirmé le soupçon que la diffusion soit le facteur limitant de la *corrosion* de SiC par le palladium.

0.5 Projets à quatre ans

L'orientation des mes projets scientifiques pour les prochaines années suivra les trois axes suivants :

1. développement des approches multi-échelle
2. identification de défauts ponctuels via le couplage théorie-simulation/expérience
3. ouverture sur l'étude de matériaux fonctionnels pour l'énergie.

Approches multi-échelle

Tous les objets que l'on doit pouvoir décrire en physique des matériaux évoluent sur des échelles de temps et d'espace couvrant plusieurs ordres de grandeur. Du nanomètre, l'échelle d'un défaut ponctuel, jusqu'à la taille d'un échantillon. Du temps typique d'une vibration atomique, de l'ordre de la picoseconde, jusqu'aux temps géologiques dans certains cas. Les couplages d'échelle et de méthodes sont incontournables pour relier les informations à l'échelle atomique aux propriétés macroscopiques des matériaux et à leurs variations dans le temps.

Dans ce contexte, je souhaite poursuivre la démarche ébauchée dans une précédente publication [4], contenant un premier modèle simplifié de cinétique chimique homogène basée sur des énergies de réaction entre défauts calculées en DFT. La suite de ce programme prévoit non seulement la prise en compte d'autres types de défauts, qui peuvent jouer un rôle important, comme des agrégats de carbone et de silicium, mais également l'inclusion de plusieurs états de charge pour un même défaut. Cela signifie également introduire l'évolution des porteurs de charge, donc du dopage (ou la position du niveau de Fermi). Cette démarche, encore totalement inexplorée, est nécessaire pour comprendre, à terme, l'évolution des populations de défauts hors équilibre dans les matériaux isolants et semiconducteurs. Connaître au cours du temps (et même sous irradiation) les concentrations moyennes de défauts de chaque type (lacunes, interstitiels, antisites, amas de taille différente) ouvre la possibilité de prédire (et de comparer aux expériences) les propriétés macroscopiques qui en dépendent, comme par exemple la conductivité thermique ou électrique, le gonflement sous irradiation, les propriétés optiques, pour ne citer que quelques exemples.

Sondes pour les matériaux sous irradiation : spectroscopies et identification de défauts

Le deuxième axe vise à développer le calcul de grandeurs permettant une comparaison plus directe avec l'expérience. À ce propos considérons l'exemple des calculs que j'ai effectués des modes de vibration de systèmes contenant des défauts ponctuels [2, 3, 13] : les résultats permettent d'obtenir des entropies vibrationnelles, mais la comparaison avec l'expérience n'est pas immédiate, puisque, d'une part, les échantillons réels contiennent plusieurs types de défauts en concentrations inconnues, mais aussi, d'autre part, parce que les techniques expérimentales ne sont pas toujours en mesure de sonder la totalité de la densité d'états. Un pas ultérieur vers la comparaison directe avec l'expérience est le calcul direct de spectres, par exemple le spectre Raman non-resonant, ce qui est aujourd'hui possible en utilisant la théorie de la réponse linéaire.

Les spectroscopies optiques sont aussi difficilement exploitables sans un support théorique. Les propriétés optiques des défauts peuvent aujourd'hui être prédites de façon de plus en plus satisfaisante grâce aux progrès dans la description des états excités (méthode GW ou théorie de la fonctionnelle de la densité dépendante du temps, TDDFT). Dans cette direction il y a un grand potentiel de synergie entre simulation et expérience que j'entends également explorer. Le but premier de cette démarche est de contribuer à l'identification expérimentale des défauts et de leur état de charge dans les matériaux non-métalliques et notamment pour les défauts qui ne peuvent pas être détectés par résonance paramagnétique électronique (EPR), technique limitée aux défauts de spin impair.

Des matériaux du nucléaire aux matériaux fonctionnels pour l'énergie

Le CEA est fortement impliqué non seulement dans les matériaux du nucléaire, mais aussi dans la recherche sur les matériaux pour l'énergie en

général. Ces derniers incluent les matériaux pour la production d'énergie photovoltaïque, les échangeurs ioniques pour les batteries au lithium, les matériaux pour le stockage d'hydrogène et pour les piles à combustible. Ces matériaux posent des problèmes complexes de physico-chimie où les connaissances acquises sur les matériaux sous irradiation (par définition hors équilibre thermodynamique) peuvent être mises à profit. Je souligne en particulier le rôle des cinétiques à l'état solide ; un exemple typique est le rôle de la diffusion de l'oxygène dans la croissance de couches d'oxyde de silicium (modèle de Deal-Grove).

Ce dernier volet à pris une place plus importante que prévu initialement, suite à ma mission de longue durée en Allemagne, à l'Université de Mayence, ou j'ai commencé un projet sur les cellules solaires en couches minces.

C'est dans le cadre d'une collaboration entre universités, centres de recherches publiques et privés que s'insère un programme de simulation des mécanismes à l'échelle atomiques qui ont une influence sur l'efficacité de ces dispositifs. En particulier, mon travail, qui devrait inclure aussi un rôle de coordination, se focalisera sur les phénomènes de diffusion du sodium sur la surface du contact métallique en face arrière et aux joints de grain de ce dernier. On sait que le sodium, présent dans ces dispositifs, améliore leur éfficacité, mais on n'en connaît pas les mécanismes.

Bibliographie

[1] Per Kofstad. *Nonstoichiometry, diffusion, and electrical conductivity in binary metal oxides*. Wiley Interscience, 1972. (Cité pages x et 1.)

[2] F. A. Kröger and H. J. Vink. Imperfections in crystalline solids. In Frederick Seitz and David Turnbull, editors, *Solid State Physics*, volume 3. Academic Press, 1956. p. 312. (Cité pages x et 1.)

[3] Georges Martin and Pascal Bellon. Driven alloys. In *Solid State Physics*, volume 50. Academic Press, 1997. (Cité pages x et 1.)

[4] A. Barbu, C. S. Becquart, J.L. Bocquet, J. Dalla Torre, and C. Domain. Comparison between three complementary approaches to simulate 'large' fluence irradiation : application to electron irradiation of thin foils. *Philos. Mag.*, 85(4-7) :541–547, 2005. (Cité pages xi, 2 et 41.)

[5] J. Dalla Torre, J.-L. Bocquet, N. V. Doan, E. Adam, and A. Barbu. Jerk, an event-based kinetic monte carlo model to predict microstructure evolution of materials under irradiation. *Philos. Mag.*, 85(4-7) :549–558, 2005. (Cité pages xi et 2.)

[6] A. S. Nowick and B. S. Berry. *Anelastic relaxation in crystalline solids*. Academic Press, New York and London, 1972. (Cité pages xi et 3.)

[7] S. Bausch, H.G. Bohn, and W. Schilling. Anelastic and dielectric relaxation measurements in the protonic conductor $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$. *Solid State Ionics*, 97 :517–521, 1997. (Cité pages xi et 3.)

[8] K. Ruschenschmidt, H. Bracht, N. A. Stolwijk, M. Laube, G. Pensl, and G. R. Brandes. Self-diffusion in isotopically enriched silicon

carbide and its correlation with dopant diffusion. *J. Appl. Phys.*, 96(3) :1458–1463, 2004. (Cité pages xi, 3 et 39.)

[9] Hartmut Bracht. Self- and foreign-atom diffusion in semiconductor isotope heterostructures. I. continuum theoretical calculations. *Phys. Rev. B*, 75 :035210, 2007. (Cité pages xi et 3.)

[10] G. Roma. Palladium in cubic silicon carbide : stability and kinetics. *J. Appl. Phys.*, 106 :123504, 2009. (Cité pages xii, xviii, 3, 11, 37, 43, 44, 50 et 77.)

[11] Fei Gao, Eric J. Bylaska, William J. Weber, and L. René Corrales. *Ab initio* and empirical-potential studies of defect properties in $3C - SiC$. *Phys. Rev. B*, 64 :245208, 2001. (Cité pages xii et 3.)

[12] Paul Erhart and Karsten Albe. Analytical potential for atomistic simulations of silicon, carbon, and silicon carbide. *Phys. Rev. B*, 71 :035211, 2005. (Cité pages xii et 3.)

[13] A. Hallil, E. Amzallag, S. Landron, and R. Tétot. Properties of rutile tio2 surfaces from a tight-binding variable-charge model. comparison with ab initio calculations. *Surf. Sci.*, 605(7-8) :738 – 745, 2011. (Cité pages xii et 4.)

[14] B. S. Thomas and N. A. Marks. Comment on "use of a variable-charge interatomic potential for atomistic simulations of bulk, oxygen vacancies, and surfaces of rutile TiO_2". *Phys. Rev. B*, 76 :167401, 2007. (Cité pages xii et 4.)

[15] Pekka Koskinen and Ville Mäkinen. Density-functional tight-binding for beginners. *Comp. Mater. Sci.*, 47 :237–253, 2009. (Cité pages xii et 4.)

[16] S. J. Zinkle and C. Kinoshita. Defect production in ceramics. *J. Nucl. Mater.*, 251 :200–217, 1997. (Cité pages xii et 5.)

[17] Yves Limoge and Alain Barbu. Aging of oxides under irradiation. *Def. Diff. Forum*, 237–240 :621, 2005. (Cité pages xii et 5.)

[18] Yves Limoge. Radiation aging of nonmetallic materials : specific aspects. *Comptes Rendus Physique*, 9 :370 – 378, 2008. (Cité pages xii et 5.)

[19] J. L. Bocquet, G. Brebec, and Y. Limoge. *Physical Metallurgy*, chapter 7 Diffusion in metals and alloys, pages 536–668. Elsevier Science, Amsterdam, 1996. p. 583. (Cité pages xiii, 7 et 8.)

[20] Peter Hänggi, Peter Talkner, and Michal Borkovec. Reaction-rate theory : fifty years after kramers. *Rev. Mod. Phys.*, 62 :251–341, 1990. (Cité pages xiii et 8.)

[21] J Mayer and M Fähnle. On the meaning of effective formation energies, entropies and volumes for atomic defects in ordered compounds. *Acta Mater.*, 45 :2207 – 2211, 1997. (Cité pages xiii et 8.)

[22] G. Roma, Y. Limoge, and S. Baroni. Oxygen self-diffusion in α-quartz. *Phys. Rev. Lett.*, 86 :4564–4567, 2001. (Cité pages xiii, xv, 17, 24, 31, 49 et 77.)

[23] G. Roma and Y. Limoge. Density functional theory investigation of native defects in SiO_2 : Self-doping and contribution to ionic conductivity. *Phys. Rev. B*, 70 :174101, 2004. (Cité pages xiii, xv, 13, 25, 49 et 77.)

[24] D. B. Laks, C. G. Van de Walle, G. F. Neumark, P. E. Blöchl, and S. T. Pantelides. Native defects and self-compensation in ZnSe. *Phys. Rev. B*, 45 :10965–10978, 1992. (Cité pages xiv et 14.)

[25] G. Makov and M. C. Payne. Periodic boundary conditions in *ab initio* calculations. *Phys. Rev. B*, 51 :4014–4022, 1995. (Cité pages xiv et 14.)

[26] Jihye Shim, Eok-Kyun Lee, Y. J. Lee, and R. M. Nieminen. Density-functional calculations of defect formation energies using supercell methods : Defects in diamond. *Phys. Rev. B*, 71 :035206, 2005. (Cité pages xiv et 14.)

[27] Stephan Lany and Alex Zunger. Assessment of correction methods for the band-gap problem and for finite-size effects in supercell defect calculations : Case studies for ZnO and GaAs. *Phys. Rev. B*, 78 :235104, 2008. (Cité pages xiv, 14 et 18.)

[28] C. Freysoldt, J. Neugebauer, and C. G. Van de Walle. Fully ab initio finite-size corrections for charged-defect supercell calculations. *Phys. Rev. Lett.*, 102 :016402, 2009. (Cité pages xiv et 14.)

[29] Samuel E. Taylor and Fabien Bruneval. Understanding and correcting the spurious interactions in charged supercells. *Phys. Rev. B*, 84 :075155, 2011. (Cité pages xiv, 14 et 15.)

[30] Walter R. L. Lambrecht. Which electronic structure method for the study of defects : A commentary. *Phys. Status Solidi B*, 248(7) :1547–1558, 2011. (Cité pages xiv et 17.)

[31] G. Roma and J.-P. Crocombette. Evidence for a kinetic bias towards antisite formation in SiC nano-decomposition. *J. Nucl. Mater.*, 403 :32–41, 2010. (Cité pages xiv, xvii, 19, 37, 40, 50, 65 et 67.)

[32] L. Martin-Samos, Y. Limoge, N. Richard, J. P. Crocombette, G. Roma, E. Anglada, and E. Artacho. Oxygen neutral defects in silica : Origin of the distribution of the formation energies. *Europhys. Lett.*, 66 :680–686, 2004. (Cité pages xv, 28 et 49.)

[33] L. Martin-Samos, Y. Limoge, J. P. Crocombette, G. Roma, N. Richard, E. Anglada, and E. Artacho. Neutral self-defects in a silica model : A first-principles study. *Phys. Rev. B*, 71 :014116, 2005. (Cité pages xv, 28 et 49.)

[34] N. Richard, L. Martin-Samos, G. Roma, Y. Limoge, and J. P. Crocombette. First principle study of neutral and charged self-defects in amorphous SiO_2. *J. Non-Cryst. Solids*, 351 :1825–1829, 2005. (Cité pages xv, 28 et 49.)

[35] L. Martin-Samos, Y. Limoge, and G. Roma. Defects in amorphous SiO_2 : Valence alternation pair model. *Phys. Rev. B*, 76 :104203, 2007. (Cité pages xv, 28, 49 et 77.)

[36] Guido Roma, Yves Limoge, and Layla Martin-Samos. Aspects of point defects energetics and diffusion in SiO_2 from first principles simulations. *Nucl. Instrum. Meth. Phys. Res. B*, 250 :54–56, 2006. (Cité pages xv, 13, 26 et 49.)

[37] Guido Roma, Yves Limoge, and Layla Martin-Samos. Oxygen and silicon self-diffusion in quartz and silica : The contribution of first principles calculations. *Def. Diff. Forum*, 258-260 :542–553, 2006. (Cité pages xv, xvi, 33 et 49.)

[38] L. Martin-Samos, G. Roma, P. Rinke, and Y. Limoge. Charged oxygen defects in SiO_2 : going beyond local and semilocal approximations to density functional theory. *Phys. Rev. Lett.*, 104 :075502, 2010. (Cité pages xv, xvi, 17, 18, 30, 31, 49 et 77.)

[39] J. C. Mikkelsen. Self-diffusivity of network oxygen in vitreous SiO_2. *Appl. Phys. Lett.*, 45 :1187, 1984. (Cité pages xv et 24.)

[40] Layla Martin-Samos. *Étude ab-initio des auto-défauts et des mécanismes d'auto-diffusion dans un verre de silice*. PhD thesis, Université de Cergy-Pontoise, 2004. (Cité pages xv et 26.)

[41] Olga Natalia Bedoya-Martínez and Guido Roma. Activation entropies for diffusion in cubic silicon carbide from first principles. *Phys. Rev. B*, 82 :134115, 2010. (Cité pages xvi, xvii, 8, 37, 39, 50, 65, 66 et 77.)

[42] C. Wert and C. Zener. Interstitial atomic diffusion coefficients. *Phys. Rev. B*, 76(1) :1169, 1949. (Cité pages xvii et 39.)

[43] C. Zener. Theory of D_0 for atomic diffusion in metals. *J. Appl. Phys.*, 22(4) :372–375, 1951. (Cité pages xvii et 39.)

[44] A. Yelon, B. Movaghar, and R. S. Crandall. Multi-excitation entropy : its role in thermodynamics and kinetics. *Rep. Prog. Phys.*, 69(4) :1145–1194, 2006. (Cité pages xvii et 39.)

[45] Ting Liao, Olga Natalia Bedoya-Martínez, and Guido Roma. Stoichiometric defects in silicon carbide. *J.Phys. Chem. C*, 114 :22691–22696, 2010. (Cité pages xvii, 37, 39, 41, 42, 50, 65, 67 et 77.)

[46] Fabien Bruneval and Guido Roma. Energetics and metastability of the silicon vacancy in cubic SiC. *Phys. Rev. B*, 83 :144116, 2011. (Cité pages xvii, 37, 41, 42, 50, 65, 66, 67 et 77.)

[47] A. Mattausch, M. Bockstedte, and O. Pankratov. Carbon antisite clusters in SiC : A possible pathway to the D_{II} center. *Phys. Rev. B*, 69 :045322, 2004. (Cité pages xviii et 43.)

[48] A. Mattausch, M. Bockstedte, and O. Pankratov. Structure and vibrational spectra of carbon clusters in SiC. *Phys. Rev. B*, 70 :235211, 2004. (Cité pages xviii, 43 et 67.)

[49] A. Gali, P. Deák, P. Ordejón N. T. Son E. Janzén, and W. J. Choyke. Aggregation of carbon interstitials in silicon carbide : A theoretical study. *Phys. Rev. B*, 68 :215201, 2003. (Cité pages xviii et 43.)

[50] T. Hornos, N. T. Son, E. Janzén, and A. Gali. Theoretical study of small silicon clusters in 4H-SiC. *Phys. Rev. B*, 76 :165209, 2007. (Cité pages xviii et 43.)

[51] T. Liao and G. Roma. Silicon di-interstitial structures in 3C-SiC. Note Technique DEN/DANS/DMN/SRMP/NT/2008-01, CEA , Service de Recherches de Métallurgie Physique, 2008. p. 23. (Cité pages xviii, 37, 43, 66, 67 et 77.)

[52] T. Liao, G. Roma, and J. Y. Wang. Neutral silicon interstitials in 3C and 4H silicon carbide : a first principles study. *Philos. Mag.*, 89 :2271–2284, 2009. (Cité pages xviii, 39, 43, 49, 65 et 66.)

[53] Guido Roma. The influence of palladium impurities on vacancy diffusion in cubic silicon carbide. In J.K. Gibson, S.K. McCall, E.D. Bauer,

L. Soderholm, T. Fanghaenel, R. Devanathan, A. Misra, C. Trautmann, and B.D. Wirth, editors, *Basic Actinide Science and Materials for Nuclear Applications*, volume 1264 of *Mater. Res. Soc. Proc.*, 2010. (Cité pages xviii, 43, 44 et 50.)

Introductory remarks 1

1.1 The role of electronic structure theory in understanding point defects and diffusion

The numerical implementation of Density Functional Theory (DFT), its application to solids and its successful achievements have been possible since the end of the seventies. Thanks to the translational invariance, and the Bloch theorem, the description of an ideal crystalline periodic solid requires to cope only with the degrees of freedom associated to one atom (for the simplest solids).

However, all solids contain defects, in particular point defects, even if one considers only materials in thermodynamic equilibrium; defects break the translational simmetry and, as such, require the description of systems containing tens or hundreds of atoms. Although point defects entail an energy penalty, they lower the configurational entropy of the solid and the trade off between energy loss and entropy gain determines the equilibrium concentration, which is given by the well known Boltzmann exponential form [1, 2]. Even at low concentrations, and neglecting the other entropic contributions, the prediction of the equilibrium concentration of an intrinsic defect or an impurity is not a trivial task, especially in an insulating material. Talking about entropic contributions, most of the time only the configurational one is implicitly considered (through the equilibrium concentration formula), neglecting the vibrational one; but also the electronic entropy, the magnetic entropy —in case of magnetic excitations— and other possible contributions could be taken into account.

Point defects are influencing properties of materials in several ways; they can change mechanical properties —for example by pinning dislocations— they influence optical and electrical properties of insulators and semiconductors, by absorbing/emitting light (e.g., coloured centres), by trapping charges, by scattering phonons and electrons.

However, a point of special interest for materials far from equilibrium, like materials under irradiation, is that point defects are mediating mass transfer, i.e., they determine diffusion properties and the kinetic paths towards a stationary state, be it of thermodynamic equilibrium or not. The point is particularly important in the case of so-called "driven materials" (or "driven alloys", see [3]), for which defect concentrations can be much higher than equilibrium ones, and for which the way a state can be practically reached and maintained depends crucially on point defect kinetics.

A characteristic feature of point defects in non-metallic materials, is the ability to trap charges. As they can occur, in these materials, in various

charge states, point defects can act as a charge reservoir, driving charge equilibration and determining the position of the Fermi level. In insulating materials where the electrical conductivity is mainly ionic, point defects control, through diffusion, also this physical property. For these reasons both the relative stability of different charge states and the energy landscape seen by each charged species is of the utmost importance in understanding kinetic properties in non-metallic materials.

Rate theory models [4] are a valuable tool allowing to make a connection between the energetic parameters controlling the formation, migration, and reactions between defects, and the macroscopic properties of a given material. They rely on a set of differential equations describing the evolution of average defect concentrations by the probability of events involving them, including defect reactions and cluster formation and dissociation; for this reason the same approach bears sometimes the name of Homogeneous Chemical Kinetics (HCK) or Cluster Dynamics (CD). An important step further, including spatial inhomogeneities of the concentrations, is given by object/event Monte Carlo approaches [5], which describe the diffusion and reaction of defect objects in a solid. Events probabilities are not single jump probabilities, although they are in general derived from them. The latter approach, sometimes referred to as Event Kinetic Monte Carlo (EKMC), still disregards the local correlation of various atomic jump mechanisms, which is, conversely, taken into account in atomic kinetic Monte Carlo (AKMC) simulations. By describing single atoms on a rigid lattice (thus disregarding lattice relaxations, except through hopping probability values), AKMC is able to treat local correlation of jumps, as long as all possibly relevant hopping events are included in the model.

The three levels of description of kinetic processes that we just mentioned (HCK, EKMC and AKMC) all rely on the knowledge of the formation and migration/reaction energy of the involved defect species, and depend in a crucial way from them. For this very reason the focus of the work presented in this manuscript is on defect energetics: the formation energy of defects, the energy barriers associated to defect transformations, migration and reactions, which are the basic bricks of any kinetic simulation of material properties. I want to stress this point because a large majority of point defects investigations in semiconductors and insulators has been driven by the microelectronic community, in order to understand the influence of defects on the electrical and optical properties of materials. However, applications in those fields are, most of the time, at relatively low temperature and without permanent creation of defects (unless dealing with hardened electronics or optoelectronics), so that the interest in the evolution of defect populations is less crucial than in the case of nuclear applications and/or very high temperatures. Moreover, the very long time behaviour of devices has not been a strong concern up to now.

At this point, there are at least two questions that could spontaneously arise to the mind of the reader. The first is: can we access directly defect energetics through experiments? And the second: what is the most appropriate level of description in order to be able to predict point defect energetics?

The most valuable tool to obtain formation and migration energies of

defects from experiments are diffusion measurements. However, even if one forgets practical and technical difficulties —like finding (and manipulating) the right isotope for tracer diffusion experiments, controlling experimental conditions (like the surrounding athmosphere), the quality of samples (to avoid the contribution of short circuits like grain boundaries)— the interpretation of diffusion experiments is difficult for several reasons:

- Many mechanisms and defects can contribute to mass transport, and through a diffusion profile is, in many cases, not possible to distinguish them.
- The determination of the charge of the defect controlling the diffusion is difficult, especially when more than one charge states is contributing; and this in spite of the fact that the shape of a profile, as well as the dependence of the activation energy with respect to the oxygen partial pressure, can give precious indications.
- Unless the diffusion measurement is coupled with other probes, the main outcome of diffusion experiments is an activation energy, including a formation and a migration part, and their relative contribution cannot be easily disentangled.

Valuable tools exist to probe the migration energy alone, but their applicability is limited to specific materials and defects. These are internal friction [6] and, for non-metals, dielectric relaxation measurements (which can be coupled in some cases to provide a more reliable answer [7]). Another possibility is to extract the migration energy of a native defect from the activation energy for the migration of an impurity which occurs through a native defect assisted mechanism (see for example the case of B in SiC [8] of As in SiO_2 [9]), but doubts may subsist on which native defect, and which mechanism, is controlling the diffusion of the impurity. Indeed the available coupling mechanisms are several, even in relatively simple cubic systems [10]. For this reason, not only the coupling of two or more probes allows to ascertain that underlining hypotheses on defect species and mechanisms are correct, but also the comparison with numerical estimates based on atomistic models is a very useful tool to confirm or exclude a given diffusion model. The work on palladium in silicon carbide, that we will discuss later, represents an attempt in this direction [11].

The answer to the second of the two questions previously mentioned, the one concerning the best methodological approach for predicting defect energetics, depends, of course, on the material. However, some general remarks can be made for insulating materials, especially when containing more than one type of atoms. The description of the solid through empirical interaction potentials has at least two very serious drawbacks: the first is that, most of the time, this approach is unable to give quantitative predictions of formation and, especially, migration energies even for neutral defects, unless they are included in the fitting set [12, 13]; the second is that they cannot describe the different possible charge states of the same defect and its electronic structure.

In the previous paragraph we were referring to the most used forms of empirical potentials, based on formal charges, like Tersoff of Born-Meyer-Higgins type or similar. We should mention that, already more than 20 years ago, variable charge potentials were proposed that should be able to describe the polarisability of molecules and atoms in solids when their en-

vironment is modified; unfortunately this approach, which is in principle very promising, has not found satisfactory applications in defect physics, and also recent calculations of defect properties in an oxide were still object of debate [14, 15].

Other approaches, based on the tight binding method, are still being developed; a convergence between approximate, light basis sets, DFT calculations and DFT-based tight binding [16] can be observed in recent developments and applications, in order to be able to describe large systems at a reasonable price. The basis set error, for many common localised basis sets, is, however, not always under control.

The application of DFT to the prediction of the properties and energetics of point defects has now reached a mature state, where calculations are now routinely performed and limitations and strengths of the approach should be well known to practitioners. The description of bulk properties for many materials of interest is reliable to a good level of accuracy for structure and energetics, a level that would be sufficient, in many cases, for profitable applications to defects. In the following I will present an overview on the applications of DFT to defects in silicon carbide and silicon dioxide that I have been involved in since more than a decade, with focus not only on successes but also on failures that made clear that, in many cases, a higher level of theory is required to achieve reliable predictions. This is linked to the fact that reliable energetics, for point defects, cannot be disentangled with a reliable description of the electronic structure, not limited to the valence band structure of the perfect bulk.

The whole approach was guided by some basic questions, related to the description of the kinetics of insulating/semiconducting materials under irradiation. Can we predict the kinetics of materials under irradiation without being able to describe mass diffusion for a material at thermodynamic equilibrium? This question is of course rethoric in nature, and explains why the following of this document will try to answer other questions like: How equilibrium (self-)diffusion depends on experimental conditions (e.g., atomic and electronic chemical potentials, impurity concentration) in some specific, model, materials? And to which extent can we predict mass diffusion in non-metallic materials through the calculation of formation and migration (free) energies of point defects obtained within a given DFT approach?

1.2 From actual nuclear materials to model insulating materials

Materials science has slowly grown as an independent discipline pushed by the need for applications in several fields. Speaking of materials for nuclear applications (in both fusion and fission reactors), the number of constraints that determine which actual material can be used for a specific function is very large. First of all, materials are submitted to high neutron flux, which produces radiation damage and transmutation. The constituent atomic species of the initial material should be such that the transmutation products are not harmful, or not too long lived, or not too difficult to get rid of. Furthermore, for components of nuclear

fuel elements for fission reactors, the neutron absorption cross sections should be low enough, to allow the chain reaction to be sustained for a given reactor design. Another point that has not always been possible to take into account, but should not be overlooked, is the fact that the transmutation products (and fission products) should be accomodated in the matrix without producing phase separation or other potentially annoying material transformations.

Leaving aside nuclear reactions, irradiation by neutrons, but also by α particles, electrons or Γ-rays, produces a variety of defects, evolving on various timescales, from the few picoseconds of a displacement cascade, to seconds, years or thousands of years. Typical consequences are swelling, modification of the mechanical, optical, electrical and thermal properties of the materials. High concentration of native defects, together with pristine or added impurities, can lead to defect clustering, to the modification of the microstructure through grain boundaries and dislocations, irradiation induced corrosion, and to segregation of new phases.

Metals, and in particular iron as main component of steels, have been for long time the privileged playground for nuclear materials scientists. However, many insulators are present in the nuclear cycle, like UO_2 of PuO_2 for the fuel, other oxides or hydrides as unwanted corrosion products, various ceramic and glassy materials used as protective coatings or disposal matrices for nuclear waste.

Although experimental studies of irradiation effects on oxides, ceramics and other insulating materials have been performed since long time [17, 18, 19], the theoretical understanding is much less advanced than for metals. The obstacles partly explain this fact: fuel oxides present strong electron correlation and are solids for which common DFT approaches are inadequate. Nuclear glasses and many other ceramic matrices are structurally too complex to be directly described at a quantum level. However, very useful insights can be obtained by studying somewhat simplified or model material.

1.2.1 Two playgrounds: silicon dioxide and silicon carbide

The main component ($\sim$ 50%) of high level nuclear waste disposal glasses is silicon dioxide; SiO_2 is also very important for many other reasons, applied and fundamental. It can be considered a prototypical ionic-covalent insulating oxide, showing both crystalline and amorphous phases, and it is a crucial material for silicon based microelectronic devices, is an important component of earth's crust [20] and is present in our everyday life. The pure bulk is quite well described by standard DFT semilocal approaches, at least in its tetrahedrally coordinated low pressure phases. Due to the large bandgap, electronic excitations can produce large relaxations and even the production of defect pairs can be expected. For those reasons, a relevant part of my work, since my first contact with CEA, was devoted to this material, whose importance cannot be overlooked.

The second material to which will be devoted part of the following pages is silicon carbide; this wide band gap semiconductor is interesting for several reasons. From the point of view of nuclear materials, it is the

main ceramic material that has been used in a fission power plant; it was employed as a fuel cladding material in Helium-cooled high temperature reactors. A layer of SiC was indeed included in so called Triso [1]-coated fuel particles, as a diffusion barrier, in order to prevent the leakage of fission products and to contribute to the mechanical integrity of the fuel element. SiC is also considered as a structural material for fusion reactors.

As SiC is also an important functional material for high temperature/high frequency electronic devices, its point defects have been studied theoretically and experimentally since the sixties and with renewed interest since the end of the nineties, making it a natural benchmark to test our understanding of defects, diffusion and irradiation damage in binary semiconductors.

1. Tri-structural isotropic

2 Point defects from first principles: approximations and open issues

2.1 Basic framework

The phenomenological theory of diffusion, based on Fick equations, has found a theoretical explanation thanks to the statistical description of the random walk of particles, Brownian motion, as developed by Einstein and Smoluchowski at the beginning of the 20th century. The fundamental expression of the mean square displacement of a particle performing such random walk in a given time allows us to understand the microscopic meaning of Fick's diffusion in term of atomic jumps on a network of atomic sites [21]. The diffusion process, in absence of concentration gradients, can then be expressed in term of an isolated diffusing particle (the tracer), from which can be calculated the Fick's diffusion coefficient. The tracer can be a foreign atom, if we are talking of impurity diffusion, or an isotope of one of the costituents of the solid (we are then talking of self-diffusion); in the latter case, in particular, atomic jumps occur through point defects, for example vacancies or interstitials.

The tracer diffusion coefficient, in the limit of low defect concentration, can be written as

$$D^* = \sum_i g_i f_i a_i^2 c_i k_i \tag{2.1}$$

where i labels a defect and a jump mechanism, a_i is the hopping distance, g_i is a factor linked to the the jump geometry, f_i is the factor taking into account the correlation of successive steps, c_i the concentration of the defect i, and k_i the respective jump rate.

The calculation of the correlation factor f_i can be non-trivial [22] for certain diffusion mechanisms, although in many simple cases it is a quantity of the order of 1 and, as such, not crucial in comparing theoretical and experimental activation energies.

In principle, the sum in 2.1 runs over all defect types able to contribute to the transport of a giver tracer, be they usual point defects (vacancies, interstitials, antisites), but also defect clusters, defect complexes, as well as coordination defects or distortions of the crystalline network induced by electronic excitations.

The basic assumptions allowing a practical implementation of formula 2.1 are low defect concentrations and transition state theory through the Eyring equation [23] to express jump probabilities.

The temperature dependence is mainly included in these two last quantities, concentrations and jump probabilities, which take the form of Boltzmann exponentials:

$$c_i = \exp\left[-\frac{{G_f}^i}{k_B T}\right] \tag{2.2}$$

$$k_i = \frac{k_B T}{h}\exp\left[-\frac{{G_m}^i}{k_B T}\right] = \Gamma_0^i \exp\left[-\frac{{H_m}^i}{k_B T}\right], \tag{2.3}$$

where $G^i_{f/m} = H^i_{f/m} - TS^i_{f/m}$ is the formation/migration free enthalpy, h is the Planck constant. Equivalent expressions, which look somewhat different and contain an attempt frequency ν_0, can be found [22]; the very difference resides in the definition of the migration entropy (S_m, H_m being the enthalpy) which depends on the choice of ν_0 [24].

The key parameters, in these expressions are the free enthalpies (or Gibbs free energies) of formation and migration for the i-th defect species. Their sum is called the activation free enthalpy: $G_{act} = G_f + G_m$.

The second exponential (eq. 2.3) comes from considering quasi-equilibrium at transitions states. This implies some assumptions, like the neglect of quantum tunnelling. The meaning of G_m is essentially the difference between the Gibbs free energies of a system at two different points of a path in a multi-dimensional space. The really limiting factor, for calculating it from first principles, is to devise a way to obtain meaningful paths in the multi-dimensional landscape with the least number of points.

The origin of the definition of G_f in 2.2 deserves a few remarks. The equilibrium state of a solid stems from the minimisation of its Gibbs free energy including defects. The defect contribution, for sufficiently low (and homogeneous) concentrations, can be written as a sum over defect species $G_{def} = \sum_i N_i {G_f}^i$, where N_i is the number of defects of type i and ${G_f}^i$ is the raise in the free enthalpy by the presence of one defect. For a metallic AB ordered compound, for example, the formation free enthalpy of a defect with a missing A atom (e.g., an A vacancy) can be written as

$$G_f^{V_A} = G^*_{(N-1)_A+N_B} - G_{N_A+N_B} + \mu_A \tag{2.4}$$

This is practically the way formation energies are obtained from first principles calculations, where G^* is the free enthalpy of a supercell containing a specific defect configuration, G is that of the undefected crystal and μ_A the appropriate chemical potential of the A species. The subscript of the supercells free enthalpies give the numbers of atoms of type A and B in the supercell.

As long as the solid contains more than one type of atoms, the treatment in the grand-canonical ensemble (through the use of chemical potentials) is necessary in order to take into account the fact that, even at low concentrations, the specific parameters for one defect species (formation energy, formation entropy and formation volumes) depend on the actual concentrations of the others [25].

As clear from the expression 2.4, if we want to calculate formation free enthalpies in a coherent way, we need not only large supercells containing a defect, but also reliable reference states, whose energy gives us the chemical potential. In the field of semiconductor science it is customary to take chemical potentials as free parameters, that can vary in a relatively restricted range. However, if one wants to compare concentrations or diffusion coefficients to experiments, one should recall that chemical potentials are indeed fixed by experimental conditions. One can cite here the case of an oxide, whose oxygen reservoir can be either a surrounding oxygen-containing athmosphere, or the oxide itself, or an interface with another oxide, or liquid water, only to cite some possibilities. The equilibrium concentration of defects (and thus the self-diffusion constants) in that material is determined by the rate constant characterising the reactions that can lead to the formation of the defects.

Let us compare two cases, that we will discuss later for silicon dioxide: the (heterogeneous) reaction with gaseous oxygen and the (homogeneous) formation of oxgen defects in a closed system. In the latter case only defects that keep the stoichiometry can be formed; then the reaction to form a vacancy (V_O) implies, for example, the formation, at the same time, of an interstitial (I_O) at another oxygen lattice site (O_x); we form thus a Frenkel pair through the reaction:

$$2O_x \rightleftharpoons V_O + I_O \Rightarrow c_{FP} = \exp\left[-\frac{G_f^{V_O} + G_f^{I_O}}{k_B T}\right] \tag{2.5}$$

In this case the expression turns out to be independent of the oxygen chemical potential, which is fixed by the mass conservation condition.

If we neglect clusters, antisites, and other defect complexes, the concentrations of isolated vacancies and interstitials are bound to be the same, as for electrons and holes in an intrinsic semiconductor [26]: $c_V = c_I = \sqrt{c_{FP}}$.

Conversely, if vacancies are formed by exchange of oxygen atoms with another phase (a gas of O_2 molecules) then the formation reaction to be considered is $O_x \leftrightarrow \frac{1}{2}O_2(\text{gas}) + V_O$.

The formation free enthalpy, $G_f^{V_O}$, depends then on the oxygen chemical potential, i.e., the Gibbs free energy of an oxygen molecule at given temperature and partial pressure. Even if one neglects the vibrational and rotational contributions to the free energy (-TS^{vib} and -TS^{rot}) there is one part that, for a gas, cannot be neglected, that is the translational contribution to the free energy, -TS^{tr}, which can be expressed by the Sackur-Tetrode formula. This leads to the following dependence for the concentration:

$$c_V \propto \exp\left[\frac{S_{O_2}^{tr}(p_{O_2})}{2k_B}\right] \quad \text{where} \quad S_{O_2}^{tr} = -k_B\left[\log(cost \times p_{O_2} T^{-\frac{5}{2}}) + \frac{3}{2}\right]; \tag{2.6}$$

A hint on the respective weights of entropic contributions in the formation entropy is given by the calculated values for an oxygen vacancy/interstitial in quartz as shown in Fig.2.1.

Whatever the reference state, it is necessary to check that the errors on the reference states are not orders of magnitude higher than for the defect supercells. For example, when taking atomic oxygen as a chemical

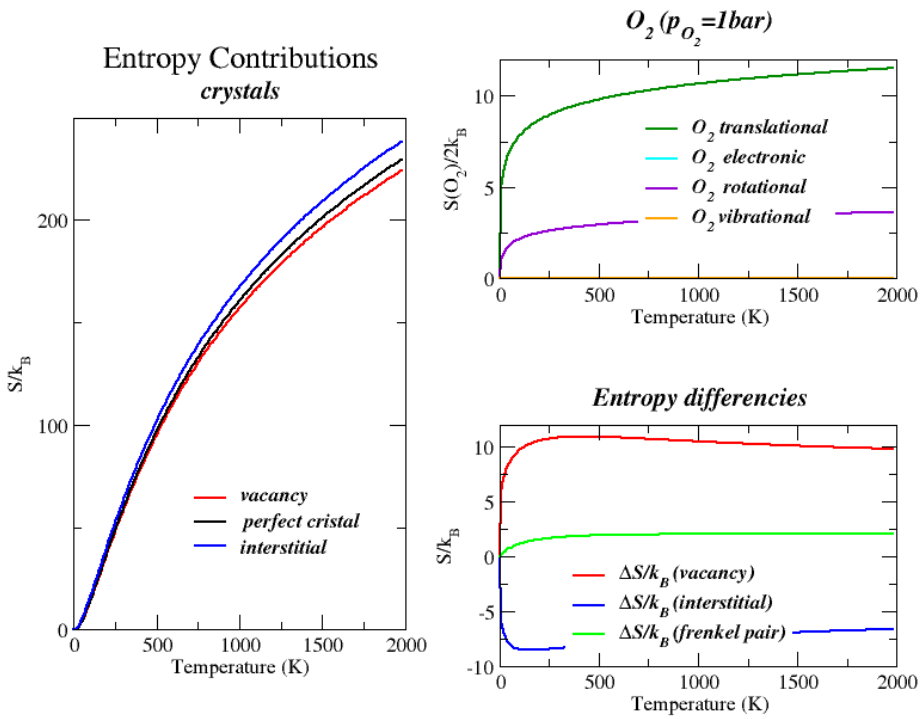


Figure 2.1 – *Various entropic contributions to the formation entropy of oxygen vacancies and interstitials in α-quartz. Left panel: vibrational entropies for a supercell containing a defect or not. Right upper panel: Contributions to the entropy of an oxygen molecule (at $p_{O_2} = 1$ bar). The electronic and vibrational contributions are negligible with respect to the rotational and configurational ones and for this reason are almost superimposed on the x axis. Right lower panel: Vibrational entropies of formation for oxygen vacancy/interstitial and for a Frenkel pair.*

potential —supposing one deals with an experimental situation in which atomic oxygen is the dominant species— the choice of the DFT functional is a more sensitive issue than for molecules or for O in a solid [27]. In general, when dealing with impurities in a material, it is wise to check that the calculated formation enthalpies of compounds of the impurity with the host atoms are reasonably well reproduced by the level of theory that we are using. As an example, in [11], a reasonably good description of Pd_2Si was a prerequisite [28] for trusting solution energies of Pd in SiC.

The calculation of formation, or migration, *free enthalpies* in most cases reduces to the calculation of formation *energies*, meaning that the TS term is neglected, as well as the PV term. The latter, although frequently indeed small, can easily be included by calculating formation energies at constant pressure P=0. We should also mention the fact that one could also work exclusively at constant volume, because a thermodynamic relation connects the Helmholtz formation free energy at constant volume with the Gibbs formation free energy at constant pressure [29]; however, a problem arises when one tries to calculate the formation entropy at constant volume for a defect in a compound, because of the reference chemical potentials of the elements by which it is constituted; it is not clear whether the workaround proposed in ref. [30] is reliable and follows a rigorous approach.

As far as entropic contributions of the solid are concerned, most of the time they are simply neglected. The most important contribution, at least for non metallic materials, is the vibrational entropy of formation, which can be calculated from the phonon dispersions of the crystal with and without defects, and from those of the reference states. The direct calculation of the vibrational entropy from first principles is possible, and has been proposed since the first applications of DFT to point defects [31, 32], but adds a considerable workload. The question arises whether this contribution can be estimated in an empirical way, at least to estimate the error that one commits by neglecting it. Two options are the Zener empirical formula and the Meyer-Neldel rule, that will be briefly discussed in connection with results obtained for silicon carbide (Sec. 4.1.1).

As a last comment to this section on general properties of point defects, we remark that, for many semiconductors or insulators, the formation energies of defects are in general larger than energy barriers relevant for diffusion; the consequence is that, at equilibrium, the entropic contribution represent a small amount on large activation energies which are, by the way, also burdened by other sources of errors. Conversely, when discussing processes occurring out of equilibrium —and in particular materials under irradiation— the migration energies are much smaller and the role played by the entropic contribution to free energy barriers can be much more important, and its omission is less justified.

2.2 Charge neutrality and the Fermi energy

In a dielectric material, point defects can, apriori, trap charges and thus assume different charge states. Then, the formation energy includes an interaction energy with an average potential. As a starting point let us take as a reference the Fermi level of an undefected crystal (conventionally at midgap at T=0), so that we have to add to the right member of equ. 2.4

the term Q(VBT+$E_{gap}/2$), where Q is the net charge of the defect and VBT the valence band top.

The long range Coulomb interaction between (more or less) localised charges and their potential has to be included in the free energy of the system, which now reads:

$$G_{def} = \int_V d\mathbf{r} \left[\sum_i n_i(\mathbf{r}) {G_f}^i + \frac{1}{2}\rho(\mathbf{r})\Phi(\mathbf{r}) \right] - TS_c \tag{2.7}$$

where n_i is the space dependent concentration of defect i, ${G_f}^i$ its formation free enthalphy, ρ the contribution to the charge density by the defects —i.e., $\rho(r) = \sum_i n_i(r)Q_i$, where Q_i are the defects net charges— and Φ the corresponding potential. V is the crystal volume, S_c the configurational entropy and T the temperature [33]. The expression for equilibrium concentrations results from the minimisation of 2.7. In some cases, namely for alkali halides, one can reduce the number of relevant defect species to two, having opposite charges ± 1. Then the variational minimisation of 2.7 leads to a Poisson-Boltzmann problem [34], with the following solutions:

$$n^+(\mathbf{r}) = N \times \exp\left[-\frac{{G_f}^+ + e\Phi(\mathbf{r})}{k_B T} \right] \tag{2.8}$$

$$n^-(\mathbf{r}) = N \times \exp\left[-\frac{{G_f}^- - e\Phi(\mathbf{r})}{k_B T} \right] \tag{2.9}$$

Here, as we said, concentrations are considered space dependent, and one can define specific boundary conditions. For example, these equations can be used to find the spatial variation of defect concentrations in specific geometric conditions, as in the case of an interface between two different dielectrics. This is indeed what was shown by Kliever and Köhler in ref. [33], where they also show that, far from the interface, concentrations can be written with a space independent Φ_∞ which corresponds to the average potential inside the solid and enforces the neutrality of the system. If we consider an infinite solid, spatial variations of concentrations are not determined by boundary conditions, but only by statistical fluctuations; we can then average out the spatial degrees of freedom and find that the constant potential enforcing the neutrality of the system is the one entering the expression for average concentrations. Using this average potential, that we recognise as the modification of the Fermi level induced by defects, $\Delta\mu_e$, average concentrations are then written, as usual, as Boltzmann exponentials in which the formation energy, $\tilde{G_f^i}$, depends on $\Delta\mu_e$:

$$\tilde{G_f^i}(Q) = G_f^i(Q) + Q_i \times \Delta\mu_e$$

where we remind that G_f^i(Q) depends on the choice of the reference Fermi level made at the beginning of this section.

What actually fixes the value of the Fermi level in an insulating material, depends on many factors. In semiconductors, in many cases, it is fixed by doping, i.e., by the concentration and type of impurities. If the level of impurity is sufficiently low (intrinsic semiconductor), then the Fermi level is fixed by the concentrations of holes in the valence band and

of electrons in the conduction band, which can be expressed by an approximated formula based on valence and conduction effective masses, whose limit for T$\rightarrow$ 0 gives midgap [26]. This comes from the fact that the formation energy of native defects is higher than the bandgap; if this is not the case, then intrinsic semiconductors are mimicked by so called compensated semiconductors, where the concentration of donors and acceptors are tuned in such a way as to pin the Fermi level at midgap.

In ionic insulators like alkali halides, the most abundant native defects pin the Fermi level somewhere inside the bandgap. For example, for NaCl, the members of the Schottky defect, V_{Na}^{-} and V_{Cl}^{+}, have relatively low formation energies, and pin the Fermi level. The distance of μ_e from midgap is $\Delta\mu_e = \frac{G_f(V_{Na}^{-})-G_f(V_{Cl}^{+})}{2}$. In this specific example the two formation energies are very similar [35], so that the Fermi level is, again, close to midgap.

In the general case, however, it is the interplay of point defects and charge carriers (electrons and holes) that determines the position of the Fermi level in the bulk of a solid, through the neutrality equation:

$$p_v(T,\mu_e) + \sum_i n_i(T,\mu_e)Q_i - n_c(T,\mu_e) = 0 \tag{2.10}$$

where p_v are holes in the valence band, n_c electrons in the conduction band, and n_i are the concentration of defects of charge Q_i (i running on all native defects and impurities). If applicable, equation 2.10 can be coupled to the analogous equation enforcing mass conservation, as formation energies depend also on atomic chemical potentials (an example is given in ref. [36]). If no impurities are present, the solution of 2.10 accounts for the *self-doping* of a material. This is how was determined the self-doping effect in quartz [37], using first principles formation energies in 2.10 .

Here we talk of bulk systems, where the influence of surfaces, interfaces, grain boundaries or dislocations is considered to be negligible. For thin films or nanostructures the role of surfaces and interfaces and the charge accumulated on them has to be considered.

It is interesting to remark that an important cause of the accumulation of charges at interfaces comes precisely from the matching, at the interface, of the electronic chemical potentials of the two respectives bulk sides, and depends directly on the formation energy of native defects (and the concentration of impurities) on each side of the interface [33].

2.3 Point defects and periodic boundary conditions, a brain teaser

The theory of diffusion previously sketched is based on the hypothesis of low concentration of the involved defects. The goal of describing an isolated defect with first principles calculations is limited, first of all, by the number of atoms that one can describe. Two main approaches have been pursued, the cluster approach, with open boundary conditions, in which a bunch of atoms in a solid are described as a molecule as large as possible, containing a point defect in its centre. The other, that has the advantage of avoiding arbitrary chemical and geometrical conditions

on the surface of the cluster, is the supercell approach; the latter relies on periodic boundary conditions and has certainly been favoured by the advantages of plane waves basis sets.

However, the use of supercells with periodic boundary conditions implies the unwanted interaction between periodic images of defects, which is a difficult problem to cope with, for several reasons, especially for charged defects:

- 1) The energy of a periodic arrangement of N charged periodic units of volume Ω is diverging in the thermodynamic limit ($\Omega N = V \to \infty$).
- 2) The analogous sum for neutral cells is still conditionally convergent
- 3) The defect charge (i.e., the difference between the charge density of the supercell with and without defect) can have different degrees of localisation for different solids/defects
- 4) The calculation of the formation energy relies on the energy difference between supercells with and without the defect, that should refer to a common zero of energy [38]

Issue number 1) is solved by introducing a compensating uniform background, which practically means omitting the G=0 terms of: the Hartree contribution (el-el interaction), the G-space contribution in the Ewald sum (ion-ion interaction), and the electron-ion interaction energy associated to the local part of the pseudopotential (this omission gives rise to the so called Z-α term of the electron-ion interaction; see, e.g., [39] p. 163).

The second point is related to the fact that, even with the addition of the uniform background, the result of the infinite Coulomb sum is not absolutely convergent, but only conditionally convergent, and the results depend on the way the limiting surface is extending to infinity [40, 41]. Moreover, if a term coming from dipole interactions were not neglected, the energy of the periodic solid would also depend on the choice of the origin of the supercell [42].

The first proposal to correct for the electrostatic interaction of an array of point charges with a neutralising background [43] is still widely followed, sometimes with the addition of a quadrupole term [42]. The problem is that it is based on the assumption that the defect charge is essentially a delta function. If this is not the case, this correction will seriously overestimate the interaction energy, which has indeed been shown in selected cases [44, 45]. For this reason other corrections schemes, based on countercharges of different shapes, have been proposed [46, 47]. Let us make a further remark: the Madelung correction term, in the limit of point charges, is free from any self-interaction, whereas the latter is not fully removed from DFT calculations with the computed charge density.

A lot of debate, in recent years, has arisen around these corrections [44, 45, 48] and some new or improved solutions have been proposed [46, 47, 49, 50, 51], however it seems that no simple solution has yet gained the preminence. As many authors recognised, the interaction of charges cannot be considered independently from the change of the average potential induced by the addition of the defect (with or without a net charge). But only very recently it was clearly stated that the average poten-

tial shift contains indeed contributions from the electrostatic interactions and that double counting has to be avoided [51].

This potential shift could in principle be evaluated by the calculation of the macroscopic average of the potential [52], but, in most cases, attainable supercell sizes do not contain really bulk like regions, especially for large band gap solids, showing wild charge oscillations and low screening. Moreover, symmetry lowering distortions make the recognition of true bulk like regions even harder. The choice that I made, for the results presented here, was to determine the potential alignment through matching of the electronic densities of states (eDOS). This was done by making a spline interpolation of the gaussian broadened eDOS for the defected and undefected supercell, and minimising the mean square error of their difference (or, equivalently, maximising their overlap). Providing that coherent **k**-point sampling are used, and that well relaxed structures are compared, the procedure is robust and independent of the chosen broadening and eDOS energy range. An example of alignement is shown in Fig. 2.2.

Would it be possible to align on some deep levels? This has been indeed suggested as another option, but one has to be careful that if the defect charge is truly localised (and the atomic positions are not relaxed) the deep level can be splitted by the difference in Coulomb energy induced by the variation of the distance between the defect charge and the various atomic sites at which the deep level can be located [51]. As we calculated the alignment only for fully relaxed structures, the alignement of the full DOS is essentially equivalent to the alignment of the deep levels (as can be seen on Fig. 2.2).

In previous works the choice of the potential alignment was not always the same. Here, as clear from Fig. 2.2, the value of ΔV is the one that brings the bulk eDOS onto the defect one. In the example ΔV=+0.53 eV, which appears in the formation energy as $+Q\Delta V$. Then, in this case, it raises the formation energy, as for the Madelung correction. This is the case in most of our results, at least in all vacancies and interstitials in quartz, where all obtained potential shifts have the same sign as the charge of the defects. A graphical sketch of this is shown in Fig. 2.3, where the energy corrections coming from the potential shift are compared with the monopole Madelung term calculated for a 72 atom supercell.

Our choice for the sign of the potential alignment, the opposite of what suggested by Taylor and Bruneval [51] but coherent with other papers cited in it, comes from the fact that we were not adding the Madelung electrostatic correction. However, in the light of ref. [51], this is only partly justified, as the electrostatic term contained in the potential alignment is the double of the Madelung correction.

The results are relaxed with respect to atomic positions and supercell volume. Elastic effects are also present, so that relaxing or not the atomic positions and the supercell volume, means that a part of the interaction energy that one would call electrostatic (for example the mentioned splitting of a deep level according to the distance to the defect [51]) in the unrelaxed structure, would be commonly called elastic energy in the relaxed system. It is needless to say that the label *elastic* or *electrostatic* comes only from the model in the framework of which these energies are calculated.

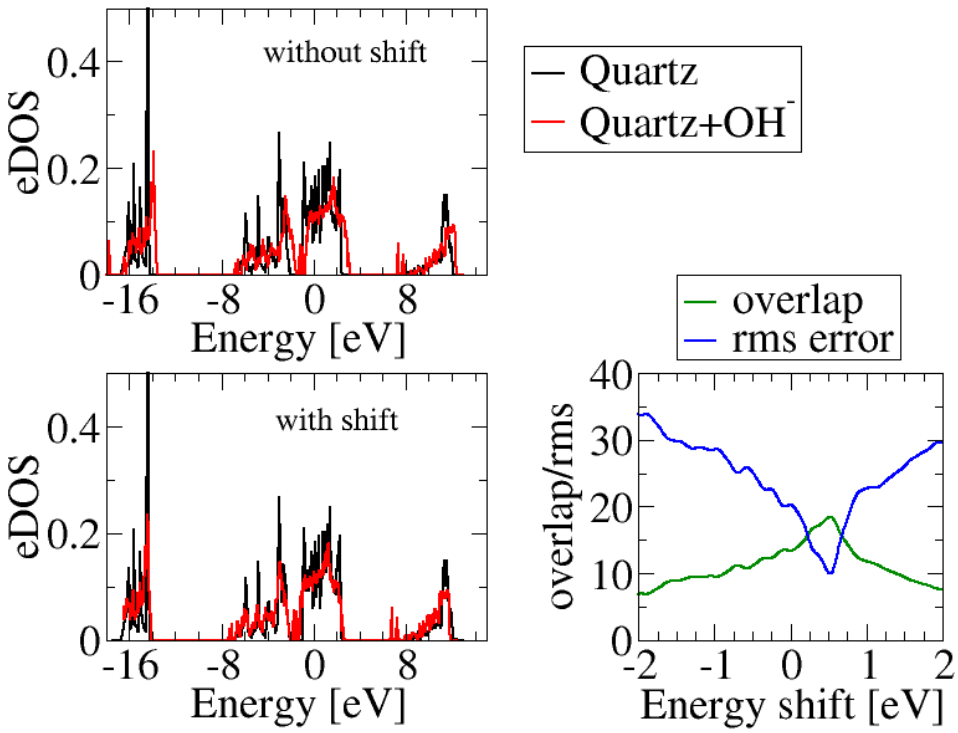


Figure 2.2 – *An example of potential alignment through the matching of electronic density of states (eDOS). Upper left: the raw eDOS of two quartz supercells, one with no defects (black) the other with an OH^- interstitial group (red). Lower left: the same except that the eDOS of the supercell with the defect has been shifted to match the undefected one. Right panel: A measure of the matching accuracy, through the overlap of the two eDOS or through the rms of their difference. The calculated potential shift is 0.53 eV.*

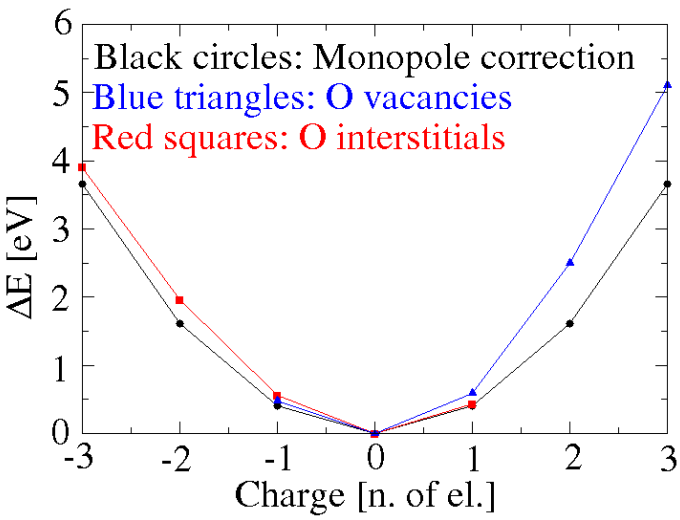


Figure 2.3 – *The comparison of potential alignment correction for oxygen vacancies and interstitials in quartz in several charge states and the Madelung monopole electrostatic interaction term.*

2.4 Standard DFT and more advanced approaches

In the last few years the discussion on the most adapted approach to describe defects in insulators has considerably grown [53, 54]. In particular, although most of the first principles calculations of defects in the last two decades were based on semilocal functionals, like LDA or various GGA flavours —this is what we mean by the *standard* approach—, it appears more and more clearly that, in many cases, such results have to be taken with care and thoroughly reevaluated through the lens of more advanced approaches.

LDA or GGA?

Almost all the results discussed in the following have been obtained with the LDA functional. It is worthwile to add a few words to justify this choice, for SiC and SiO_2, with respect to the nowadays widespread use of gradient corrected functionals of different flavours. For the bulk properties of the various polytypes of silicon dioxide a thorough comparison of LDA and GGA [55] had shown that the LDA gives better structural properties than the GGA and predicts the correct relative stability for all tetrahedrally coodinated phases, which is not true for the GGA. The latter, however, describes correctly the high pressure phase stability, for which the LDA fails. On this basis it is not clear which one is better for point defects, as defects can imply positive or negative local stresses. In practice, the results for which we can compare are very similar. The migration energy of the neutral oxygen interstitial is 1.3 eV with GGA [56], to be compared to our 1.2 eV [57] (1.4 in a larger supercell [58]); the difference could well be due more to the details of the calculation (pseudopotential, cutoff, supercell size) than to the functional itself. The charged oxygen interstitial migration for Q=-1 and Q=-2, calculated by Jin and Chang with GGA [59], are 0.27 and 0.11 eV respectively, to be compared with 0.10 and 0.37 [58] found with LDA. The formation energies are also close, although slightly lower for the LDA (1.8 *vs* 2-2.1 eV for GGA) and the problematic 0/-2 charge transition level, as far as it can be estimated from the plot in ref. [59], is very close to our result. The claimed difference in the oxygen vacancy formation energy between LDA and GGA [27] is actually entirely due to the difference in the *atomic* reference: if the formation energy is referred to the oxygen molecule (a more sensible reference state), the two results become very close.

As far as silicon carbide is concerned, the choice of the LDA has been made by most of the groups active in the field of defects calculation and does not seem to have been the subject of controversies. In the cases where a comparison has been made [60], the differences do not seem to be larger, on average, than the discrepancies between existing LDA calculations [61].

As a last remark, the band gap, whose underestimation affects the position of several defect levels, is practically identical between LDA and GGA in quartz (5.8 eV with PBE [62] *vs* our 5.75 eV), as well as for β-SiC (1.34 eV with LDA *vs* 1.40 eV with PBE, and the difference is even smaller at fixed geometry). It seems then that there are no premises for a systematic improvement of defect formation/migration energies and/or charge transition levels by a gradient corrected functional in silicon carbide and silicon dioxide.

Actually, warnings on the limitations of the LDA approach for the descriptions of the electronic structure of defects, had appeared since the

first applications [63] [1]; however, the method has been largely used to shed light on defect levels in semiconductors. Much later came the awareness that the band gap issue, and consequent errors on the position of defect levels inside the band gap, could have an influence on calculated total energies. A clear indication came out with the case of the Al impurity in SiO_2, for which the symmetric equilibrium structure predicted by LDA/GGA calculations (but also by the B3LYP hybrid functional) turned out to be wrong due to the unphysical self-interaction [64, 65]. Why the energetics of a native defect, in a material for which DFT gives a good description of the ground state properties, including linear response, should be affected by significantly larger errors? Why couldn't one trust the thermodynamic charge transition levels (tCTL), which are issued from ground state calculations, in materials like silicon, carbon, binary semiconductors like SiC or those of the III-V family, or silicon dioxide?

The reason is, in my opinion, essentially related to the localised nature of point defects and the incomplete removal of self-interaction. Indeed the charge of a defect (in the sense mentioned in the previous chapter 2.3) can be so much localised that the residual self-interaction, not canceled in standard semilocal approaches of DFT, becomes unphysical; in this case a DFT optimisation may end in a more delocalised electronic configuration, which will falsely appear as lower in energy. However, a simple model based on the exchange energy alone is not sufficient to predict the behaviour of different defect levels [58].

The prediction of defect levels affects the prediction of total energies. Even in the case that, say, the neutral state of a defect is correctly described in terms of charge distribution and formation energy, its stability has to be assessed in comparison with other charge states, whose description is not necessarily as good. The fact that the LDA or GGA approximations (but to a certain extent also hybrid functionals [66]) do not respect the linearity of the energy with orbital occupation [67], influences the positioning of defect levels (corresponding to *vertical* transition levels, or vCTL, due to the Janak's theorem) and thus of total energies. How to correct for these effects? Some solutions were already proposed long ago, in the spirit of the scissor correction for the band gap, and consisted in evaluating the amount of scissor correction to be added to a given defect level on the basis of the projection of the corresponding wavefunction on the valence/conduction manifolds [68]. Similar correction schemes have been reviewed recently [48], but the reliability of such empirical approaches is not clearly established.

Two directions are emerging: hybrid functionals and many body techniques. The first has the advantage of naturally providing total energy and forces. The main drawback is the somewhat arbitrary portion of Hartree-Fock (HF) exchange in the xc functional; the evolution towards tuning this fraction to the current material (and/or problem?) [69] underlines the empirical side of the approach. Many body techniques like the GW approximation, on the other hand, provide a more rigorous description of

1. One can read in this early paper by Baraff and Schlüther: "We are aware that localized states, such as those associated with a vacancy, might possibly give rise to specific correlation effects and multiplet structures which lie beyond the single-particle approximation we are using here."

the screening and dynamical correlation effects, but the direct calculation of total energy and forces, in the framework of the Random Phase Approximation (RPA) is still in its infancy [70]. Most common applications of the GW approximation are based on the perturbative one shot scheme, G_0W_0, relying thus on LDA or GGA wavefunctions; but this approach can be in trouble when the LDA/GGA description of the wave function is not satisfactory. Possible solutions are the use of hybrids as a starting point for the perturbative calculation [71] or a self-consistent approximated many body approach (like COHSEX) on which to perform the one shot GW calculation [72].

Both the hybrid functionals and the GW (even the G_0W_0) are presently computationally still very demanding and, as such, difficult to apply systematically to the description of point defects.

2.5 Following slopes in energy landscapes

A crucial point in understanding diffusion at the atomic scale is detecting jump trajectories and the associated energies. These are, actually, paths in the 3N-dimensional space spanned by the 3N coordinates of the atoms of the supercell used to describe the defect. The search of paths and saddle points of a function of 3N variables (the energy) is a formidable task, especially when the calculation of the function itself is a time consuming task.

Even with automatic methods, meant to extensively explore an energy landscape, like the Activation Relaxation Technique [73], the finding of the relevant saddle point is not given in advance. When these techniques are not applicable, as it is frequently the case for large supercells described by DFT, one has to rely on symmetry arguments and intuitive tentative paths as a starting point for path optimisation.

When using the Nudged Elastic Band [74, 75] (NEB) method, for example, the outcome depends on the starting path, which is generally obtained by linear interpolation between two points in the 3Nd space. Even the choice of the arrival point is a clear bias in path search. For this reason I used the NEB method mostly for cases for which the symmetry of the system and/or previous works were suggesting a determinate path.

The use of constrained relaxations is more flexible, although sometimes more time consuming and, in cases when the chosen constraint is not appropriate, leading to a setback. A very flexible constraint that I have used in several works is a generalisation of the one proposed long time ago by C. H. Bennett for describing atomic jumps in an FCC lattice [76]. After realising that this reference alone was leading to discussion between colleagues about the real nature of the constraint, and especially about its relation to the so-called "drag-method", I decided to describe it in detail in a paper on Frenkel-pair recombination in silicon carbide, where it had been extensively used [77]. The essence of the method is that, as in the "drag-method", an atom is *pushed* in a given direction by letting all the other atoms relax; but the additional freedom is given by the possibility of modifying the direction along the path, turn around obstacles, and not being bound to a given arrival point, which makes the method more adapted

to low symmetry, flexible networks, like the one of silicon dioxide. A disadvantage is that paths look sometimes abrupt, i.e., the sampling points are not chosen according to the nature of the path itself.

The variety of possible paths could be taken into account by path sampling approaches [78], which would, however, considerably burden the study of migration barriers. As far I know this method has not yet been applied to point defects in solids with an ab initio description. Another approach consists in a biased sampling of phase space by constrained first principles molecular dynamics, which keeps full account of anharmonic processes. Another promising approach, that samples the potential energy surface on the basis of some well chosen biasing functions keeping some memory of previously explored paths, is the *metadynamics* [79], which also includes the full anharmonicity of the atomic vibrations. A simpler approach, is to rely on the quasi-harmonic phonon frequencies to add the vibrational contribution to the free energy. This point will be discussed in chapter 4, devoted to silicon carbide.

3 Silicon dioxide: native defects and self-diffusion

As surprising as it may seem, in spite of the importance of SiO_2 in several domains, the knowledge about the self-diffusion of its very constituents, silicon and oxygen, is still very partial. Experimental results are relatively numerous, but, at least at first sight, they do not always agree with one another, both on the order of magnitude of the self-diffusion coefficient and on the activation energies. This is evident from the the variation on the results on oxygen mobility in silicate glasses as summarised in the the review by Lamkin and coworkers [80, 81, 82]. The situation is slightly clearer for silicon self-diffusion, although the identified variation of the self-diffusion coefficient with sample thickness is not clearly explained. The scattering of self-diffusion data for silicon and oxygen leads to two suggestions: the first is that, to interpret them, a broader theoretical framework is necessary; the second is that experimental conditions may differ between different experiments that seem similar and that some parameters have not been sufficiently kept under control. A further remark is necessary: the charge of species is in general not discussed in the interpretation of experiments, maybe considering a formal charge Q=-2 for oxygen species and Q=+4 for silicon. Ionic conductivity in quartz and silica is generally attributed to alkaline impurities [83].

3.1 Oxygen self-diffusion: a starting point

The results cited by Lamkin [80] concerning oxygen self-diffusion span activation energies between 0.9 to 4.7 eV. The highest value can be taken apart, as concerning a sample capped with Si_3N_4; the latter is a diffusion barrier for athmospheric oxygen, employed in order to monitor only the contribution of network oxygen (self-diffusion in closed conditions). However, also other results feature relatively high activation energies (see for example Ref. [84], 3.1 eV). Experiments giving the lowest activation energies, close to 1 eV, are probably measuring the diffusion of oxygen *molecules* through the SiO_2 network [85, 86], as this regime is supposed to be dominant for partial pressures close to 1 bar [87]; but even in this case it is not clear if the charge of the diffusing molecules is neutral or negative. However, at the end of the nineties the question of the charge state was not even clearly asked.

From the theoretical point of view, many informations were already known on defects, for example about the configurations of the oxygen vacancy in the neutral and +1 charged states and their identification as the E′ centre through EPR [1] (see [88] for a review), and also some formation energies for neutral defects [89, 90, 91]; the focus was clearly on the vacancy and with no much interest for diffusion properties. Only a notable paper, by Hamann, was addressing the problem of diffusion and showing that neutral oxygen dumbells should play a major role [56]. However, nothing was known on the migration energy of vacancies. Valence alternation pair (VAP) defects had been proposed [92], but no first principles studies were available for them.

Several questions were then open at the end of the nineties concerning oxygen self-diffusion: is the mechanism of self-diffusion a vacancy or an interstitial one, or in what condition is one or the other? In which regimes is molecular diffusion dominant? What are the differences between the crystalline and amorphous forms of SiO_2? Which is the contribution of VAP defects to self-diffusion? Futhermore it became rapidly clear that other important questions were: what are the charges of the defects mediating diffusion? What controls charge compensation and the Fermi level? What is the influence of impurity levels (especially OH) on oxygen self-diffusion? These questions guided the work that gave rise to the results summarised in the rest of the chapter.

3.2 Oxygen self-diffusion: achievements and open questions

3.2.1 Neutral defects

At first the focus was on neutral defects and the goal was to evaluate the respective contribution of vacancies and interstitials to oxygen self-diffusion in a coherent model. For a meaningful comparison, the calculation of formation and migration energies of oxygen vacancies and interstitials had to be undertaken on the same footings. The results lead

1. Electron Paramagnetic Resonance

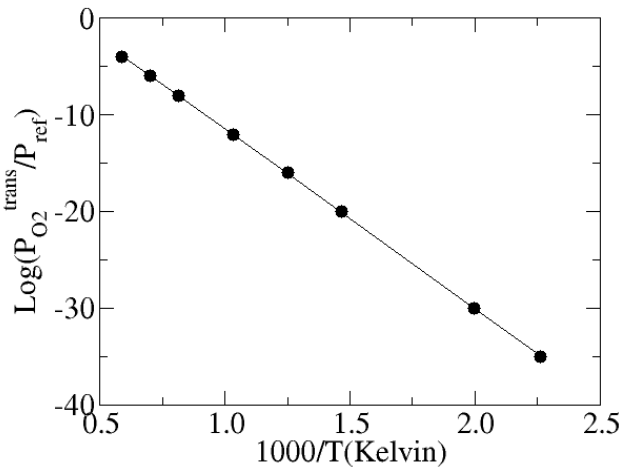


Figure 3.1 – *The transition partial oxygen pressure at which the oxygen vacancies and interstitials have equal concentrations. The vibrational entropies of formation of the defects have been taken into account. (P_{ref}=1 bar).*

to the results presented in [57]. The most important result of this paper is the prediction of the relative contribution of vacancies and interstitials to self-diffusion as a function of the oxygen partial pressure (for an open system) and the explanation of the higher activation energy found by Mikkelsen [93] (for a capped sample, i.e., a closed system) as the contribution by the interstitial side of a Frenkel pair. A notable ingredient for this outcome was the migration energy of the neutral oxygen vacancy (3.2 eV), unknown until then.

The contribution of the vibrational entropy to the free energy of formation had to be estimated, which lead us to the use of linear response phonon calculations to account for the vibrational entropy; the contribution to the free energy is small, but has a non-negligible influence on some parameter that one can calculate, namely the transition pressure (we mean here "oxygen partial pressure") at which vacancies and interstitials have equal concentrations. We show this quantity as a function of the inverse temperature in Fig. 3.1. The awareness of these regimes driven by the oxygen partial pressure allowed us to estimate the frozen-in disorder in samples according to their preparation conditions *before* the diffusion annealings. In the case of Mikkelsen experiment, for example, the sample was annealed in vacuum before the Si_3N_4 capping. From our results we could estimate the corresponding defects supersaturation and its influence on the subsequent diffusion annealing. The measured activation energy is expected then to present a change in slope, which is shown in Fig. 3.2. The fact that this elbow was not observed by Mikkelsen is readily explained by the temperature range in which the measurements were performed.

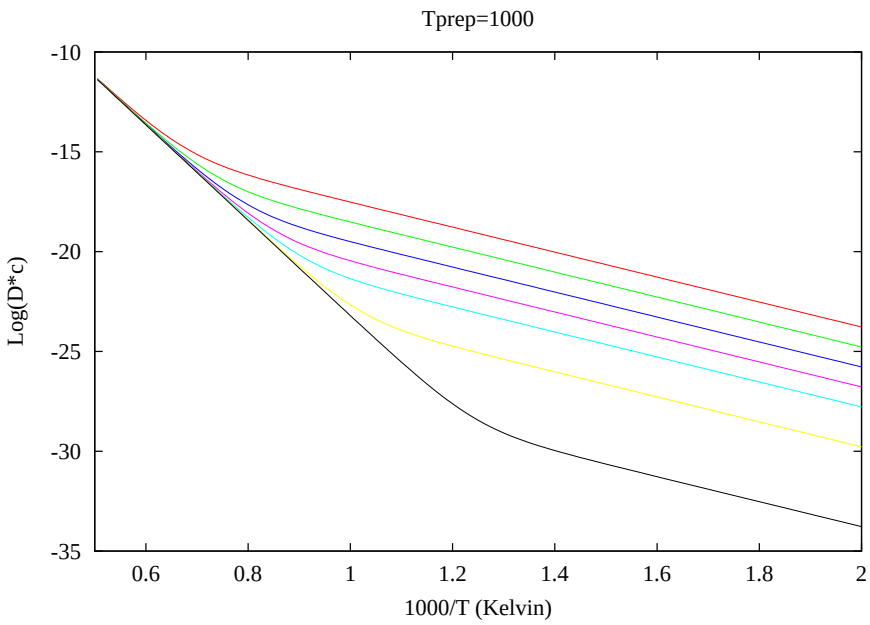


Figure 3.2 – *The expected inflection in the activation energy for oxygen self-diffusion on a sample prepared at 1000K and various oxygen partial pressures, then capped before the diffusion annealing. The pressures, in bar, are 1 (red), 10^{-2}, 10^{-4}, 10^{-6}, 10^{-8}, 10^{-12}, 10^{-20} (black).*

3.2.2 Charged defects and the Fermi level

The question of the role of charged defects was of course quickly raised, but the main concern was, initially, the positively charged vacancy, the well known E′ defect. As we had found for it a much higher formation energy, it was excluded that it could give significant a contribution to self-diffusion at equilibrium. Moreover, one point was not clear at that time: the fact that in Mikkelsen experiment the system was closed with respect to oxygen exchange, but, most probably, open with respect to charge equilibration, the silicon substrate playing the role of a charge reservoir. Nevertheless, the importance of negatively charged interstitials became immediately clear after two papers [59, 94] that were published in the same volume of the Physical Review Letters as our paper. The first paper [59] found much lower migration energies for the negative interstitials (Q=-1 and Q=-2) than for neutral ones. The second paper, although quantitatively in disagreement with the first, confirmed that the (thermodynamic) charge transition level 0/-1 and 0/-2 were well below midgap; however, they did not fully recognise the strong implications for self-diffusion, as their main focus was the stability of the E′ centre. The issue of the charge states of defects lead us to a thorough study of charge states of native defects in quartz, the outcome of which is in ref. [37]. The paper contains several new results, including the formation energy and structures of silicon vacancies and interstitials, not only neutral but also in various charge states, and the formation energy of neutral antisites. But the main advance of this work is, in my opinion, the discussion of the mechanisms of charge compensation and self-doping in intrinsic quartz and the estimate of the contribution of negative oxygen self-interstitials to ionic conductivity in

the material. The mixed (electronic/ionic) charge compensation was indeed surprising and called for further verification. The results were still compatible with the activation energies for self-diffusion in open mode. A summary of DFT-LDA formation energies in open and closed mode are show in Fig.3.3. In order to further appreciate the consequences of the calculated formation energies and self-consistent Fermi level we estimated, using the migration energies from ref. [59], the intrinsic contribution to ionic conductivity, which, in quartz and silica, is traditionally attributed to Na impurities [83]. The calculated value for intrinsic quartz was indeed lower than measured values, but it was clear that relatively small changes in the Fermi level (for example due to impurities) would strongly influence ionic charge transport, and easily make the intrinsic contribution comparable to the extrinsic one, due to sodium.

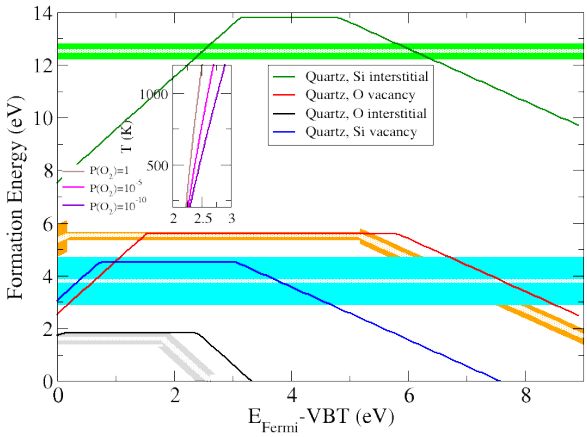
3.2.3 Answers raising new questions

The doubt about the dominant charge state of oxygen interstitials led to suggestions of possible experimental checks, based either on the different formation volumes of neutral and charged interstitials, or on the P_{O_2} dependence of the diffusivity, which for a -1 (resp. -2) charged defect would be $\propto P_{O_2}^{-1/4}$ (resp. $\propto P_{O_2}^{-1/6}$) [95].

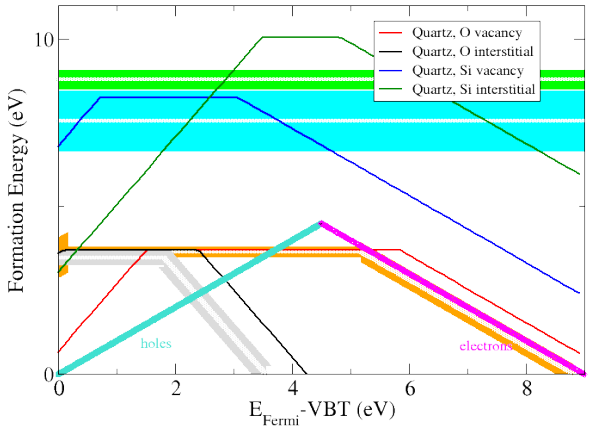
The puzzle became apparent when, once more, we revisited the interpretation of Mikkelsen experiment for a closed system: here the charge compensation lead to an activation energy (for the negative interstitial side of a Frenkel pair) which was more than 1 eV lower than the 4.7 eV by Mikkelsen. [36] What could explain this? The first possible solution was that, due to the presence of some impurity, the Fermi level was further lowered, so to suppress the concentration of negative interstitials. But which impurity? Na and Al are generally kept such as to approximately compensate each other. Moreover, a too low Fermi level would raise the equilibrium concentration of holes, making silica a *p* self-doped transparent semiconductor (sic!). Another hypothesis, discussed in ref. [36], was the influence of hydrogen, forming neutral OH group by passivating negative interstitials. But then further difficulties would arise, because the apparent activation of oxygen would have been given by the migration barrier of OH groups, known to be around $1 \div 1.5$ eV [96, 97, 98]. A further reason to exclude this hypothesis was the fact that H impurities had accurately been eliminated from Mikkelsen's samples.

3.2.4 Amorphous silica

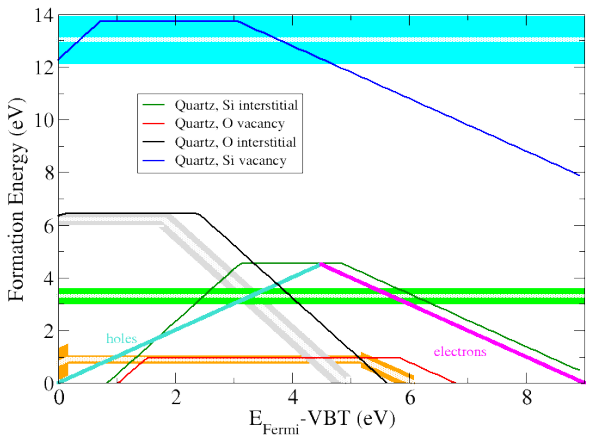
The diffusion experiments that we discussed previously were mostly performed, actually, on silica samples. The comparison was justified by the similarity of the local coordination in the two forms of SiO_2, and based on the assumption that, due to that similarity, formation and migration energies were close. The PhD thesis of Layla-Martin Samos [99] dealt with the study of amorphous SiO_2 in close connection with the work devoted to quartz. The distribution of formation energies is, at least for neutral oxygen defects, gaussian and essentially centred around the values obtained for quartz. This fact can be seen on Fig. 3.3, where the width of the



(a) Open (extrinsic): eq. with O_2



(b) Closed (intrinsic) conditions.



(c) Open (extrinsic): eq. with bulk Si.

Figure 3.3 – *Formation energies of vacancies and interstitials in quartz and silica as a function of the electronic chemical potential, for open and closed systems. The coloured bands concern silica; their width is that of the distribution of the corresponding formation energies. Charged silicon defects have been calculated only for quartz. The inset in the top panel shows the position of the self-consistent Fermi level as a function of temperature for three oxygen partial pressures.*

coloured bands represents the full width at half maximum of the distributions. The model for the amorphous, as well as the results for the spread in defect formation energies and their interpretation, are summarised in a few papers [100, 101, 102, 103]. The prediction of a dominant diffusion mechanism for oxygen driven by *negative* oxygen interstitials is not only still valid for silica, but it leads to even lower activation energy, and as such in even stronger disagreement with Mikkelsen experiment. The results, for the amorphous, are based on the assumption that one can apply a model for random walk in a random network where the distributions of formation and migration energies on sites are random and not connected with each other [104]; although a systematic study for migration energies is still missing, this assumption seems, however, well founded, at least for oxygen defects, on the basis of formation energies and a few migration ones.

A typical reason for disagreement between calculated and measured activation energy lies in the fact that the search for configurations and migration paths is always very limited, and the theoretical approach could have missed an important diffusion mechanism. However, this would of course lead in calculated activation energies higher than experimental ones. For this reason, the contribution of different kind of defects, present only in the amorphous, cannot easily solve the puzzle, as the calculated activation energy is too low, and not to high. Nevertheless, the study of the amorphous gave the opportunity of gaining further understanding of possible diffusion mechanisms looking at coordination defects [105]. In thatr study we employed Maximally Localised Wannier Functions (MLWF) [106] in order to have a visual idea of electron localisation on defects; the blue inset briefly describes the essential features and gives some examples.

Visualizing electrons in silica through Maximally localised Wannier Functions

A common way of visualising the bonds around a point defect, in an insulating material, is to show the Bloch functions associated to defect levels in the band gap. However, in many cases the comparison with the characteristics of other bonds in the material is not straightfoward and this view cannot be easily used for a classification of defects. The tools of Maximally Localised Wannier Functions [106], already used for the characterisation of bonding in amorphous structures [107, 108], or the dipole moment in condensed phases [109], seems well suited to the task. In the case of a well localised level inside the gap the Wannier function coincides with the Block function (at Γ), but the advantage is that one can easily compare, on equal footings, with the localisation of MLWF in the bulk without defects; moreover, some comparisons of defects in the crystal and the amorphous are at hand. As an example we show some defect configurations including the Wannier functions centres (in some cases with MLWF isosurfaces). The distribution of distances and spreads for crystalline and amorphous silica is also shown in Fig. 3.4. Some examples are shown in the shaded inset containing Fig. 3.5. We applied this characterisation also to valence alternation pair defects in amorphous silica [105].

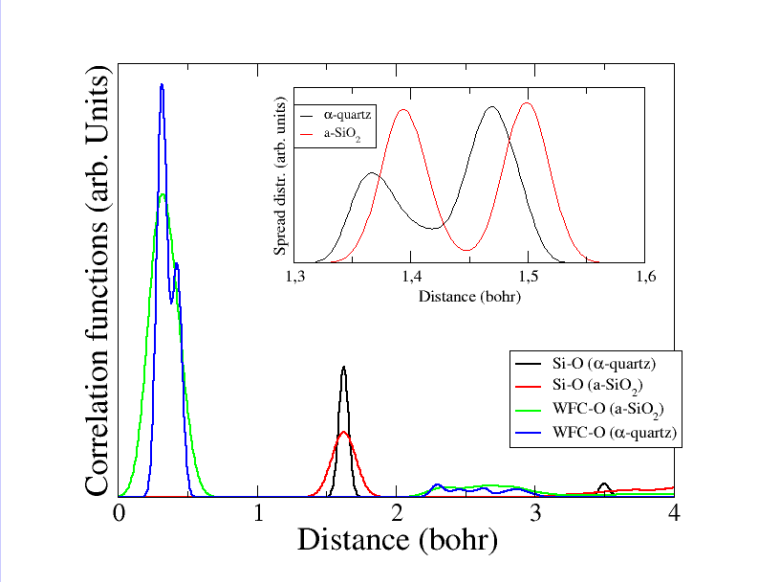
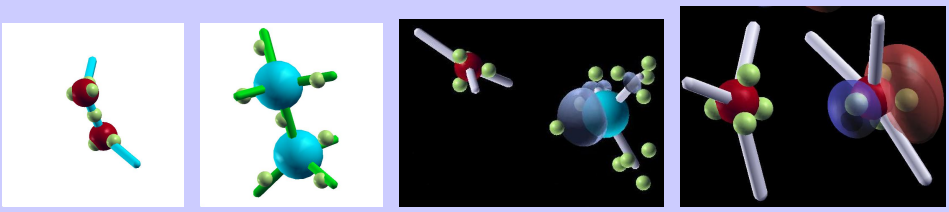


Figure 3.4 – *Pair correlation functions between Wannier centres and oxygen atoms in quartz and silica; the inset shows the distribution of MLWF spreads for the two systems.*



(a) I_O^0 (b) V_O^0 (c) V_O^{+1} (d) V_O^{+2}

Figure 3.5 – *Atomic structures and Wannier centres for defects in quartz. From left to right: neutral oxygen interstitial, oxygen vacancy in neutral, +1 and +2 charge states. Oxygens are red, silicons are light blue, Wannier centres are yellow. For the charged vacancies it is shown the isosurface containing 80% of the charge of a Wannier function.*

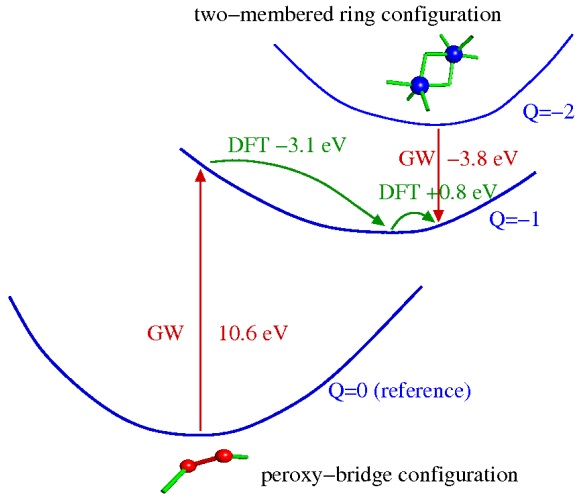


Figure 3.6 – *The GW correction scheme for an oxygen interstitial in silica. Vertical excitation energies are calculated within the GW approximation (in red), relaxation energies within DFT-LDA (in green).*

3.2.5 GW corrections: an important step forward

For quartz as for amorphous silica, the peculiar charge compensation mechanism and the puzzle discussed in Sec. 3.2.3 called for further investigation. The doubts concerning the description of negatively charged interstitials within the DFT-LDA approach suggested to switch to a method at the state of the art for the description of electronic excitations. Assuming that the main source of error were associated with an erroneous position of defect levels in the band gap, the GW approximation would have allowed to correct the result only by correcting the single particle energies associated with some pathological defect levels. The idea of using the position of defect levels, calculated with more advanced and reliable approaches (hybrid functionals and/or GW), in order to correct total energies had been already used [110, 111]; however, the first coherent approach for correcting formation energies on the basis of GW calculations was explained by Rinke and coworkers [112]. Thanks to the newly written GW code, SaX [113], by Layla Martin-Samos, we applied the same procedure [58], to the oxygen interstitial in quartz and silica; the adopted correction scheme is shown in Fig. 3.6. The choice of the neutral interstitial as the reference state to which the *vertical excitation/relaxation* procedure is applied, is justified by the fact that the position of the HOMO (wrt the VBT) is confirmed by the 0/+1 excitation as calculated by G_0W_0. The picture is now radically changed: the negative interstitial was found to be much higher in energy than the DFT-LDA prediction, so that the tCTLs 0/-1 and 0/-2 are above midgap; this is compatible with a Fermi level around midgap, and with the experimental Si/SiO_2 band offset; we remark that the DFT valence band offset is largely underestimated ($\sim$ 2.5 eV), while the same quantity calculated within the GW approximation is close to experiment (4.3 eV above the VBT [114]). In Ref. [58] no corrections to the migration energies of oxygen interstitials were taken into account, assuming that they are much smaller than the corrections to the formation

energies. Following this hypothesis, which should, however, be tested, we showed that the calculated *dynamical* CTLs [2] predict a large range of Fermi levels around midgap for which the dominant contribution to oxygen-self-diffusion comes from neutral interstitials, now firmly supporting the view previously discussed in [57].

Before concluding this section on oxygen self-diffusion, I would like to discuss some questions that are, however, still open. One is related to the fact that the picture is, now, somewhat incoherent. Indeed, although one can speculate that the formation energy for neutral oxygen vacancies is probably reliable, because the HOMO is a level very close to the VBT, the charge transition levels are not necessarily reliable. this could have an effect on the predicted activation energies for oxygen self-diffusion for samples in equilibrium with bulk silicon. For silicon self-diffusion similar questions are again to be addressed. We will nevertheless give a brief overview, in the following section, of the picture coming out from DFT-LDA results, which to some extent seems to explain experimental findings.

One serious technical issue is related to the approximation used, the G_0W_0 perturbative approach: what is the influence of the starting DFT-LDA wave functions on the final result? How this influence changes from one defect to another? An illustration of possible pathological situations comes from the same oxygen interstitial discussed in ref. [58]: in the negative charge state (but in the equilibrium geometry of the neutral one) the HOMO is hybridised with the conduction band (see Fig. 3.7). A GW calculation on top of this configuration would probably be strongly affected by the shape of the DFT-LDA wave function. As a consequence, if the path (excitation/relaxation) for the correction scheme were not the one sketched in Fig. 3.6, but an alternative one, the result could have been doubtful.

The comparison with hybrid functionals calculations could also give new insights. It would certainly be a very powerful approach if one could, as suggested in ref. [62], extract the right vertical CTLs from DFT-LDA adding the PBE0 *vs* LDA shift in the valence band top. Unfortunately the approach seems not to work for shallow levels and its accuracy depends strongly on the material, as suggested by the results on the band gap. As already mentioned, the approach consisting in adapting the portion of exact exchange to match the bandgap is, to my personal feeling, unsatisfactory [69].

3.3 Silicon self-diffusion

The first results on silicon self-diffusion were obtained in more recent times than those for oxygen, probably due to the obstacles to performing experiments at high temperature and/or on long times, which are needed to measure lower diffusion coefficients. The result of Brebec and coworkers [115], which came well before the others, in 1980, is still a reference

2. The *dynamical* tCTL is an extension of the usual definition of tCTL to diffusion activation energies (see Ref. [58]).

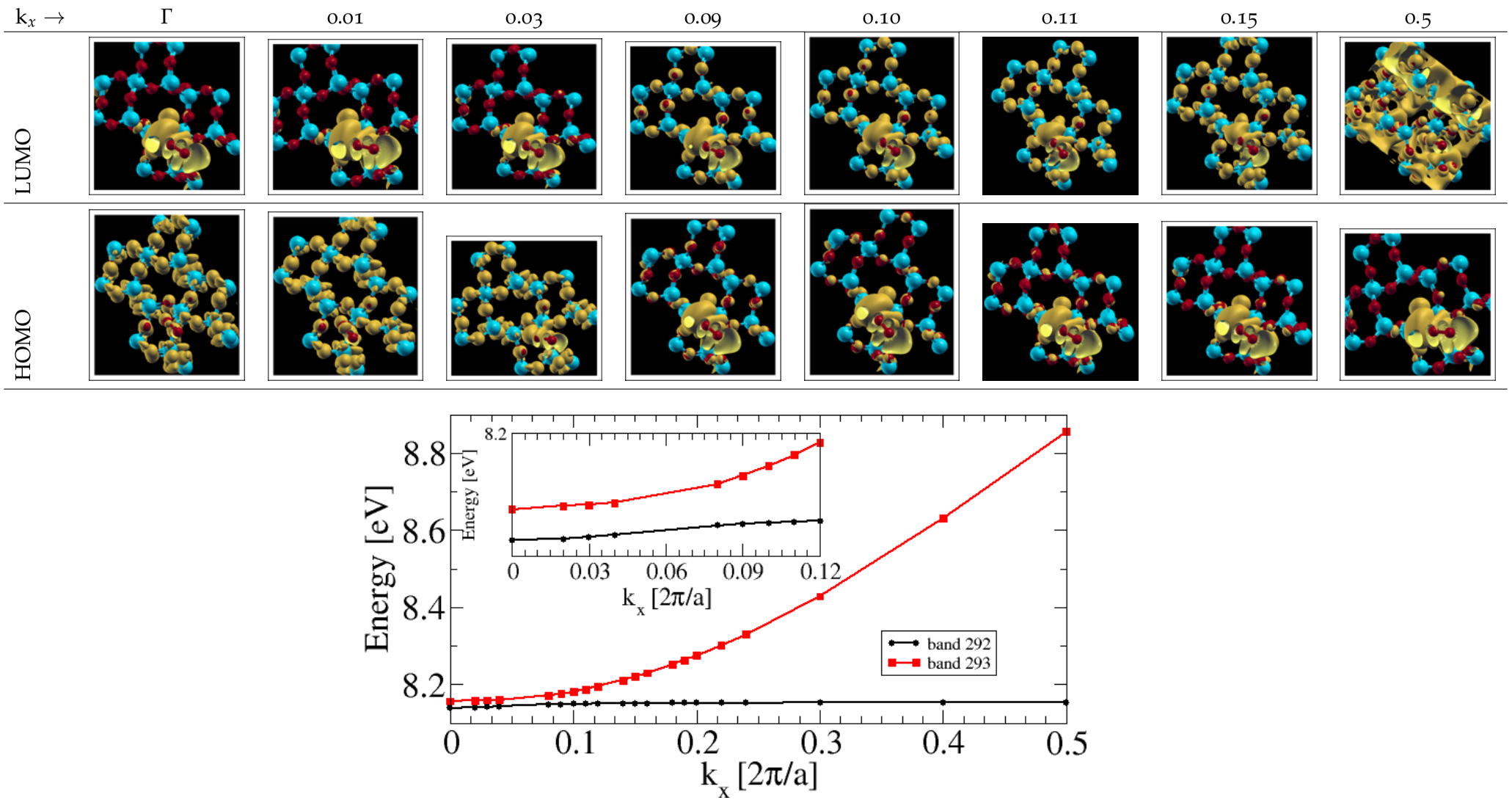


Figure 3.7 – *Hybridisation of the HOMO with the conduction band for a negative (Q=-1) oxygen interstitial in the geometry of the neutral one in SiO_2. Above: Density isosurfaces at $\rho = 0.0002$ of the HOMO (half filled) and LUMO (empty) for a negative oxygen interstitial in the geometry of the neutral one. Below: the corresponding energy bands along the $\langle 100 \rangle$ direction of the BZ. $\mathbf{k}_x = \frac{2\pi}{a}(x, 0, 0)$.*

for silica glass and gives an activation energy of 6 eV. For quartz the result arrived much later, with a diffusion coefficient close to Brebec's results in magnitude, but with an activation energy somewhat higher (7.6 eV). Both these results were obtained on bulk samples, in conditions which are, however, not really comparable. After 1988 [9], several works have been published reporting on silicon mobility in silicon dioxide thin films on a silicon substrate. The outcome were diffusion coefficients some orders of magnitude higher than for bulk samples and with a lower activation energy, as low as 4.4 eV. An interpretation based on the SiO_2 decomposition at the interface [116], following the reaction $Si + SiO_2 \rightleftharpoons 2SiO$, lead to consider SiO molecules as the species mediating silicon mobility. However, similar results have been attributed to silicon interstitials [117]. More recent results ([118, 119] and in particular [120, 121]) using samples with various thicknesses, concluded that the diffusion coefficient was getting lower the thicker the samples, and with an activation energies of 5-5.5 eV. In spite of having shown this variation of diffusivity and activation energy with the sample thickness, these works still give very partial answers to the question of the mediating defect and the dominant charge states for silicon self-diffusion.

A preliminary discussion of predictions based on our DFT-LDA results is contained in [122] and we sumarise and complement it here with some further remarks; it is clear, however, that a few limitations make the discussion only semiquantitative: 1) the data for the amorphous are incomplete concerning charged defects 2) the CTL for silicon defects in quartz may be enticed by LDA failures as for the oxygen interstitial (in particular the silicon vacancy, whose structure is that of a double oxygen dumb-bell) 3) the migration energy of the silicon vacancy should be further investigated. Nevertheless, the low migration energy of the silicon interstitial (1.2 eV) and the formation energy of silicon defects in different conditions (see Fig. 3.3) suggest that, in closed mode, the diffusion regime should be controled by the silicon interstitial of an anti-Schottky triplet. The calculated activation energy for quartz, 7 eV, is not far from the experimental value given by Jaoul and coworkers [123]. The result for silica is lower (approx. 6.5 eV) but we cannot compare it to Brebec's results, which in principle are for an open system, in an oxygen athmosphere. According to our results, in that case one should expect a regime with a higher activation energy, at least 9 eV. This estimation is based on the fact that we were unable to find a migration mechanism with a migration barrier lower than 5 eV. But such a regime is not attainable for silica, as can be extracted from the correspondence between profile width and annealing time at the melting point for a few activated mechanisms shown in Fig. 3.8.

Similarly, for thick uncapped samples on a silicon substrate, the equilibrium with oxygen is probably not attained even very close to the external surface, as far as silicon self-diffusion is concerned. Conversely, sufficiently close to the substrate the conditions can be genuinely those of equilibrium with silicon. The fitting of profiles will then lead to an activation energy which is in between silicon equilibrium (with an activation energy, for silica, close to 4.5 eV) and that of a closed system. This explains why an analysis of experiments in thin films shows lower diffusivities and higher activation energies the thicker the film. Qualitatively similar behaviour is

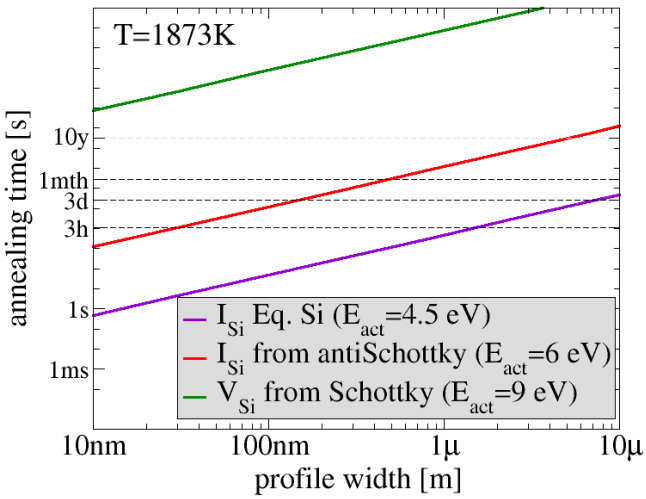


Figure 3.8 – *The annealing time needed to obtain a given profile width for a few activation energies related to some silicon diffusion mechanisms in silica. The temperature is taken at the melting point.*

expected for capped samples, where the diffusivity far from the Si/SiO_2 interface should approach the antiSchottky regime. The influence of the closed regime in measurements for thick samples should be further investigated; however, again from Fig. 3.8, one can predict that measuring the diffusion regime controlled by interstitials formed by antiSchottky triplets, whose activation energy is higher than 6 eV, produces very narrow profiles even with long annealing times.

4 Silicon Carbide: prediction of selected defect properties in a wide band gap semiconductor

The defects studies summarised in the following were mainly driven by the need of understanding the behaviour of silicon carbide under irradiation, the evolution of radiation damage with time and, as a consequence, the modification of material properties that are strongly influenced by the type and amount of damage. As the first quantities of interest are formation and migration energies of point defects, a natural benchmark is the comparison with self-diffusion data. But the interest for radiation damage drove us towards defect clusters/complexes, various forms of stoichiometric defects, including Frenkel pairs and their recombinations, and in general with a focus on kinetic mechanisms.

4.1 Defect free energies and self-diffusion

The formation energies of native defects in various polytypes of silicon carbide have been calculated by several authors. Although we know at least one review describing the achievements in defects identifications through the comparison of measured and calculated spectroscopic properties [124], we are not aware of detailed reviews focusing on defect energetics in SiC, except for an internal note [125], that we wrote for an EFDA [1] project, and a recent conference proceedings paper[61]. Although many discrepancies exist between different papers that appeared in the last 10-15 years, a global remark that can be made is that native defects in SiC have quite high formation energies, almost always higher than 4 eV in intrinsic conditions, and in some cases (for interstitial defects) up to 9 or 10 eV. Conversely, migration energies can be quite low, as low as 1 eV or even less (again for interstitials defects).

Having gathered data in the literature in order to evaluate the possibility of performing chemical kinetics simulations of the evolution of defect populations in silicon carbide under irradiation, it was necessary to choose a common convention to compare them: this implies having the same Fermi energy and the same Si/C chemical potentials. It is interesting, then, to represent them graphically; the plot in Fig. 4.1 gives a global idea of how defect formation and migration energies are distributed. The distribution of barriers is strictly connected to the behaviour of a material under stepwise annealing after irradiation, identifying the temperature stages at which determinate transformations are activated. The understanding of the evolution of the properties of silicon carbide under/after irradiation is the main goal of the works presented here, from the understanding of silicon clustering [126], to the kinetics of recombination of Frenkel pairs and antisite pairs [77, 127], as well as the transformation of the silicon vacancy in its metastable counterpart, $V_C C_{Si}$ [128], and of course the chemical and kinetic behaviour of fission products, like Pd [11]. The necessary study of basic energetics, like formation and migration energies of simple defects, leads also, naturally, to a comparison with self-diffusion at equilibrium.

4.1.1 Free energies of migration for interstitials

The paper on vibrational entropies of interstitials[24] is no exception to this programme, as the goal was to start from ab-initio phonons (in the quasi-harmonic approximation) and phonons-phonons interactions to model thermotransport and the contribution of point defects to thermal conductivity. However, a natural benchmark for vibrational entropy calculations is the comparison with diffusion activation energies.

The interpretation of self-diffusion experiments in silicon carbide still leaves some open questions. The ab-initio calculation of a diffusion coefficient (including prefactors) leads to a direct comparison with experimental results. Our results do not allow to solve the question of silicon self-diffusion, for which measured activation energies are compatible with a vacancy mechanism as well as an interstitial one [129]. Furthermore, for the latter, the reliability of DFT calculations, are questionable, especially

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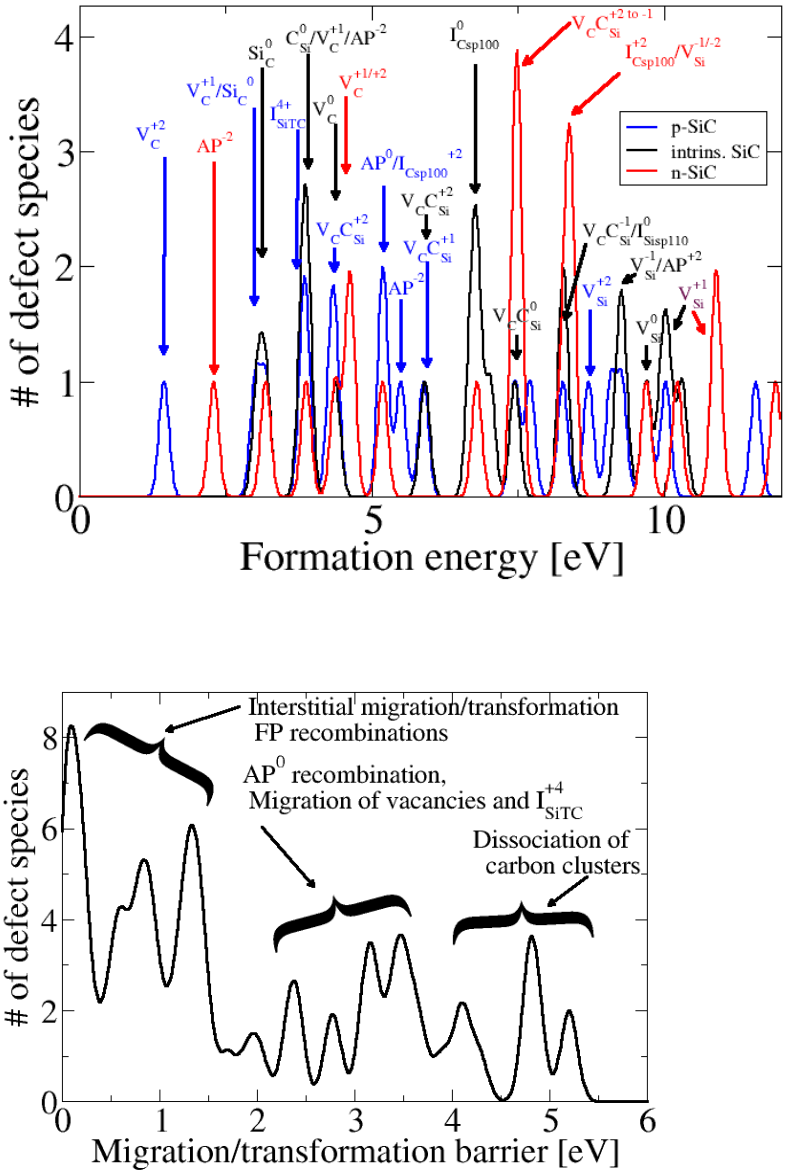

Figure 4.1 – *A graphical summary of formation energies and defect reactions barriers in cubic silicon carbide. Above: the distribution of formation energies for intrinsic (μ_e =midgap, black), p-type (μ_e =VBT+0.4 eV, blue), and n-type (μ_e =CBM-0.4 eV, red) conditions. Below: Distribution of several energy barriers, including migration barriers, recombination barriers and some other defect reactions. The data on which the figures are based are in the appendix A.1. They are broadened with gaussians whose FWHM is 0.2 eV.*

for the tetrahedral configuration, as in this case the HOMO is found in the conduction band for charge states lower than 4+ [130]. For carbon self-diffusion, the results confirm that the mechanism is an interstitial one; the agreement with one set of experimental data [8], although obtained on the 4H polytype, is very satysfying. Still doubts subsist on the charge of the interstitial, that could be neutral or charged 2+.

Incidentally, it can be remarked that the migration energy can vary considerably with the charge state for the same defect; this is probably the main reason why the amorphisation temperature threshold of silicon carbide is considerably lowered when the ratio of electronic to ionic damage is raised [131]. No clear relationship has been established between this effect and one peculiar migration mechanism, but the behaviour of the silicon interstitial, which seems to undergo a Bourgoin-like mechanism [132] when switching from neutral to the -2 charge state, could be able to explain this point. There are other cases where the trapping of holes or electrons can lead to an accelerated migration or defect reaction; this is for example the case of the antisite pair recombination that we will discuss later.

The results obtained for silicon carbide can be used to evaluate some empirical relations meant to evaluate vibrational entropies without explicitely calculating them. The pioneering empirical formula by Zener [133, 134], relating the migration entropy to the temperature variation of the elastic shear modulus, seems to work well for neutral defects, but fails for charged ones. However, the assumption was based on the classical model by Eshelby, for which the defect formation energy was entirely of elastic origin. It would be interesting to understand if one could extend it by adding to the original Zener expression the temperature variation of the dielectric constant.

The so called Meyer-Neldel rule, initially found, and somewhat justified, for electronic processes, is frequently applied to atomic jumps [135]. It postulates a linear relationship between the energy and the entropy of an activated process. It is thus interesting to check if the results of DFT calculations for interstitial migration in SiC fulfill the rule. It turns out that the rule is approximately fullfilled. A defect that is somewhat out of trend, in the Meyer-Neldel plot of ref. [24], is the neutral silicon interstitial; if this has to be ascribed to the peculiar electronic structure of that defect along its the migration path, would be worth investigating.

Considering the free energy barriers that we found for the annealing of some stoichiometric defects [127], we remark that theMeyer-Neldel rule seems to hold also for atomic jumps not involving interstitials defects. For this group of barriers, the obtained Γ_{00} and Δ_0 values [2] are quite close to those of the curve of the first panel of figure 8 in ref. [24]. Anyhow, even for this group of barriers, the rule is only approximately fulfilled. The results are shown in Fig. 4.2; it is clear that the calculated Γ_0 values are relatively strongly temperature dependent, but the Arrhenius picture is perfectly sound when one fits the full reaction rate. The fitted Γ_0, which are temperature independent, are those shown on the right panel, containing the Meyer-Neldel plot, where also the activation energies are the fitted ones,

2. The parameters of the energy/entropy linear relationship; for the definitions of Γ_{00}, Γ_0 and Δ_0 see ref. [24]

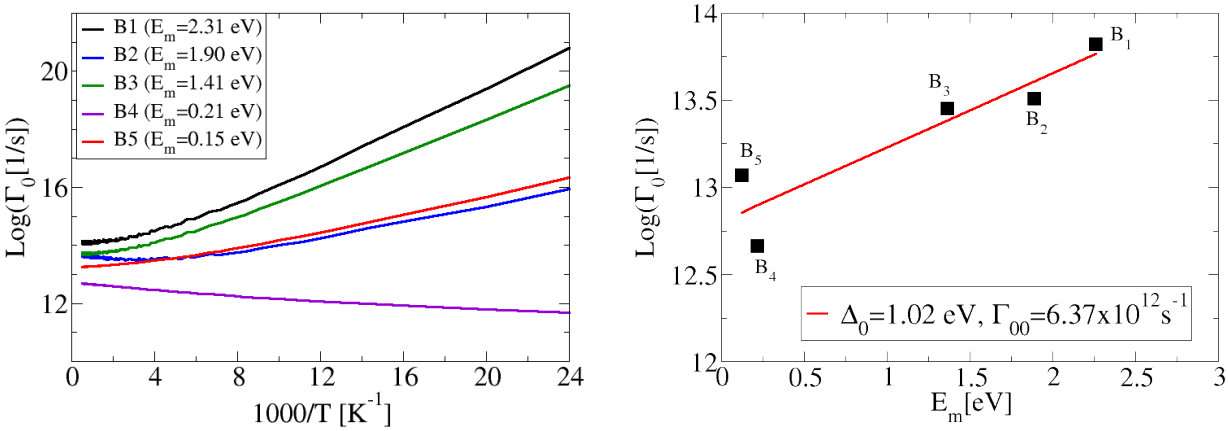

Figure 4.2 – *Prefactors for five barriers along the recombination path of neutral antisite pairs in silicon carbide, ordered according to their activation energy. Left Panel:* Γ_0 *as a function of inverse temperature, as directly calculated from first principles vibrational entropies. Right Panel: Meyer-Neldel plot containing the* Γ_0 *obtained from fitting the ab-initio reaction rate with an Arrhenius equation, shown as a function of the activation energy obtained from the same fit. The red line is a linear fit to the black squares.*

slightly different from those calculated from first principles and shown in the legend of the left panel.

4.2 Annealing of Frenkel pairs, stoichiometric defects, and the silicon vacancy

The lifetime of defects produced by irradiation is important for the establishment of materials properties under irradiation and for their evolution after it. A striking example of the effect of irradiation on material properties, is the evolution of the thermal conductivity in silicon carbide, which drops by orders of magnitude during irradiation. [136]. This is a major concern for the use of SiC in nuclear fission and fusion applications. Defects can disappear either by annihilating on sinks (surfaces, dislocations, grain boundaries ...) or by recombination with, or transformation into, other defects. In any of these cases the limiting factor can be either the diffusivity of the fastest species, or the last barrier to be overcome for the annihilation —if it is higher than the migration energy. Although, in metals, the recombination barrier for Frenkel-pairs is commonly assumed to be zero (or lower than the migration energy), this is not a general feature.

4.2.1 Frenkel pairs recombination: a kinetic bias towards decomposition?

The interesting point that we wanted to stress in ref. [77] is that, for an ordered binary compound, with a given pattern of recombination energies, the annealing of supersaturated Frenkel pair concentrations can lead to the production of antisites. The complexity of recombination paths hinted to limit the study to neutral pairs; nevertheless, it was interesting

to draw some consequences for the long term evolution using a simple model of chemical kinetics. The expression for the recombination rate, taking into account diffusion and recombination, is known since the sixties [137], but their use for the evolution of point defects in a non-metallic material are very rare. The results evidence the fact that the outcome of the kinetic evolution depends crucially on the initial structure of the silicon vacancy, whose metastability is a notable feature of silicon carbide. If the vacancies assume their stable form, the $V_C C_{Si}$ complex, a tendency towards nanoscale decomposition is expected. Otherwise, the silicon vacancies are annealed to give normal silicon sites and the initial damage is almost completely healed after a certain time. The compilation of data in the appendix A.1 is intended as a first step towards a more complete model for the evolution of defect populations under/after irradiation, either by a homogeneous chemical kinetics approach, or by a spatially informed event Monte Carlo kinetic simulation. In both cases improvements are needed with respect to existing procedures [4] in order to cope with charges and long range Coulomb interactions.

4.2.2 Coordination defects

Coordination defects are, like homogeneous Frenkel pairs, defects which are stoichiometric. Between them antisite pairs received much attention, even very recently [138]. Still, there were details of the annealing of these defects that had not been investigated. In particular, along the recombination path of antisite pairs, shown in Fig. 4.3, we found two shallow minima; they correspond to coordination defects, containing 5- and 7-membered rings, similar to Stone–Wales defects in carbon nanostructures. These apparently minor features could be of importance in determining the amorphisation threshold in SiC under irradiation. The calculation of their lifetime [127], including an ab-initio evaluation of the prefactor, as mentioned in Sec. 4.1.1, suggests how defects that are virtually absent before and *after* irradiation, can play a role in the modification of the material *during* irradiation, and in determining a non-equilibrium stationary state. The lowering of the recombination barrier for the 2+ charge state is a notable feature that had not been reported previously; it could give an important contribution to the lowering of the amorphisation threshold accompanying the raise of electronic to ionic damage ratio.

4.2.3 The metastability of the silicon vacancy

The metastability of the silicon vacancy in silicon carbide is an interesting feature which, as mentioned previously in this section, is important for the determination of kinetic paths in irradiated SiC. The conversion mechanism from V_{Si} to $V_C C_{Si}$ has also the advantage of presenting a relatively simple reaction path [139] and have been probed by several experimental techniques. It is, thus, an ideal candidate to attempt the application of advanced electronic structure approaches like GW, not only to the equilibrium position, but also to a saddle point, something that had never been done before. The two major outcomes of the study [128] are a reinterpreta-

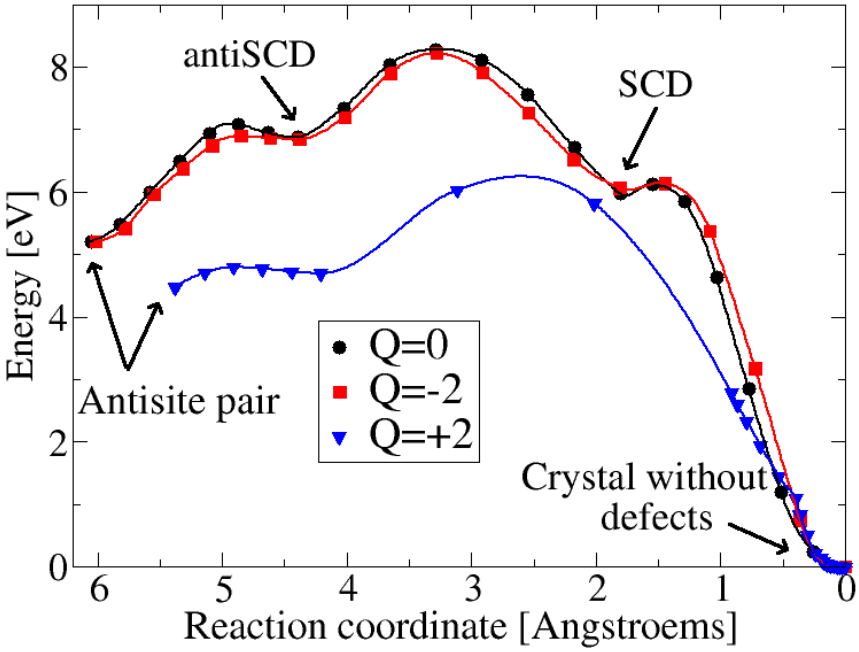

Figure 4.3 – *Energy profile along the recombination path of antisite pairs in cubic silicon carbide. Three charge states are shown. The stoichiometric coordination defects, called SCD and antiSCD, and their lifetimes have been discussed in Ref. [127]. The reaction coordinate is the distance in the 3N dimensional space, N being the number of atoms in the supercell.*

tion of some experimental results and new insights on the role of charged states in the conversion mechanisms.

For the first outcome, related to the electronic properties of the vacancy, the accurately calculated vCTL showed that the agreement of the LDA 0/-1 vCTL with the energy of the so-called E-line in the photoluminescence (PL) spectra was fortuitous; the new results, instead of a conduction-acceptor recombination, point towards a donor-valence recombination, corresponding thus to the -2/-1 transition of the vacancy.

Concerning the second point, related to the conversion kinetics, we found that GW corrections to the migration barriers are not negligible. Furthermore, although each jump is assumed to occur in a definite charge state, the statistical contribution of conversions for all the available charge states of the silicon vacancy has the effect of lowering the overall barrier, and leads to a much better agreement with experiment for an intrinsic (or compensated) SiC, provided that GW corrected barriers are considered. With respect to the GW calculations for the oxygen interstitial in SiO_2, here the advantage is that the starting wave functions for the G_0W_0 calculations are less affected by localisation errors, because of the nature of the material and of the defect. In general, the findings for the $V_{Si} \rightleftharpoons V_C C_{Si}$ transformation stress the following fact: when the differences in formation energy between different charge states are comparable to the differences in their migration energy, a global view on all available reaction processes is necessary.

Although we did not develop this point in ref. [128], it is clear that,

for different doping conditions, the relative weight of charged states at the stable position and at the saddle point will be different; one has to expect, thus, a lower barrier for *p*-type SiC which, combined with results on FP recombination, would suggest a higher build-up of antisites during/after irradiation. Conversely, for *n*-type SiC, the barrier is expected to be higher, and the build-up of antisites reduced. This qualitative remark is based on the assumption that the fraction of $V_C C_{Si}$ complexes *vs* metastable V_{Si} vacancies is controlled, even under irradiation, by the energy barrier for the conversion.

4.2.4 The importance of clustering

It was clear from papers published in 2003/2004 [140, 141, 142] that carbon interstitials have a strong tendency to cluster in silicon carbide, at least looking at the thermodynamics. However, at the time when I started working on silicon carbide, nothing was known about silicon clusters. The clustering of silicon interstitials, from the point of view of irradiation, is not less important than that of carbon. This fact suggested to investigate silicon di-interstitials, checking several possible configurations, barriers for transformations and migrations. The results, summarised in an internal report [126], are in agreement with a paper which came out in the meanwhile [143] on their stability: silicon di-interstitials have lower binding energy then carbon ones, but still a relatively large one (1.6 eV/atom). The migration energy of a di-interstitial as a whole is 1.2 eV, not far from the calculated value for the single interstitial. We have calculated it together with some rotation and transformation barriers, which are shown in Fig. 4.4. However, these barriers could suffer from similar drawbacks as the migration energy of single silicon interstitials; the latter is a challenge for DFT calculations, because the transformation to the tetrahedral configuration pushes the HOMO (in the neutral state) above the DFT-LDA CBM, raising objections on the reliability of the obtained values. We have discussed this point in ref. [130]; in that paper we found a jump mechanism with a migration energy of 0.8 eV, which is lower than a previously calculated value of 1.4 eV [129]; however, the very reason for this reduced barrier is probably an enhanced cell-size and **k**-point sampling. The tests that I made with reduced localised basis sets on the neutral silicon interstitials suggest that the formation energy of the tetrahedral configuration depends strongly on the description of the conduction band.

4.3 Palladium impurities in SiC : from an applied problem to fundamental understanding of diffusion

The study of palladium impurities in cubic SiC [11, 28, 144] was conceived in response to a genuinely applied issue related to nuclear fission applications. As the SiC layer in Triso-coated particles is supposed to retain fission products and insure against mechanical failures of the fuel particles in gas-cooled reactors, palladium, as a fission product, was one of the major concerns for very high temperature reactors of that kind. Not because it is a particularly harmful one from the point of view of

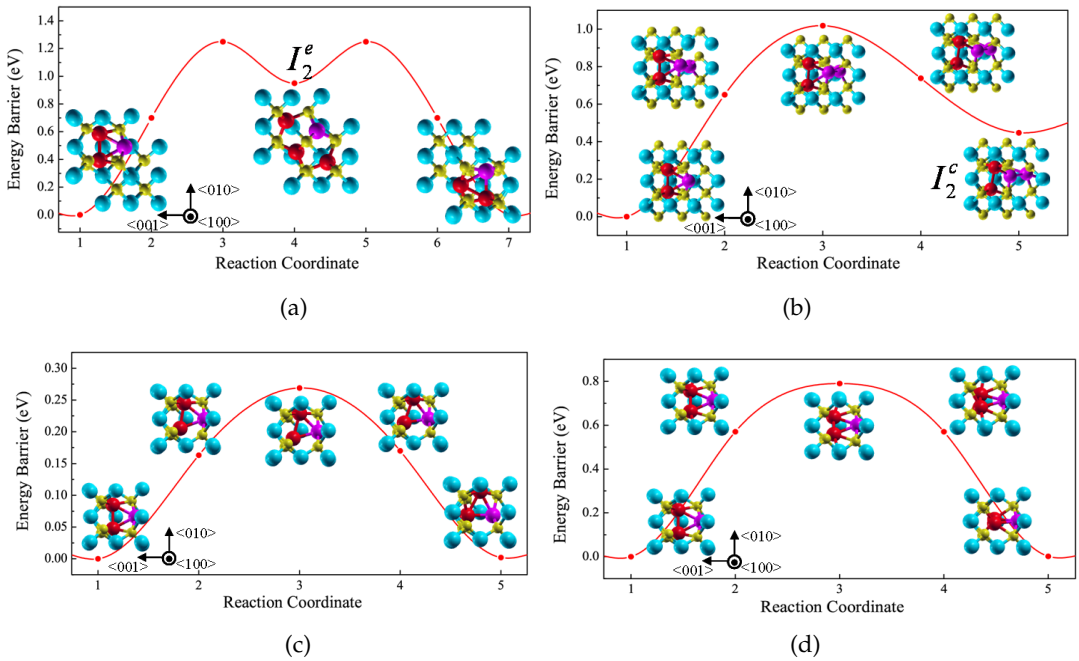

Figure 4.4 – *Energy profiles for migration and transformation pathways of the silicon di-interstitial in silicon carbide. (a) Migration of the di-interstitial. (b) transformation to a metastable configuration. (c) in-plane rotation of the triangular ground state configuration. (d) twist of the triangular configuration. Silicon atoms are blue, carbons are yellow. Badly coordinated silicons are highlighted.*

radioactivity, but because it had been detected in some damaged regions at the interface between carbon and SiC. The suggestion that Pd could have formed some Pd silicide [145] was readily confirmed not only by the enthalpy of formation of Pd_2Si wrt to SiC, but also by the high solution energies that I found with DFT. It was clear then that the kinetics of the impurities was the limiting factor for the *corrosion* of SiC by palladium. Interestingly enough, the only attempt to measure the diffusion of palladium in silicon carbide dates from the beginning of the eighties [146] and exactly in the same framework, in spite of the fact that the Pd/SiC system has been studied for several others applications for which diffusion properties are also important[3]. The study of Pd diffusion gave me the opportunity to tackle impurity diffusion problems and to realise the importance of native defect assisted mechanisms. Apart from some interstitial assisted migration mechanisms, the vacancy mechanism is worth citing. First, for the application of a well known diffusion model (the five frequency model) to a material very different from those to which it is commonly applied (metallic alloys in FCC structure). Second, because it revealed that the effective activation energy was comparable to that of the interstitialcy mechanism, although native interstitials in SiC have much lower migration energies than vacancies.

Moreover, the implications for the vacancy contribution to carbon self-diffusion [144] are equally surprising, and can give hints of a similar be-

3. See the introduction of ref. [11].

haviour for some of the numerous impurities [147], especially transition metals [148, 149], that have been considered in SiC.

Conclusions and future directions

5

The document for which I write here some concluding remarks has been already written as a backward view over the past ten years of my research activity at CEA. One of the goals was to show how this activity is part of a unitary approach towards atomic scale understanding of diffusion properties and kinetic mechanisms in general, in spite of (but even partially thanks to) the specific interests of the service (SRMP), the department (DMN), and the direction (DEN) of CEA to which I belong.

Nevertheless, I will, for completeness, further summarise, taking the risk of repeting myself. I will then first briefly remind the main achievements and possible further work on SiO_2 and SiC. Then I will express some of my feelings about possible future research directions.

5.0.1 Silicon dioxide

The work devoted to SiO_2 has clarified the diffusion regimes that are to be expected in given temperature/P_{O_2} domains [57, 37, 36, 122]. It is now clear, after overcoming a tough *impasse*, that the interstitial regime is controlled by charge neutral interstitials [58]. I would like to remind that when I started on this subject some of the most renowned specialists in the field of diffusion in glasses still considered that the charge of diffusing oxygens had to be the formal charge Q=-2.

Concerning silicon diffusion, we predict three regimes: interstitial for open systems in equilibrium with silicon, antiSchottky (again via the silicon interstitial) for a closed system, and a vacancy mecanism for an open system in *hypothetical* equilibrium with gaseous oxygen — hypothetical because probably not easily attainable. For the case of silicon, further investigations are necessary to confirm that the dominant charge of the diffusing species is again neutral. However, we have provided a first explanation of the origin of the variation of the activation energy with the thickness of samples. The similarities and differencies between quartz and silica are now much better known thanks to our results [100, 102, 103, 101, 122, 105, 58], for what concerns defects and diffusion. The variety of defect configurations for some silicon defects and some charged oxygen vacancies in the amorphous could deserve further detailed investigations. The frequently invoked role of coordination defects, and their possible role for diffusion, is now more than an hypothesis, firmly supported by our first principles calculations [105].

It would certainly be desirable to have, on the theoretical side, a set of coherent data obtained with the most reliable level of theory. It is still probably somewhat too heavy computationally, especially if one plans to do a systematic sampling of defect sites on amorphous SiO_2, to use state of the art GW corrections. However, one could devise reasonable approximations, maybe using tight-binding fitted on GW quasiparticle energies [150] (including at least the most important defect configurations) or some GW ontop of tight binding approaches [151]. Further developments could be directed to investigate excitonic effects associated to point defects through the Bethe-Salpeter equation, also in comparison to optical experiments on SiO_2.

Of course such a set of coherent data would allow to predict diffusion activation energies for samples in a variety of environmental conditions, assess the attainability of given conditions as a function of sample sizes, annealing times and temperatures. Such information would greatly ease the comparison with recent [82], more controlled, experimental investigations and other that could be performed in the future.

5.0.2 Silicon Carbide

The first principles calculation of migration/reaction barriers in silicon carbide, apart from a low energy mechanism for the silicon interstitial [130], which should be confirmed with methods able to correctly describe the band gap, evidence at least three features

– the comparison of heterogeneous and homogeneous recombinations

mechanisms and the subsequent importance of the silicon vacancy structure for the annealing of interstitials [77]
- the presence of shallow minima along the antisite pair recombination path that could influence the irradiation behaviour [127]
- the contribution of different charge states in the annealing of the silicon vacancy and the difference between LDA and GW corrected results for this reaction barrier [128]

The study of formation and migration entropies gave a careful evaluation of vibrational entropies for interstitial defects and allowed to propose, through the Meyer-Neldel rule, a way to estimate migration entropies in SiC [24].

The investigation of palladium impurities revealed quantitative features of native defect assisted impurity diffusion that were somewhat unexpected [11, 144], like the low effective migration energy for the vacancy mechanism, a point that could be checked (theoretically and experimentally) for other impurities.

There are at least two future developments that I would be interested in: the first is the mentioned use of the database of first principles data in higher scale simulations, a more realistic model of the type of that sketched in ref. [77].

The second development, that was the motivation at the origin of the study of vibrational properties of defects in SiC, is the first principles investigation of thermotransport [152] and the influence of point defects on the thermal conductivity of SiC. This could be achieved through the calculation of phonon lifetimes. The main limitation would be probably the need for a very fine **k**-point sampling.

5.0.3 Interconnections and future directions

I would like to make a general remark that emerges out of the whole work summarised in this manuscript: the various formation/migration mechanisms studied for each material are generally interconnected in a more or less indirect way. The electron chemical potential establishes a feedback connection between the concentrations of various defects and impurities. From the point of view of kinetics, we have seen how the outcome of the recombination of Frenkel pairs is dependent on the structure assumed by the silicon vacancy. The position of the Fermi level influences its conversion rate. Part of the interstitials will also be captured by clusters (as well as, of course, by any kind of sinks). Here, too, the concentration of impurities will influence the global kinetic evolution by binding to native defects, assisting or hindering their migration, and modifying the Fermi level.

I am convinced that, in spite of the somewhat heterogeneous and incomplete data available nowadays, kinetic simulations based on ab initio data (at AKMC, EKMC or HCK level) should be performed and will give very valuable hints on possible kinetic paths and unexpected evolutions of non equilibrium defect populations. Moreover, one could check the assumption that is implicitely made all over the work described here: the point defects model, i.e., the hypothesis of non-interacting defects and

how far one can go with it. This assumption is in the background of almost all first principles calculations of point defects.

On the methodological side, there is room for improvements and major advances. Concerning boundary conditions, the spurious interaction of periodic images could be better understood, also by comparison with free boundary conditions (cluster) calculations. The latter are also a valuable tool to improve our understanding of defect interactions with surfaces. In the same direction also the interaction of point defects with dislocations or grain boundaries could be further investigated; in this respect methods coupling quantum and classical descriptions on different scales, like QMMM (Quantum Mechanics-Molecular Mechanics), should become a valuable tool.

Concerning improvements in the description of the quantum nature of the electron-electron interaction, the already mentioned hybrid functionals, as well as GW corrections, should be further checked as a valuable tool for defect calculations; they will allow to gain a better understanding of the role of screening and self-interaction in the energetics of defects. As Quantum Monte Carlo methods seem to be now applicable to systems with a relatively large number of atoms (at least at fixed atomic positions) they will probably become useful to provide reference calculations [153]. The study of excitonic effects associated to defects will certainly develop in the future, in particular in connection with optical experiments [154].

Talking about optical absorption/emission in the range of electronic excitations, they provide an important connection between experimental probes and defect calculations. Another tool for fruitful experimental/theoretical comparisons for defects is the calculation of g tensors [138], well suited for the identification of EPR-active defects. Other theoretical/experimental comparisons could be explored for other probes, one of those is connected with Raman spectroscopy. The calculation of Raman-active peaks that are specific for defects (provided the Placzek approximation is still valid) could lead to interesting comparisons with experiments.

For all the mentioned techniques, the coupling of multi-scale simulation with the calculation of experimental signatures of defects could lead to very interesting results also in the design of new materials. One could indeed try to predict, for example, in which peculiar irradiation conditions a material would present a given optical response.

A few of the developments that I just mentioned are indeed described in the four years project that I submitted as a *pre-dossier* meant as a prerequisite for the habilitation. This four year project is reproduced, with some updates, as a conclusion to the french summary (Sec. 0.5). In the last part of this project I envisage to study other functional materials for energy applications from the same point of view that I described for SiO_2 and SiC. In particular, I am now involved in a project focusing on kinetic mechanisms taking place at surfaces/interfaces of thin films chalcopyrite photovoltaic devices, in collaboration with the University of Mainz, where I am now since may 2011.

In this english conclusion, with respect to the french one, I gave a slightly more general view of possible developments, not necessarily part of my personal activity in the near future. Indeed an habilitation thesis is the place where to show independent thinking and ability to propose

innovative subjects to promising students. The precise definition of these subjects will depend not only on my personal interest, but on the importance they have in the CEA scientific strategy, their formative character for students, and the opportunities they can offer to integrate them into the scientific community in a larger sense, in an academic or industrial environment.

Bibliography

[1] Per Kofstad. *Nonstoichiometry, diffusion, and electrical conductivity in binary metal oxides*. Wiley Interscience, 1972. (Cited pages x and 1.)

[2] F. A. Kröger and H. J. Vink. Imperfections in crystalline solids. In Frederick Seitz and David Turnbull, editors, *Solid State Physics*, volume 3. Academic Press, 1956. p. 312. (Cited pages x and 1.)

[3] Georges Martin and Pascal Bellon. Driven alloys. In *Solid State Physics*, volume 50. Academic Press, 1997. (Cited pages x and 1.)

[4] A. Barbu, C. S. Becquart, J.L. Bocquet, J. Dalla Torre, and C. Domain. Comparison between three complementary approaches to simulate 'large' fluence irradiation: application to electron irradiation of thin foils. *Philos. Mag.*, 85(4-7):541–547, 2005. (Cited pages xi, 2, and 41.)

[5] J. Dalla Torre, J.-L. Bocquet, N. V. Doan, E. Adam, and A. Barbu. Jerk, an event-based kinetic monte carlo model to predict microstructure evolution of materials under irradiation. *Philos. Mag.*, 85(4-7):549–558, 2005. (Cited pages xi and 2.)

[6] A. S. Nowick and B. S. Berry. *Anelastic relaxation in crystalline solids*. Academic Press, New York and London, 1972. (Cited pages xi and 3.)

[7] S. Bausch, H.G. Bohn, and W. Schilling. Anelastic and dielectric relaxation measurements in the protonic conductor $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$. *Solid State Ionics*, 97:517–521, 1997. (Cited pages xi and 3.)

[8] K. Ruschenschmidt, H. Bracht, N. A. Stolwijk, M. Laube, G. Pensl, and G. R. Brandes. Self-diffusion in isotopically enriched silicon carbide and its correlation with dopant diffusion. *J. Appl. Phys.*, 96(3):1458–1463, 2004. (Cited pages xi, 3, and 39.)

[9] G. K. Celler and L. E. Trimble. High-temperature stability of Si/SiO_2 interfaces and the influence of SiO flux on thermomigration of impurities in SiO_2. *Appl. Phys. Lett.*, 53:2492–2494, 1988. (Cited pages 3 and 33.)

[10] Hartmut Bracht. Self- and foreign-atom diffusion in semiconductor isotope heterostructures. I. continuum theoretical calculations. *Phys. Rev. B*, 75:035210, 2007. (Cited pages xi and 3.)

[11] G. Roma. Palladium in cubic silicon carbide: stability and kinetics. *J. Appl. Phys.*, 106:123504, 2009. (Cited pages xii, xviii, 3, 11, 37, 43, 44, 50, and 77.)

[12] Fei Gao, Eric J. Bylaska, William J. Weber, and L. René Corrales. *Ab initio* and empirical-potential studies of defect properties in $3C-$SiC. *Phys. Rev. B*, 64:245208, 2001. (Cited pages xii and 3.)

[13] Paul Erhart and Karsten Albe. Analytical potential for atomistic simulations of silicon, carbon, and silicon carbide. *Phys. Rev. B*, 71:035211, 2005. (Cited pages xii and 3.)

[14] A. Hallil, E. Amzallag, S. Landron, and R. Tétot. Properties of rutile tio2 surfaces from a tight-binding variable-charge model. comparison with ab initio calculations. *Surf. Sci.*, 605(7-8):738 – 745, 2011. (Cited pages xii and 4.)

[15] B. S. Thomas and N. A. Marks. Comment on "use of a variable-charge interatomic potential for atomistic simulations of bulk, oxygen vacancies, and surfaces of rutile TiO_2". *Phys. Rev. B*, 76:167401, 2007. (Cited pages xii and 4.)

[16] Pekka Koskinen and Ville Mäkinen. Density-functional tight-binding for beginners. *Comp. Mater. Sci.*, 47:237–253, 2009. (Cited pages xii and 4.)

[17] S. J. Zinkle and C. Kinoshita. Defect production in ceramics. *J. Nucl. Mater.*, 251:200–217, 1997. (Cited pages xii and 5.)

[18] Yves Limoge and Alain Barbu. Aging of oxides under irradiation. *Def. Diff. Forum*, 237–240:621, 2005. (Cited pages xii and 5.)

[19] Yves Limoge. Radiation aging of nonmetallic materials: specific aspects. *Comptes Rendus Physique*, 9:370 – 378, 2008. (Cited pages xii and 5.)

[20] K. P. Driver, R. E. Cohen, Zhigang Wu, B. Militzer, P. López Ríos, M. D. Towler, R. J. Needs, and J. W. Wilkinsa. Quantum monte carlo computations of phase stability, equations of state, and elasticity of high-pressure silica. *Proc. Natl. Acad. Sci.*, 107:9519, 2010. (Cited page 5.)

[21] Y. Adda and J. Philibert. *La diffusion dans les solides*. Bibliothèque de Sciences et Techniques Nucléaires. Presses Universitaires de France, 1966. (Cited page 7.)

[22] J. L. Bocquet, G. Brebec, and Y. Limoge. *Physical Metallurgy*, chapter 7 Diffusion in metals and alloys, pages 536–668. Elsevier Science, Amsterdam, 1996. p. 583. (Cited pages xiii, 7, and 8.)

[23] Peter Hänggi, Peter Talkner, and Michal Borkovec. Reaction-rate theory: fifty years after kramers. *Rev. Mod. Phys.*, 62:251–341, 1990. (Cited pages xiii and 8.)

[24] Olga Natalia Bedoya-Martínez and Guido Roma. Activation entropies for diffusion in cubic silicon carbide from first principles. *Phys. Rev. B*, 82:134115, 2010. (Cited pages xvi, xvii, 8, 37, 39, 50, 65, 66, and 77.)

[25] J Mayer and M Fähnle. On the meaning of effective formation energies, entropies and volumes for atomic defects in ordered compounds. *Acta Mater.*, 45:2207 – 2211, 1997. (Cited pages xiii and 8.)

[26] Neil W. Ashcroft and David N. Mermin. *Solid State Physics*. Saunders College Publishing, international edition edition, 1976. p. 574-575. (Cited pages 9 and 13.)

[27] N. Capron, S. Carniato, A. Lagraa, G. Boureau, and A. Pasturel. Local density approximation and generalized gradient approximation calculations for oxygen and silicon vacancies in silica. *J. Chem. Phys.*, 112(21):9543–9548, 2000. (Cited pages 11 and 17.)

[28] Guido Roma. A first principles study of palladium impurities in silicon carbide. *Adv. Sci. Technol.*, 45:1969–1973, 2006. (Cited pages 11 and 43.)

[29] G. Jacucci and R. Taylor. Calculation of vacancy formation energies in the alkali-metals Li, Na and K. *J. Phys. F: Met. Phys.*, 9(8):1489–1502, 1979. (Cited page 11.)

[30] Peter Agoston and Karsten Albe. Formation entropies of intrinsic point defects in cubic In_2O_3 from first-principles density functional theory calculations. *Phys. Chem. Chem. Phys.*, 11(17):3226–3232, 2009. (Cited page 11.)

[31] G. B. Bachelet, G. Jacucci, R. Car, and M. Parrinello. Free energy of formation of lattice vacancies in silicon. In Olof Engstrom, editor, *Proceedings of the 18th International Conference on The Physics of Semiconductors*, volume 2, page 801, Singapore, 1987. World Scientific. (Cited page 11.)

[32] Matthias Scheffler and Jaroslaw Dabrowski. Parameter-free calculations of total energies, interatomic forces and vibrational entropies of defects in semiconductors. *Philos. Mag.*, 58:107–121, 1988. (Cited page 11.)

[33] K. L. Kliewer and J. S. Koehler. Space charge in ionic crystals. I. general approach with application to NaCl. *Phys. Rev.*, 140:A1226–A1240, 1965. (Cited pages 12 and 13.)

[34] J. Frenkel. *Kinetic Thoery of Liquids*. Oxford at the Clarendon Press, 1946. (Cited page 12.)

[35] S. K. Wonnell and L. M. Slifkin. Individual point defect formation parameters for AgBr, AgCl, and NaCl. *Radiation Effects and Defects in Solids*, 119-121(1):135–140, 1991. (Cited page 13.)

[36] Guido Roma, Yves Limoge, and Layla Martin-Samos. Aspects of point defects energetics and diffusion in SiO_2 from first principles simulations. *Nucl. Instrum. Meth. Phys. Res. B*, 250:54–56, 2006. (Cited pages xv, 13, 26, and 49.)

[37] G. Roma and Y. Limoge. Density functional theory investigation of native defects in SiO_2: Self-doping and contribution to ionic conductivity. *Phys. Rev. B*, 70:174101, 2004. (Cited pages xiii, xv, 13, 25, 49, and 77.)

[38] D. B. Laks, C. G. Van de Walle, G. F. Neumark, P. E. Blöchl, and S. T. Pantelides. Native defects and self-compensation in ZnSe. *Phys. Rev. B*, 45:10965–10978, 1992. (Cited pages xiv and 14.)

[39] Warren E. Pickett. Pseudopotential methods in condensed matter applications. *Computer Physics Reports*, 9(3):115 – 197, 1989. (Cited page 14.)

[40] S. W. de Leeuw, J. W. Perram, and E. R. Smith. Simulation of electrostatic systems in periodic boundary conditions. i. lattice sums and

dielectric constants. *Proc. R. Soc. Lond.*, A373:27–56, 1980. (Cited page 14.)

[41] Leonard Kleinman. Comment on the average potential of a Wigner solid. *Phys. Rev. B*, 24:7412–7414, 1981. (Cited page 14.)

[42] G. Makov and M. C. Payne. Periodic boundary conditions in *ab initio* calculations. *Phys. Rev. B*, 51:4014–4022, 1995. (Cited pages xiv and 14.)

[43] M. Leslie and M. J. Gillan. The energy and elastic dipole tensor of defects in ionic crystals calculated by the supercell method. *J. Phys. C*, 18:973, 1985. (Cited page 14.)

[44] Jihye Shim, Eok-Kyun Lee, Y. J. Lee, and R. M. Nieminen. Density-functional calculations of defect formation energies using supercell methods: Defects in diamond. *Phys. Rev. B*, 71:035206, 2005. (Cited pages xiv and 14.)

[45] U. Gerstmann, P. Déak, R. Rurali, B. Aradi, Th. Frauenheim, and H. Overhof. Charge corrections for supercell calculations of defects in semiconductors. *Physica B*, 340-342:190, (2003). (Cited page 14.)

[46] Peter A. Schultz. Charged local defects in extended systems. *Phys. Rev. Lett.*, 84:1942–1945, 2000. (Cited page 14.)

[47] Ismaila Dabo, Boris Kozinsky, Nicholas E. Singh-Miller, and Nicola Marzari. Electrostatics in periodic boundary conditions and real-space corrections. *Phys. Rev. B*, 77:115139, 2008. (Cited page 14.)

[48] Stephan Lany and Alex Zunger. Assessment of correction methods for the band-gap problem and for finite-size effects in supercell defect calculations: Case studies for ZnO and GaAs. *Phys. Rev. B*, 78:235104, 2008. (Cited pages xiv, 14, and 18.)

[49] C. Freysoldt, J. Neugebauer, and C. G. Van de Walle. Fully ab initio finite-size corrections for charged-defect supercell calculations. *Phys. Rev. Lett.*, 102:016402, 2009. (Cited pages xiv and 14.)

[50] N. D. M. Hine, K. Frensch, W. M. C. Foulkes, and M. W. Finnis. Supercell size scaling of density functional theory formation energies of charged defects. *Phys. Rev. B*, 79:024112, 2009. (Cited page 14.)

[51] Samuel E. Taylor and Fabien Bruneval. Understanding and correcting the spurious interactions in charged supercells. *Phys. Rev. B*, 84:075155, 2011. (Cited pages xiv, 14, and 15.)

[52] Alfonso Baldereschi, Stefano Baroni, and Raffaele Resta. Band offsets in lattice-matched heterojunctions: A model and first-principles calculations for GaAs/AlAs. *Phys. Rev. Lett.*, 61:734–737, 1988. (Cited page 15.)

[53] Walter R. L. Lambrecht. Which electronic structure method for the study of defects: A commentary. *Phys. Status Solidi B*, 248(7):1547–1558, 2011. (Cited pages xiv and 17.)

[54] Audrius Alkauskas, Peter Deák, Jörg Neugebauer, Alfredo Pasquarello, and Chris G. Van de Walle, editors. *Advanced Calculations for Defects in Materials: Electronic Structure Methods*. Wiley-VCH Verlag GmbH & Co., 2011. (Cited page 17.)

[55] Th. Demuth, Y. Jeanvoine, J. Hafner, and J. G. Àngyàn. Polymorphism in silica studied in the local density and generalized-gradient approximations. *J. Phys.: Cond. Matt.*, 11(19):3833, 1999. (Cited page 17.)

[56] D. R. Hamann. Diffusion of atomic oxygen in SiO_2. *Phys. Rev. Lett.*, 81:3447–3450, 1998. (Cited pages 17 and 23.)

[57] G. Roma, Y. Limoge, and S. Baroni. Oxygen self-diffusion in α-quartz. *Phys. Rev. Lett.*, 86:4564–4567, 2001. (Cited pages xiii, xv, 17, 24, 31, 49, and 77.)

[58] L. Martin-Samos, G. Roma, P. Rinke, and Y. Limoge. Charged oxygen defects in SiO_2: going beyond local and semilocal approximations to density functional theory. *Phys. Rev. Lett.*, 104:075502, 2010. (Cited pages xv, xvi, 17, 18, 30, 31, 49, and 77.)

[59] Young-Gu Jin and K. J. Chang. Mechanism for the enhanced diffusion of charged oxygen ions in SiO_2. *Phys. Rev. Lett.*, 86:1793, 2001. (Cited pages 17, 25, and 26.)

[60] G. Lucas and L. Pizzagalli. Structure and stability of irradiation-induced frenkel pairs in 3C-SiC using first principles calculations. *Nucl. Instrum. Meth. Phys. Res. B*, 255:124, 2007. (Cited page 17.)

[61] Guido Roma, Fabien Bruneval, Ting Liao, Olga Natalia Bedoya Martínez, and Jean-Paul Crocombette. Formation and migration energy of native defects in silicon carbide from first principles: an overview. *Def. Diff. Forum*, 323-325:11, 2012. (Cited pages 17 and 37.)

[62] A. Alkauskas, P. Broqvist, and A. Pasquarello. Defect energy levels in density functional calculations: Alignment and band gap problem. *Phys. Rev. Lett.*, 101:046405, 2008. (Cited pages 17 and 31.)

[63] G. A. Baraff and M. Schlüter. New self-consistent approach to the electronic structure of localized defects in solids. *Phys. Rev. B*, 19:4965–4979, 1979. (Cited page 18.)

[64] Gianfranco Pacchioni, Fabiano Frigoli, Davide Ricci, and John A. Weil. Theoretical description of hole localization in a quartz Al center: The importance of exact electron exchange. *Phys. Rev. B*, 63:054102, 2000. (Cited page 18.)

[65] J. Lægsgaard and K. Stokbro. Hole trapping at al impurities in silica: A challenge for density functional theories. *Phys. Rev. Lett.*, 86:2834–2837, Mar 2001. (Cited page 18.)

[66] Fabien Bruneval. *GW* approximation of the many-body problem and changes in the particle number. *Phys. Rev. Lett.*, 103:176403, 2009. (Cited page 18.)

[67] Ismaila Dabo, Andrea Ferretti, Nicolas Poilvert, Yanli Li, Nicola Marzari, and Matteo Cococcioni. Koopmans' condition for density-functional theory. *Phys. Rev. B*, 82:115121, 2010. (Cited page 18.)

[68] G. A. Baraff and M. Schlüter. Calculation of the total energy of charged point defects using the Green's-function technique. *Phys. Rev. B*, 30:1853–1866, 1984. (Cited page 18.)

[69] Fabien Devynck, Audrius Alkauskas, Peter Broqvist, and Alfredo Pasquarello. Charge transition levels of carbon-, oxygen-, and hydrogen-related defects at the SiC/SiO_2 interface through hybrid functionals. *Phys. Rev. B*, 84:235320, 2011. (Cited pages 18 and 31.)

[70] Fabien Bruneval. Private communication. (Cited page 19.)

[71] S. Botti and J. Vidal. *Electronic excitations in solar cells from GW approaches*. Wiley-Blackwell, 2012. (Cited page 19.)

[72] Julien Vidal, Silvana Botti, Pär Olsson, Jean-François Guillemoles, and Lucia Reining. Strong interplay between structure and electronic properties in $CuIn(S,Se)_2$: A first-principles study. *Phys. Rev. Lett.*, 104:056401, 2010. (Cited page 19.)

[73] Normand Mousseau and G. T. Barkema. Traveling through potential energy landscapes of disordered materials: The activation-relaxation technique. *Phys. Rev. E*, 57:2419–2424, 1998. (Cited page 19.)

[74] G. Mills and H. Jónsson. Quantum and thermal effects in H_2 dissociative adsorption: Evaluation of free energy barriers in multidimensional quantum systems. *Phys. Rev. Lett.*, 72:1124, 1994. (Cited page 19.)

[75] G. Henkelman, B. P. Uberuaga, and H. Jónsson. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.*, 113:9901, 2000. (Cited page 19.)

[76] C. H. Bennett. *Diffusion in Solids: Recent developments*, page 73. Academic Press, New York, 1975. (Cited page 19.)

[77] G. Roma and J.-P. Crocombette. Evidence for a kinetic bias towards antisite formation in SiC nano-decomposition. *J. Nucl. Mater.*, 403:32–41, 2010. (Cited pages xiv, xvii, 19, 37, 40, 50, 65, and 67.)

[78] Christoph Dellago, Peter G. Bolhuis, and Phillip L. Geissler. *Transition Path Sampling*, pages 1–78. John Wiley & Sons, Inc., 2003. (Cited page 20.)

[79] Alssandro Laio and Michele Parrinello. Escaping free-energy minima. *Proc. Natl. Acad. Sci.*, 99:12562, 2002. (Cited page 20.)

[80] M. A. Lamkin, F. L. Riley, and R. J. Fordham. Oxygen mobility in silicon dioxide and silicate glasses: a review. *J. Europ. Cer. Soc.*, 10:347–367, 1992. (Cited pages 21 and 23.)

[81] J. D. Kalen, R. S. Boyce, and J. D. Cawley. Oxygen tracer diffusion in vitreous silica. *J. Amer. Ceram. Soc.*, 74:203, 1991. (Cited page 21.)

[82] Kirsten Sunder and Hartmut Bracht. Oxygen and silicon diffusion in silica under varying ambient conditions. *Def. Diff. Forum*, 289–292:531–539, 2009. (Cited pages 21 and 49.)

[83] H. Jain and A. S. Nowick. Electrical conductivity of synthetic quartz and natural quartz crystals. *J. Appl. Phys.*, 53:477, 1982. (Cited pages 21 and 26.)

[84] Eugene. W. Sucov. Diffusion of oxygen in vitreous silica. *J. Amer. Cer. Soc.*, 46:14, 1963. (Cited page 23.)

[85] E. L. Williams. Diffusion of oxygen in fused silica. *J. Amer. Cer. Soc.*, 48(4):190–194, 1965. (Cited page 23.)

[86] A. Bongiorno and A. Pasquarello. Oxygen diffusion through the disordered oxide network during silicon oxidation. *Phys. Rev. Lett.*, 88:125901, 2002. (Cited page 23.)

[87] G. Roma, Y. Limoge, and S. Baroni. Oxygen self-diffusion in SiO_2: An ab-initio approach. *Def. Diff. Forum*, 194-1:287–293, 2001. (Cited page 23.)

[88] S.T. Pantelides, Z.-Y. Lu, C. Nicklaw, T. Bakos, S.N. Rashkeev, D.M. Fleetwood, and R.D. Schrimpf. The E′ center and oxygen vacancies in SiO_2. *J. Non-Cryst. Sol.*, 354:217 – 223, 2008. (Cited page 23.)

[89] Gianfranco Pacchioni and Gianluigi Ieranò. *Ab initio* formation energies of point defects in pure and Ge-doped SiO_2. *Phys. Rev. B*, 56:7304–7312, 1997. (Cited page 23.)

[90] C. M. Carbonaro, Vincenzo Fiorentini, and S. Massidda. Ab-initio study of oxygen vacancies in α-quartz. *J. Non-Cryst. Solids*, 221:89, 1997. (Cited page 23.)

[91] Mauro Boero, Alfredo Pasquarello, Johannes Sarnthein, and Roberto Car. Structure and hyperfine parameters of E_1' centers in α-quartz and in vitreous SiO_2. *Phys. Rev. Lett.*, 78:887–890, 1997. (Cited page 23.)

[92] Eoin P. O'Reilly and John Robertson. Theory of defects in vitreous silicon dioxide. *Phys. Rev. B*, 27:3780–3795, 1983. (Cited page 23.)

[93] J. C. Mikkelsen. Self-diffusivity of network oxygen in vitreous SiO_2. *Appl. Phys. Lett.*, 45:1187, 1984. (Cited pages xv and 24.)

[94] Carlo Maria Carbonaro, Vincenzo Fiorentini, and Fabio Bernardini. Proof of the thermodynamical stability of the E′ center in SiO_2. *Phys. Rev. Lett.*, 86:3064, 2001. (Cited page 25.)

[95] G. Roma and Y. Limoge. First principles suggestions of targeted diffusion experiments on SiO_2. *Def. Diff. Forum*, 237-240:127–132, 2005. (Cited page 26.)

[96] Renée M. Van Ginhoven, Hannes Jónsson, Byeongwon Park, and L. René Corrales. Cleavage and recovery of molecular water in silica. *J. Phys. Chem. B*, 109(21):10936–10945, 2005. (Cited page 26.)

[97] Hajimu Wakabayashi and Minoru Tomozawa. Diffusion of water into silica glass at low temperature. *J. Amer. Cer. Soc.*, 72(10):1850–1855, 1989. (Cited page 26.)

[98] A. Rosa, A. El-Barbary, M. Heggie, and P. Briddon. Structural and thermodynamic properties of water related defects in α-quartz. *Phys. Chem. Miner.*, 32:323–331, 2005. (Cited page 26.)

[99] Layla Martin-Samos. *Étude ab-initio des auto-défauts et des mécanismes d'auto-diffusion dans un verre de silice*. PhD thesis, Université de Cergy-Pontoise, 2004. (Cited pages xv and 26.)

[100] L. Martin-Samos, Y. Limoge, N. Richard, J. P. Crocombette, G. Roma, E. Anglada, and E. Artacho. Oxygen neutral defects in silica: Origin of the distribution of the formation energies. *Europhys. Lett.*, 66:680–686, 2004. (Cited pages xv, 28, and 49.)

[101] N. Richard, L. Martin-Samos, G. Roma, Y. Limoge, and J. P. Crocombette. First principle study of neutral and charged self-defects in amorphous SiO_2. *J. Non-Cryst. Solids*, 351:1825–1829, 2005. (Cited pages xv, 28, and 49.)

[102] L. Martin-Samos, Y. Limoge, J. P. Crocombette, G. Roma, and N. Richard. Oxygen self-diffusion mechanisms in silica by first-principles. *Def. Diff. Forum*, 237-240:115–120, 2005. (Cited pages 28 and 49.)

[103] L. Martin-Samos, Y. Limoge, J. P. Crocombette, G. Roma, N. Richard, E. Anglada, and E. Artacho. Neutral self-defects in a silica model: A first-principles study. *Phys. Rev. B*, 71:014116, 2005. (Cited pages xv, 28, and 49.)

[104] Y. Limoge and J. L. Bocquet. Temperature behavior of tracer diffusion in amorphous materials: A random-walk approach. *Phys. Rev. Lett.*, 65:60–63, Jul 1990. (Cited page 28.)

[105] L. Martin-Samos, Y. Limoge, and G. Roma. Defects in amorphous SiO_2: Valence alternation pair model. *Phys. Rev. B*, 76:104203, 2007. (Cited pages xv, 28, 49, and 77.)

[106] N. Marzari and D. Vanderbilt. Maximally localized generalized wannier functions for composite energy bands. *Phys. Rev. B*, 56:12847, 1997. (Cited page 28.)

[107] P. Fitzhenry, M. M. M. Bilek, N. A. Marks, N. C. Cooper, and D. R. McKenzie. Wannier function analysis of silicon-carbon alloys. *J. Phys. Cond. Matter*, 15(2):165, 2003. (Cited page 28.)

[108] D.G. McCulloch, A.R. Merchant, N.A. Marks, N.C. Cooper, P. Fitzhenry, M.M.M. Bilek, and D.R. McKenzie. Wannier function analysis of tetrahedral amorphous networks. *Diamond and Related Materials*, 12:2026 – 2031, 2003. (Cited page 28.)

[109] Pier Luigi Silvestrelli and Michele Parrinello. Water molecule dipole in the gas and in the liquid phase. *Phys. Rev. Lett.*, 82:3308–3311, 1999. (Cited page 28.)

[110] A. Gali, T. Hornos, N. T. Son, E. Janzén, and W. J. Choyke. *Ab initio* supercell calculations on aluminum-related defects in SiC. *Phys. Rev. B*, 75:045211, 2007. (Cited page 30.)

[111] P. Deák, Th. Frauenheim, and A. Gali. Limits of the scaled shift correction to levels of interstitial defects in semiconductors. *Phys. Rev. B*, 75:153204, 2007. (Cited page 30.)

[112] P. Rinke, A. Janotti, M. Scheffler, and C. G. Van de Walle. Defect formation energies without the band-gap problem: Combining density-functional theory and the GW approach for the silicon self-interstitial. *Phys. Rev. Lett.*, 102:026402, 2009. (Cited page 30.)

[113] Layla Martin-Samos and Giovanni Bussi. SaX: An open source package for electronic-structure and optical-properties calculations in the GW approximation. *Comp. Phys. Commun.*, 180(8):1416 – 1425, 2009. (Cited page 30.)

[114] R. Shaltaf, G.-M. Rignanese, X. Gonze, Feliciano Giustino, and Alfredo Pasquarello. Band offsets at the Si/SiO_2 interface from many-body perturbation theory. *Phys. Rev. Lett.*, 100:186401, 2008. (Cited page 30.)

[115] G. Brebec, R. Seguin, C. Sella, J. Bevenot, and J. C. Martin. Diffusion du silicium dans la silice amorphe. *Acta Metall.*, 28:327–333, 1980. (Cited page 31.)

[116] R. Tromp, G. D. Rubloff, P. Balk, F. K. LeGoues, and E. J. van Loenen. High-temperature SiO_2 decomposition at the SiO_2/Si interface. *Phys. Rev. Lett.*, 55:2332–2335, 1985. (Cited page 33.)

[117] D. Tsoukalas, C. Tsamis, and J. Stoemenos. Investigation of silicon interstitial reactions with insulating films using the silicon wafer bonding technique. *Appl. Phys. Lett.*, 63:3167–3169, 1993. (Cited page 33.)

[118] D. Tsoukalas, C. Tsamis, and P. Normand. Diffusivity measurements of silicon in silicon dioxide layers using isotopically pure material. *J. Appl. Phys.*, 89:7809–7813, 2001. (Cited page 33.)

[119] D. Mathiot, J. P. Schunck, M. Perego, M. Fanciulli, P. Normand, C. Tsamis, and D. Tsoukalas. Silicon self-diffusivity measurement in thermal SiO_2 by ^{30}Si/^{28}Si isotopic exchange. *J. Appl. Phys.*, 94:2136–2138, 2003. (Cited page 33.)

[120] T. Takahashi, S. Fukatsu, K. M. Itoh, M. Uematsu, A. Fujiwara, H. Kageshima, and Y. Takahashi. Self-diffusion of Si in thermally grown SiO_2 under equilibrium conditions. *J. Appl. Phys.*, 93:3674–3676, 2003. (Cited page 33.)

[121] M. Uematsu, H. Kageshima, Y. Takahashi, S. Fukatsu, K. M. Itoh, K. Shiraishi, and U. Gösele. Modeling of si self-diffusion in SiO_2: Effect of the Si/SiO_2 interface including time-dependent diffusivity. *Appl. Phys. Lett.*, 84:876, 2004. (Cited page 33.)

[122] Guido Roma, Yves Limoge, and Layla Martin-Samos. Oxygen and silicon self-diffusion in quartz and silica: The contribution of first principles calculations. *Def. Diff. Forum*, 258-260:542–553, 2006. (Cited pages xv, xvi, 33, and 49.)

[123] O. Jaoul, F. Béjina, F. Élie, and F. Abel. Silicon self-diffusion in quartz. *Phys. Rev. Lett.*, 74:2038, 1995. (Cited page 33.)

[124] M. Bockstedte, A. Gali, A. Mattausch, O. Pankratov, and J. W. Steeds. Identification of intrinsic defects in sic: Towards an understanding of defect aggregates by combining theoretical and experimental approaches. *Physica Status Solidi B-Basic Solid State Physics*, 245(7):1281–1297, 2008. (Cited page 37.)

[125] J.-P. Crocombette and G. Roma. Étude bibliographique sur les simulations à l'échelle atomique des défauts et dégats d'irradiation dans le carbure de silicium. Note Technique DEN/DANS/DMN/SRMP/NT/2009-21, CEA, Service de Recherches de Métalurgie Physique, 2009. (Cited page 37.)

[126] T. Liao and G. Roma. Silicon di-interstitial structures in 3C-SiC. Note Technique DEN/DANS/DMN/SRMP/NT/2008-01, CEA

, Service de Recherches de Métallurgie Physique, 2008. p. 23. (Cited pages xviii, 37, 43, 66, 67, and 77.)

[127] Ting Liao, Olga Natalia Bedoya-Martínez, and Guido Roma. Stoichiometric defects in silicon carbide. *J.Phys. Chem. C*, 114:22691–22696, 2010. (Cited pages xvii, 37, 39, 41, 42, 50, 65, 67, and 77.)

[128] Fabien Bruneval and Guido Roma. Energetics and metastability of the silicon vacancy in cubic SiC. *Phys. Rev. B*, 83:144116, 2011. (Cited pages xvii, 37, 41, 42, 50, 65, 66, 67, and 77.)

[129] M. Bockstedte, A. Mattausch, and O. Pankratov. Ab initio study of the migration of intrinsic defects in 3C-SiC. *Phys. Rev. B*, 68:205201, 2003. (Cited pages 37, 43, and 66.)

[130] T. Liao, G. Roma, and J. Y. Wang. Neutral silicon interstitials in 3C and 4H silicon carbide: a first principles study. *Philos. Mag.*, 89:2271–2284, 2009. (Cited pages xviii, 39, 43, 49, 65, and 66.)

[131] In-Tae Bae, William J. Weber, Manabu Ishimaru, and Yoshihiko Hirotsu. Effect of ionization rates on dynamic recovery processes during electron-beam irradiation of 6H-SiC. *Appl. Phys. Lett.*, 90(12):121910, 2007. (Cited page 39.)

[132] J. C. Bourgoin and J. W. Corbett. Enhanced diffusion mechanisms. *Radiation Effects*, 36:157–188, 1978. (Cited page 39.)

[133] C. Wert and C. Zener. Interstitial atomic diffusion coefficients. *Phys. Rev. B*, 76(1):1169, 1949. (Cited pages xvii and 39.)

[134] C. Zener. Theory of D_0 for atomic diffusion in metals. *J. Appl. Phys.*, 22(4):372–375, 1951. (Cited pages xvii and 39.)

[135] A. Yelon, B. Movaghar, and R. S. Crandall. Multi-excitation entropy: its role in thermodynamics and kinetics. *Rep. Prog. Phys.*, 69(4):1145–1194, 2006. (Cited pages xvii and 39.)

[136] Lance L. Snead, Takashi Nozawa, Yutai Katoh, Thak-Sang Byun, Sosuke Kondo, and David A. Petti. Handbook of SiC properties for fuel performance modeling. *J. Nucl. Mater.*, 371:329–377, 2007. (Cited page 40.)

[137] Thomas R. Waite. Bimolecular reaction rates in solids and liquids. *J. Chem. Phys.*, 32:21, 1960. (Cited page 41.)

[138] U. Gerstmann, A. P. Seitsonen, D. Ceresoli, F. Mauri, H. J. von Bardeleben, J. L. Cantin, and J. Garcia Lopez. $Si_C C_{Si}$ antisite pairs in SiC identified as paramagnetic defects with strongly anisotropic orbital quenching. *Phys. Rev. B*, 81:195208, 2010. (Cited pages 41 and 51.)

[139] M. Bockstedte, A. Mattausch, and O. Pankratov. Ab initio study of the annealing of vacancies and interstitials in cubic SiC: Vacancy-interstitial recombination and aggregation of carbon interstitials. *Phys. Rev. B*, 69:235202, 2004. (Cited page 41.)

[140] A. Mattausch, M. Bockstedte, and O. Pankratov. Carbon antisite clusters in SiC: A possible pathway to the D_{II} center. *Phys. Rev. B*, 69:045322, 2004. (Cited pages xviii and 43.)

[141] A. Mattausch, M. Bockstedte, and O. Pankratov. Structure and vibrational spectra of carbon clusters in SiC. *Phys. Rev. B*, 70:235211, 2004. (Cited pages xviii, 43, and 67.)

[142] A. Gali, P. Deák, P. Ordejón N. T. Son E. Janzén, and W. J. Choyke. Aggregation of carbon interstitials in silicon carbide: A theoretical study. *Phys. Rev. B*, 68:215201, 2003. (Cited pages xviii and 43.)

[143] T. Hornos, N. T. Son, E. Janzén, and A. Gali. Theoretical study of small silicon clusters in 4H-SiC. *Phys. Rev. B*, 76:165209, 2007. (Cited pages xviii and 43.)

[144] Guido Roma. The influence of palladium impurities on vacancy diffusion in cubic silicon carbide. In J.K. Gibson, S.K. McCall, E.D. Bauer, L. Soderholm, T. Fanghaenel, R. Devanathan, A. Misra, C. Trautmann, and B.D. Wirth, editors, *Basic Actinide Science and Materials for Nuclear Applications*, volume 1264 of *Mater. Res. Soc. Proc.*, 2010. (Cited pages xviii, 43, 44, and 50.)

[145] K. Minato, Toru Ogawa, Sotoru Kashimura, Kousaku Fukuda, Michio Shimizu, Yoshinobu Tayama, and Ishio Takahashi. Fission product palladium-silicon carbide interaction in HTGR fuel particles. *J. Nucl. Mater.*, 172:184–196, 1990. (Cited page 44.)

[146] R. L. Pearson, R. J. Lauf, and T. B. Lindemer. The interaction of palladium, the rare earths and silver with silicon carbide in HTGR fuel particles. Technical Report ORNL/TM–8059, Oak Ridge National Laboratory, Oak Ridge, Tennesse 37830, April 1982. (Cited page 44.)

[147] M. Miyata, Y. Higashiguchi, and Y. Hayafuji. Ab initio study of substitutional impurity atoms in 4H-SiC. *J. Appl. Phys.*, 104:123702, 2008. (Cited page 45.)

[148] M. S. Miao and Walter R. L. Lambrecht. Electronic structure and magnetic properties of transition-metal-doped 3*C* and 4*H* silicon carbide. *Phys. Rev. B*, 74:235218, 2006. (Cited page 45.)

[149] Andrei Los and Victor Los. Magnetic states of transition metal impurities in silicon carbide. *J. Phys.: Condens. Matter*, 21(20):206004, 2009. (Cited page 45.)

[150] A. Grüneis, C. Attaccalite, L. Wirtz, H. Shiozawa, R. Saito, T. Pichler, and A. Rubio. Tight-binding description of the quasiparticle dispersion of graphite and few-layer graphene. *Phys. Rev. B*, 78:205425, Nov 2008. (Cited page 49.)

[151] T. A. Niehaus, M. Rohlfing, F. Della Sala, A. Di Carlo, and Th. Frauenheim. Quasiparticle energies for large molecules: A tight-binding-based green's-function approach. *Phys. Rev. A*, 71:022508, Feb 2005. (Cited page 49.)

[152] M. J. Gillan. The heat of transport in solids : A new theoretical approach. *J. Phys. C*, 10:1641, 1977. (Cited page 50.)

[153] D. Alfè and M. J. Gillan. Schottky defect formation energy in MgO calculated by diffusion Monte Carlo. *Phys. Rev. B*, 71:220101R, 2005. (Cited page 51.)

[154] M. Bockstedte, A. Marini O. Pankratov, and A. Rubio. Many-body effects in the excitation spectrum of a defect in SiC. *Phys. Rev. Lett.*, 105:026401, 2010. (Cited page 51.)

Annexes A

Table A.1 – *Formation energies of native defects in cubic silicon carbide. The conventions are silicon-rich conditions and Fermi energy at the valence band top.*

Defect formation energies			
Defect	Charge	Formation energy	Reference
V_{Si}	+2	7.91	[2]
V_{Si}	+1	8.88	[2]
V_{Si}	0	9.70	[2]
V_{Si}	-1	10.43	[2]
V_{Si}	-2	12.37	[2]
$V_C C_{Si}$	+2	3.51	[2]
$V_C C_{Si}$	+1	5.49	[2]
$V_C C_{Si}$	0	7.45	[2]
$V_C C_{Si}$	-1	9.49	[2]
V_C	0	4.38	[3]
V_C	+1	2.61	[3]
V_C	+2	0.65	[3]
$I_{Sisp110}$	0	8.27	[4]
I_{SiTC}	+4	2.23	[5]
I_{Csp100}	0	6.80	[6]
I_{Csp100}	+2	4.40	[6]
C_{Si}	0	3.88	[7]
Si_C	0	3.19	[7]
AP	0	5.19	[8]
AP	+2	6.91	[8]
AP	-2	6.30	[8]

A.1 Point defect energies in cubic SiC

In order to understand the behaviour of a material under irradiation multi-scale models, able to cover several length and time scales, are absolutely necessary. The study of irradiation effects in metals have lead to use several models of this kind, coupling, for example, event/object-based Monte Carlo simulations with first principles data for defects (the "objects") [1]. For non-metallic materials such approaches are less developed until now, partly because of intrinsic difficulties. However, silicon carbide, for which a number of defect properties have been calculated from first principles, seems to be a good candidate for applying such multi-scale approaches. Here below I have gathered results on formation energies and migration barriers from my personal calculations and completed with results obtained in the literature and from colleagues at SRMP. The set is inevitably heterogeneous, but it can be taken as a starting point for an iterative improvement, alternating kinetic simulations, which would suggest which mechanisms enter in competition in given conditions, and further improved first principles calculations, aiming at a more uniform and more reliable data set.

Table A.2 – *Defect reactions barriers in cubic SiC, including ordinary migrations, Frenkel-pair recombinations, some cluster dissociations and some other transformations. The bullet (•) indicates an undefected crystal.*

Defect migrations and reactions							
Ordinary migration mechanisms (A⇌C)							
Defect A	Charge	Defect B	Charge	Defect C	Charge	Barrier	Reference
V_{Si}	0	—	—	V_{Si}	0	3.4	[9]
V_{Si}	+1	—	—	V_{Si}	+1	3.6	[9]
V_{Si}	-1	—	—	V_{Si}	-1	3.2	[9]
V_{Si}	-2	—	—	V_{Si}	-2	2.4	[9]
V_C	0	—	—	V_C	0	3.5	[9]
V_C	+1	—	—	V_C	+1	4.1	[9]
V_C	+2	—	—	V_C	+2	5.2	[9]
I_{Csp100}	0	—	—	I_{Csp100}	0	0.57	[6]
I_{Csp100}	+2	—	—	I_{Csp100}	+2	1.37	[6]
I_{Csp100}	+1	—	—	I_{Csp100}	+1	0.9	[9]
I_{Csp100}	-1	—	—	I_{Csp100}	-1	0.6	[9]
I_{Csp100}	+2	—	—	$I_{CspSi100}$	+2	1.7	[9]
I_{Csp100}	+1	—	—	$I_{CspSi100}$	+1	0.9	[9]
I_{Csp100}	0	—	—	$I_{CspSi100}$	0	0.5	[9]
I_{Csp100}	-1	—	—	$I_{CspSi100}$	-1	0.7	[9]
$I_{CspSi100}$	+2	—	—	I_{Csp100}	+2	0.9	[9]
$I_{CspSi100}$	+1	—	—	I_{Csp100}	+1	0.2	[9]
$I_{CspSi100}$	0	—	—	I_{Csp100}	0	0.2	[9]
$I_{CspSi100}$	-1	—	—	I_{Csp100}	-1	0.1	[9]
$I_{Sisp110}$	0	—	—	$I_{Sisp1\bar{1}0}$	0	1.27	[6]
$I_{Sisp110}$	0	—	—	$I_{Sisp110}$	0	1.4	[9]
$I_{Sisp110}$	+1	—	—	$I_{Sisp110}$	+1	1.0	[9]
$I_{Sisp110}$	0	—	—	I_{SiTC}	0	0.8	[4]
I_{SiTC}	0	—	—	$I_{Sisp110}$	0	0.6	[4]
I_{SiTC}	+4	—	—	I_{SiTSi}	+4	3.10	[6]
I_{SiTSi}	+4	—	—	I_{SiTC}	+4	0.40	[6]
I_{SiTC}	+4	—	—	$I_{Sisp100}$	+4	3.50	[9]
$I_{Sisp100}$	+4	—	—	I_{SiTC}	+4	0.03	[9]
I_{SiTC}	+4	—	—	$I_{Sisp110}$	+4	3.40	[9]
$I_{Sisp110}$	+4	—	—	I_{SiTC}	+4	0.05	[9]
I_{SiTSi}	+2	—	—	$I_{Sisp100}$	+2	0.10	[9]
$I_{Sisp100}$	+2	—	—	I_{SiTSi}	+2	0.25	[9]
I_{SiTSi}	+2	—	—	I_{SiTC}	+2	0.03	[9]
I_{SiTSi}	+3	—	—	I_{SiTC}	+3	0.04	[9]
$(I_{Si})_2$	0	—	—	$(I_{Si})_2$	0	1.2	[10]
Defects transformations (A⇌C)							
Defect A	Charge	Defect B	Charge	Defect C	Charge	Barrier	Reference
V_{Si}	0	—	—	V_CC_{Si}	0	2.03	[2]
V_{Si}	+1	—	—	V_CC_{Si}	+1	1.50	[2]
V_{Si}	-1	—	—	V_CC_{Si}	-1	2.75	[2]
V_CC_{Si}	0	—	—	V_{Si}	0	4.28	[2]
V_CC_{Si}	+1	—	—	V_{Si}	+1	4.89	[2]

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Defect migration and reactions				*continued from previous page*			
Defect A	Charge	Defect B	Charge	Defect C	Charge	Barrier	Reference
$V_C C_{Si}$	-1	—	—	V_{Si}	-1	3.69	[2]
AP	0	—	—	•	0	3.12	[7]
AP	0	—	—	antiSCD	0	1.90	[8]
AP	+2	—	—	antiSCD	+2	0.32	[8]
AP	-2	—	—	antiSCD	-2	1.68	[8]
antiSCD	0	—	—	AP	0	0.21	[8]
antiSCD	+2	—	—	AP	+2	0.10	[8]
antiSCD	-2	—	—	AP	-2	0.05	[8]
antiSCD	0	—	—	SCD	0	1.41	[8]
antiSCD	+2	—	—	•	+2	1.33	[8]
antiSCD	-2	—	—	SCD	-2	1.37	[8]
SCD	0	—	—	antiSCD	0	2.31	[8]
•	+2	—	—	antiSCD	+2	6.02	[8]
SCD	-2	—	—	antiSCD	-2	2.20	[8]
SCD	0	—	—	•	0	0.15	[8]
SCD	-2	—	—	•	0	0.08	[8]
Binary defects association reactions (A+B⇌C)							
Defect A	Charge	Defect B	Charge	Defect C	Charge	Barrier	Reference
V_{Si}	0	I_{Si}	0	•	0	0.03	[7]
V_{Si}	-1	I_{Si}	+4	•	+3	2.4	[11]
V_{Si}	0	I_C	0	C_{Si}	0	1.25	[7]
V_C	0	I_C	0	•	0	1.35	[7]
V_C	0	I_{Si}	0	Si_C	0	1.11	[7]
$V_C C_{Si}$	0	I_{Si}	0	AP	0	0.77	[7]
$V_C C_{Si}$	0	I_C	0	C_{Si}	0	0.80	[7]
Dissociation reactions (A⇌B+C)							
Defect A	Charge	Defect B	Charge	Defect C	Charge	Barrier	Reference
$(C_2)_{Si}$	+2	I_{Csp100}	+2?	C_{Si}	0?	3.9	[12]
$(C_2)_{Si}$	+1	I_{Csp100}	+1?	C_{Si}	0?	1.3	[12]
$(C_2)_{Si}$	0	I_{Csp100}	0	C_{Si}	0	4.1	[12]
$(C_3)_{Si}$	0	I_{Csp100}	0	$(C_2)_{Si}$	0	4.8	[12]
$(C_4)_{Si}$	0	I_{Csp100}	0	$(C_3)_{Si}$	0	5.2	[12]
$(I_C)_2$	0	I_{Csp100}	0	I_{Csp100}	0	4.8	[12]
$(I_C)_3$	0	$(I_C)_2$	0	I_{Csp100}	0	4.8	[12]
$(I_C)_4$	0	$(I_C)_3$	0	I_{Csp100}	0	2.8	[12]
$(I_{Si})_2$	0	$I_{Sisp110}$	0	$I_{Sisp110}$	0	3.2	[10]

Bibliography

[1] C.C. Fu, J. Dalla Torre, F. Willaime, J.L. Bocquet, and A. Barbu. Multiscale modelling of defect kinetics in irradiated iron. *Nat. Mater.*, 4:68–74, 2005. (Cited page 65.)

[2] Fabien Bruneval and Guido Roma. Energetics and metastability of the silicon vacancy in cubic SiC. *Phys. Rev. B*, 83:144116, 2011. (Cited pages xvii, 37, 41, 42, 50, 65, 66, 67, and 77.)

[3] Fabien Bruneval. Methodological aspects of the GW calculation of the carbon vacancy in 3C-SiC. *Nucl. Instrum. Meth. Phys. Res. B*, 277:77–79, 2012. (Cited page 65.)

[4] T. Liao, G. Roma, and J. Y. Wang. Neutral silicon interstitials in 3C and 4H silicon carbide: a first principles study. *Philos. Mag.*, 89:2271–2284, 2009. (Cited pages xviii, 39, 43, 49, 65, and 66.)

[5] G. Roma. Data for chemical kinetics in SiC. Unpublished results, 2012. (Cited page 65.)

[6] Olga Natalia Bedoya-Martínez and Guido Roma. Activation entropies for diffusion in cubic silicon carbide from first principles. *Phys. Rev. B*, 82:134115, 2010. (Cited pages xvi, xvii, 8, 37, 39, 50, 65, 66, and 77.)

[7] G. Roma and J.-P. Crocombette. Evidence for a kinetic bias towards antisite formation in SiC nano-decomposition. *J. Nucl. Mater.*, 403:32–41, 2010. (Cited pages xiv, xvii, 19, 37, 40, 50, 65, and 67.)

[8] Ting Liao, Olga Natalia Bedoya-Martínez, and Guido Roma. Stoichiometric defects in silicon carbide. *J.Phys. Chem. C*, 114:22691–22696, 2010. (Cited pages xvii, 37, 39, 41, 42, 50, 65, 67, and 77.)

[9] M. Bockstedte, A. Mattausch, and O. Pankratov. Ab initio study of the migration of intrinsic defects in 3C-SiC. *Phys. Rev. B*, 68:205201, 2003. (Cited pages 37, 43, and 66.)

[10] T. Liao and G. Roma. Silicon di-interstitial structures in 3C-SiC. Note Technique DEN/DANS/DMN/SRMP/NT/2008-01, CEA , Service de Recherches de Métallurgie Physique, 2008. p. 23. (Cited pages xviii, 37, 43, 66, 67, and 77.)

[11] N. T. Son, E. Janzén, J. Isoya, N. Morishita, H. Hanaya, H. Takizawa, T. Ohshima, and A. Gali. Identification of a Frenkel-pair defect in electron irradiated 3C SiC. *Phys. Rev. B*, 80:125201, 2009. (Cited page 67.)

[12] A. Mattausch, M. Bockstedte, and O. Pankratov. Structure and vibrational spectra of carbon clusters in SiC. *Phys. Rev. B*, 70:235211, 2004. (Cited pages xviii, 43, and 67.)

B Curriculum Vitæ

B.1 Informations personnelles, parcours scolaire et professionnel

B.1.1 Informations personnelles

Prénom NOM : **Guido ROMA**
Né le : 11 Février 1966
État-civil : marié, deux enfants
Nationalité : italienne
Tel. (Saclay) : +[33] 1 69081857
Tel. (Mayence) : +[49] 6131 3922703
Mobile : +[49] 176 3230 4235
Affectation :
Service de Recherches de Métallurgie Physique
CEA-Saclay (France)
Actuellement à l'Université de Mayence (Allemagne)
Institut de Chimie Analytique et Inorganique
email : `guido.roma@cea.fr`
email : `roma@uni-mainz.de`

B.1.2 Études

1993-1995 Doctorat en Physique (Université de Rome *Tor Vergata*).
Titre de la thèse de Doctorat : *Calcul ab-initio de propriétés électroniques et vibrationnelles de graphite intercalé et de matériaux simples à base de lithium*, en italien. Mention : *Ottimo* (très bien)
Directeurs de thèse : Prof. Carlo Maria Bertoni et Prof. Stefano Baroni

1992 Service Civil (en substitution du service militaire)

1985-1991 Laurea en Physique (Université de Modène) :
Titre de la thèse de Laurea : *La contribution de la relaxation au processus de photoionisation double*, en italien. Note : 109/110
Tuteur : Prof. Olmes Bisi

1979-1984 Lycée *L.A. Muratori* de Modène (Italie). Diplôme : *Maturità Classica*. Note : 55/60

B.1.3 Parcours professionnel

Depuis mai 2011 En mission de longue durée à l'Université Johannes Gutenberg de Mayence (Allemagne), Institut de Chimie Analytique et Inorganique.

Depuis Octobre 2001 Ingénieur-chercheur (CDI) au CEA/SRMP [1], à Saclay.

Août 2000 - Octobre 2001 Collaborateur Temporaire Étranger (CDD) au CEA/SRMP[3], à Saclay.

1. Commissariat à l'Énergie Atomique/Service de Recherches de Métallurgie Physique

Janvier 1998 - Juillet 2000 CDD au Centre Européen de Calcul Atomique et Moléculaire (CECAM) [2] - Lyon, dans le cadre d'une collaboration avec le CEA/SRMP[3].

Année 1997 Stage post-doctoral au Centre Européen de Calcul Atomique et Moléculaire (CECAM)[4] - Lyon.

Juin - Décembre 1996 Stage de perfectionnement au CECAM financé par une bourse de l'Université de Modène (Italie).

Avril - May 1996 Contrat de recherche à l'Université de Modène dans le cadre d'une collaboration avec l'INFM (Istituto Nazionale di Fisica della Materia), section de physique des surfaces.

2. en même temps administrateur de système du CECAM entre juin 1997 et juillet 2000

B.2 Publications et communications

B.2.1 Articles dans des revues internationales avec comité de lecture

1. Fabien Bruneval and Guido Roma. Energetics and metastability of the silicon vacancy in cubic SiC. *Phys. Rev. B*, 83 :144116, 2011. (Cité pages xvii, 37, 41, 42, 50, 65, 66, 67 et 77.)
2. Ting Liao, Olga Natalia Bedoya-Martínez, and Guido Roma. Stoichiometric defects in silicon carbide. *J.Phys. Chem. C*, 114 :22691–22696, 2010. (Cité pages xvii, 37, 39, 41, 42, 50, 65, 67 et 77.)
3. Olga Natalia Bedoya-Martínez and Guido Roma. Activation entropies for diffusion in cubic silicon carbide from first principles. *Phys. Rev. B*, 82 :134115, 2010. (Cité pages xvi, xvii, 8, 37, 39, 50, 65, 66 et 77.)
4. G. Roma and J.-P. Crocombette. Evidence for a kinetic bias towards antisite formation in SiC nano-decomposition. *J. Nucl. Mater.*, 403 :32–41, 2010. (Cité pages xiv, xvii, 19, 37, 40, 50, 65 et 67.)
5. L. Martin-Samos, G. Roma, P. Rinke, and Y. Limoge. Charged oxygen defects in SiO_2 : going beyond local and semilocal approximations to density functional theory. *Phys. Rev. Lett.*, 104 :075502, 2010. (Cité pages xv, xvi, 17, 18, 30, 31, 49 et 77.)
6. G. Roma. Palladium in cubic silicon carbide : stability and kinetics. *J. Appl. Phys.*, 106 :123504, 2009. (Cité pages xii, xviii, 3, 11, 37, 43, 44, 50 et 77.)
7. T. Liao, G. Roma, and J. Y. Wang. Neutral silicon interstitials in 3C and 4H silicon carbide : a first principles study. *Philos. Mag.*, 89 :2271–2284, 2009. (Cité pages xviii, 39, 43, 49, 65 et 66.)
8. L. Martin-Samos, Y. Limoge, and G. Roma. Defects in amorphous SiO_2 : Valence alternation pair model. *Phys. Rev. B*, 76 :104203, 2007. (Cité pages xv, 28, 49 et 77.)
9. N. Richard, L. Martin-Samos, G. Roma, Y. Limoge, and J. P. Crocombette. First principle study of neutral and charged self-defects in amorphous SiO_2. *J. Non-Cryst. Solids*, 351 :1825–1829, 2005. (Cité pages xv, 28 et 49.)
10. L. Martin-Samos, Y. Limoge, J. P. Crocombette, G. Roma, N. Richard, E. Anglada, and E. Artacho. Neutral self-defects in a silica model : A first-principles study. *Phys. Rev. B*, 71 :014116, 2005. (Cité pages xv, 28 et 49.)
11. L. Martin-Samos, Y. Limoge, N. Richard, J. P. Crocombette, G. Roma, E. Anglada, and E. Artacho. Oxygen neutral defects in silica : Origin of the distribution of the formation energies. *Europhys. Lett.*, 66 :680–686, 2004. (Cité pages xv, 28 et 49.)
12. G. Roma and Y. Limoge. Density functional theory investigation of native defects in SiO_2 : Self-doping and contribution to ionic conductivity. *Phys. Rev. B*, 70 :174101, NOV 2004. (Cité pages xiii, xv, 13, 25, 49 et 77.)

13. G. Roma, Y. Limoge, and S. Baroni. Oxygen self-diffusion in α-quartz. *Phys. Rev. Lett.*, 86 :4564–4567, 2001. (Cité pages xiii, xv, 17, 24, 31, 49 et 77.)
14. S. Ossicini, C. M. Bertoni, M. Biagini, A. Lugli, G. Roma, and O. Bisi. Optical properties of isolated and interacting silicon quantum wires. *Thin Solid Films*, 297 :154–162, 1997.
15. G. Roma, C. M. Bertoni, and S. Baroni. The phonon spectra of LiH and LiD from density-functional perturbation theory. *Sol. State Commun.*, 98 :203–207, 1996.

B.2.2 Articles pour des conférences internationales avec comité de lecture

16. Guido Roma, Fabien Bruneval, Ting Liao, Olga Natalia Bedoya Martínez, and Jean-Paul Crocombette. Formation and migration energy of native defects in silicon carbide from first principles : an overview. *Def. Diff. Forum*, 2012. in Press. (Cité pages 17 et 37.)
17. Guido Roma. The influence of palladium impurities on vacancy diffusion in cubic silicon carbide. In J.K. Gibson, S.K. McCall, E.D. Bauer, L. Soderholm, T. Fanghaenel, R. Devanathan, A. Misra, C. Trautmann, and B.D. Wirth, editors, *Basic Actinide Science and Materials for Nuclear Applications*, volume 1264 of *Mater. Res. Soc. Proc.*, 2010. (Cité pages xviii, 43, 44 et 50.)
18. T. Liao and G. Roma. Stability of neutral silicon interstitials in 3C- and 4H-SiC : A first-principles study. *Def. Diff. Forum*, 283-286 :74–83, 2009.
19. Guido Roma, Yves Limoge, and Layla Martin-Samos. Oxygen and silicon self-diffusion in quartz and silica : The contribution of first principles calculations. *Def. Diff. Forum*, 258-260 :542–553, 2006. (Cité pages xv, xvi, 33 et 49.)
20. Guido Roma. A first principles study of palladium impurities in silicon carbide. *Adv. Sci. Technol.*, 45 :1969–1973, 2006. (Cité pages 11 et 43.)
21. Guido Roma, Yves Limoge, and Layla Martin-Samos. Aspects of point defects energetics and diffusion in SiO_2 from first principles simulations. *Nucl. Instrum. Meth. Phys. Res. B*, 250 :54–56, 2006. (Cité pages xv, 13, 26 et 49.)
22. G. Roma and Y. Limoge. First principles suggestions of targeted diffusion experiments on SiO_2. *Def. Diff. Forum*, 237-240 :127–132, 2005. (Cité page 26.)
23. L. Martin-Samos, Y. Limoge, J. P. Crocombette, G. Roma, and N. Richard. Oxygen self-diffusion mechanisms in silica by first-principles. *Def. Diff. Forum*, 237-240 :115–120, 2005. (Cité pages 28 et 49.)
24. G. Roma and Y. Limoge. A first principles study of native defects in α-quartz. *Nucl. Instrum. Meth. Phys. Res. B*, 202 :120–124, 2003.
25. G. Roma, Y. Limoge, and S. Baroni. Oxygen self-diffusion in SiO_2 : An ab-initio approach. *Def. Diff. Forum*, 194-1 :287–293, 2001. (Cité page 23.)

26. S. Ossicini, M. Biagini, C. M. Bertoni, G. Roma, and O. Bisi. Ab-initio calculation of the optical properties of silicon quantum wires. In Robert W. Collins, Philippe M. Fauchet, Isamu Shimizu, Jean-Claude Vial, Toshikazu Shimada, and A. Paul, editors, *Advances in Microcrystalline and Nanocrystalline Semiconductors – 1996*, volume 452 of *Mater. Res. Soc. Proc.*, pages 63–68, Pittsburgh, PA, 1997.
27. S. Ossicini, M. Biagini, C. M. Bertoni, G. Roma, and O. Bisi. Confinement and passivation in isolated and coupled silicon quantum wires. In M. Scheffler and R. Zimmermann, editors, *23rd International Conference on the Physics of Semiconductors*, pages 1205–1208, Berlin, Germany, July 1996. World Scientific.

B.2.3 Articles dans volumes

28. C. M. Bertoni, G. Roma, and R. Di Felice. Electronic structure of adsorbates on surfaces. Adsorption on semiconductors. In M. Scheffler and K. Horn, editors, *Electronic Structure*, volume II of *Handbook of Surface Science*, pages 247–283. Elsevier Science B. V., The Netherlands, 2000.

B.2.4 Conférences invitées

- Colloques internationaux :
  - DIMAT 2011, 8th international conference on Diffusion in Materials, Dijon 7/2011, Conférence plénière :
    Understanding defect kinetics from first principles calculations in insulators and semiconductors : selected problems in silicon carbide and silicon dioxide
  - Diffusion in Solids and Liquids 2008, Barcelona, Espagne, Juillet 2008,
    First principles studies of defects and defect clusters in silicon carbide : recent results
  - Diffusion in Solids and Liquids 2007, Alvor, Portugal, Juillet 2007,
    The contribution of first principles calculations to the study of diffusion in insulators : selected open problems and achievements
  - Diffusion in Solids and Liquids 2006, Aveiro, Portugal, Juillet 2006,
    Diffusion mechanisms in SiO_2 : from defects to Fermi level role.
  - CECAM Workshop : Understanding the similarities of SiO_2, H_2O and other systems with tetrahedral local order, organisé par J. Horbach et M. Mueser), Juillet 2002.
    Native defects in α-quartz : structure and concentrations
- Colloques nationaux :
  - Troisième colloque Matériaux, Mécanique, Microstructure (3M), INSTN/CEA-Saclay, Juin 2008,
    Quelques propriétés des défauts intrinsèques et du palladium dans SiC obtenues par une étude à l'échelle atomique
  - Réunion plénière du GNR Matinex, Avignon 2008
    Etude ab initio de défauts de silicium dans SiC

B.3 Activités d'encadrement

B.3.1 Post-doctorants

Nom : Natalia Olga Bedoya Martinez
Durée : 2 ans (11/2008-11/2010)
Sujet : Mécanismes du thermotransport dans le carbure de silicium à l'échelle atomique

B.3.2 Étudiants en thèse de Doctorat

Nom : Layla Martin-Samos
Durée : 3 ans (10/2001-10/2004), coencadrement (20%)
École Doctorale : Orsay, Paris XI
Sujet : Étude *ab-initio* des auto-défauts et des mécanismes d'auto-diffusion dans un verre de silice

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Nom : Ting Liao
Durée : 1 an (2/2007-1/2008)
École Doctorale : Académie des Sciences Chinoise, Institute of Metal Research, Shenyang, Chine (cotutelle).
Sujet : Étude ab-initio de défauts ponctuels et agrégats de défauts dans le carbure de silicium

B.3.3 Étudiants en Master

Nom : Eric Verfaillie
Durée : 6 mois (4-9/2004)
Master 2, Université de Cergy Pontoise, Techniques de Modélisation et Simulation
Sujet : Visualisation interactive de grandeurs caractérisant des défauts ponctuels dans les solides.

Nom : Ouro-Nile Mama-Touré
Durée : 6 mois (4-9/2006)
Master 2, Université de Paris VI, Systèmes Dynamiques et Statistique de la Matière Complexe
Sujet : Application de méthodes statistiques à la paramétrisation de modèles simplifiés pour la description atomistique des matériaux

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Nom : Alexandre Volgin
Durée : 5 mois (4-8/2008)
Master 1, Université de Orsay - Paris XI, Physique Fondamentale
Sujet : Étude ab-initio de défauts intrinsèques dans le carbure de silicium

B.4 Activités et compétences complémentaires

B.4.1 Activités d'expertise

– Membre de comité de lecture pour le journaux suivants :
  Physical Review B
  Journal of Applied Physics

Applied Physics Letters

Defects and Diffusion Forum

Nuclear Instruments and Methods in Physical Research B

Zeitschrift für Physikalische Chemie

- Nommé *Expert du CEA* dans le domaine Matériaux, physique du solide et des semi-conducteurs à partir du 1/1/2010
- Membre du Groupe Benchmarks pour un appel d'offre CCRT[3] (2006)

B.4.2 Organisation de workshops et de conférences

- Co-organisation, dans le cadre du GNR MATINEX, de l'atelier "Modélisation à l'échelle atomique du comportement des matériaux céramiques soumis à des conditions extrêmes" 7 novembre 2008, Aix-en-Provence
- Membre, de 2007 à 2009, du Comité Scientifique de la conférence internationale *Diffusion in Solids and Liquids*

B.4.3 Contrats

- Responsable d'action pour la tâche *"First principles study of intrinsic defects in SiC : role of Frenkel pair recombination & defects clusters"* d'un projet de l'European Fusion Development Agreement (EFDA)
  Financement demandé et obtenu en 2008, 2009 et 2010 (32k€,142k€,142k€ en "baseline support")
- Responsable d'une fiche d'action pour le GNR MATINEX (MAtériaux INnovants en conditions EXtrêmes). Financement en 2008 et 2010.

B.4.4 Formations complémentaires

Formation Nucléaire de Base de la Direction de l'Énergie Nucléaire du CEA. Durée : 3 mois à plein temps (suivie en 2005).

B.4.5 Informatique et calcul scientifique

- Représentant au comité utilisateurs du CCRT de 2002 à 2011 (avant fin 2003 Centre de Calcul du CEA à Grenoble).
- Correspondant Informatique du Service de Recherches de Métallurgie Physique
- Admistration de systèmes UNIX/Linux, machines parallèles et vectorielles
- Rédaction d'un cahier des charges d'appel d'offre pour l'achat d'un cluster de calcul (200000 € en 2007)

3. Centre de Calcul de Recherche et Technologie

Selection d'articles

C

Dans cette annexe sont reproduits [1] les articles [1, 2, 3, 4, 5, 6, 7, 8] suivants. Nous reproduisons aussi, par commodité, le document technique [9].

Liste des articles joints

[1] G. Roma, Y. Limoge, and S. Baroni. Oxygen self-diffusion in α-quartz. *Phys. Rev. Lett.*, 86 :4564–4567, 2001. (Cité pages xiii, xv, 17, 24, 31, 49 et 77.)

[2] G. Roma and Y. Limoge. Density functional theory investigation of native defects in SiO_2 : Self-doping and contribution to ionic conductivity. *Phys. Rev. B*, 70 :174101, 2004. (Cité pages xiii, xv, 13, 25, 49 et 77.)

[3] L. Martin-Samos, Y. Limoge, and G. Roma. Defects in amorphous SiO_2 : Valence alternation pair model. *Phys. Rev. B*, 76 :104203, 2007. (Cité pages xv, 28, 49 et 77.)

[4] G. Roma. Palladium in cubic silicon carbide : stability and kinetics. *J. Appl. Phys.*, 106 :123504, 2009. (Cité pages xii, xviii, 3, 11, 37, 43, 44, 50 et 77.)

[5] L. Martin-Samos, G. Roma, P. Rinke, and Y. Limoge. Charged oxygen defects in SiO_2 : going beyond local and semilocal approximations to density functional theory. *Phys. Rev. Lett.*, 104 :075502, 2010. (Cité pages xv, xvi, 17, 18, 30, 31, 49 et 77.)

[6] Olga Natalia Bedoya-Martínez and Guido Roma. Activation entropies for diffusion in cubic silicon carbide from first principles. *Phys. Rev. B*, 82 :134115, 2010. (Cité pages xvi, xvii, 8, 37, 39, 50, 65, 66 et 77.)

[7] Ting Liao, Olga Natalia Bedoya-Martínez, and Guido Roma. Stoichiometric defects in silicon carbide. *J.Phys. Chem. C*, 114 :22691–22696, 2010. (Cité pages xvii, 37, 39, 41, 42, 50, 65, 67 et 77.)

[8] Fabien Bruneval and Guido Roma. Energetics and metastability of the silicon vacancy in cubic SiC. *Phys. Rev. B*, 83 :144116, 2011. (Cité pages xvii, 37, 41, 42, 50, 65, 66, 67 et 77.)

[9] T. Liao and G. Roma. Silicon di-interstitial structures in 3C-SiC. Note Technique DEN/DANS/DMN/SRMP/NT/2008-01, CEA , Service de Recherches de Métallurgie Physique, 2008. p. 23. (Cité pages xviii, 37, 43, 66, 67 et 77.)

1. Uniquement dans la version pour les rapporteurs ; dans le Rapport CEA ces articles ne sont pas inclus pour des raisons de Copyright

Remerciements

Écrire des remerciements est une tâche difficile pour plusieurs raisons. Le remerciement peut paraître déplacé ou trop froid, la liste des personnes citées explicitement peut paraître trop longue ou trop courte. Naturellement l'impression donnée à chacun des lecteurs ne peut qu'être influencée, à tort ou à raison, par la comparaison avec les autres remerciements. C'est en particulier cet aspect d'un remerciement public, tel que je suis en train d'écrire, qui en fait quelque chose de très différent d'un remerciement privé, personnel, dont la gratuité est plus évidente, puisqu'elle n'est pas conditionnée par une habitude, une coutume, que l'on respecte, entre autres, aussi pour éviter de paraître excessivement original. Je préfère toutefois ne pas me dérober à cet exercice, maintenant, une fois la soutenance passée, puisque, parmi les différents risques, celui d'irriter ou de flatter ceux qui auraient pu en influencer l'issue n'est plus d'actualité.

S'il y a une personne à qui je dois la démarche d'utiliser les calculs de structure électronique au service de véritables problèmes de science de matériaux, un aspect clairement apprécié par le Jury, c'est bien Yves Limoge, qui m'a non seulement transmis, au fil des ans, l'essentiel de l'esprit de "la SRMP", mais aussi m'a considéré, déjà à l'occasion de mes premières visites à Saclay, comme un collègue et, très vite, comme un ami. Son encouragement pour me lancer dans les démarches de l'HDR a été évidemment très important.

Tous les collègues du SRMP, chacun avec sa personnalité, forment un groupe où l'échange scientifique est toujours profitable et plaisant. Je voudrais tous les remercier. Je voudrais remercier en particulier Jean-Paul Crocombette et Fabien Bruneval, avec qui j'ai eu la chance de collaborer de plus près, ce qui a donné lieu à des articles en commun.

Les chefs de service successifs du SRMP, Georges Martin, Michel Guttmann et François Willaime, ont influencé discrètement l'orientation de mes travaux, je les remercie de leur confiance. À François je dois aussi des conseils précieux pour atteindre l'objectif de l'Habilitation à Diriger des Recherches. Je remercie aussi Claudia Felser, qui m'a accueilli comme visiteur dans son groupe de recherche à Mayence, où j'ai rédigé ce document en grande partie.

Mais je n'aurais pu atteindre le but sans avoir enfreint l'esprit du diplôme, c'est à dire sans avoir encadré des étudiants avant d'en être habilité. En effet, non seulement une activité d'encadrement est requise pour pouvoir soutenir une HDR, mais elle est aussi très utile pour prendre du recul par rapport aux sujets de recherche que l'on attaque, parfois, "le nez dans le guidon". Ainsi je remercie Layla Martin-Samos Colomer, qui a souvent discuté avec moi de son sujet de thèse et avec qui la collaboration a continué après. Je remercie Ting Liao, qui pendant l'année passée à Saclay a produit beaucoup de résultats, sans pour autant oublier le contexte et la

connaissance de la littérature associée. Elle m'a aussi permis de percevoir personnellement à quel point la culture chinoise chérit la figure de l'enseignant. Nous, les occidentaux, avons quelques choses à apprendre dans ce domaine. Il y a au moins deux raisons principales pour lesquelles je remercie de tout coeur Natalia Olga Bedoya-Martínez : elle m'a fait confiance en choisissant son sujet de post-doctorat (parmi d'autres très intéressants au SRMP) et elle a toujours abordé les sujets de recherche avec enthousiasme. Mes remerciements vont aussi aux stagiares que j'ai encadrés précédemment ; avec des charactères et des attitudes différentes ils m'ont fait comprendre l'intérêt de l'activité d'encadrement non seulement du point de vue scientifique mais aussi humain.
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