

Basic mechanisms of atomic displacement production in cubic silicon carbide: A molecular dynamics study

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Studying the effects of radiation in silicon carbide (SiC) is important for its possible use in both nuclear and electronic technology. One of the most important parameters to describe radiation damage in a material is the threshold displacement energy (TDE). In this paper, the computational technique known as molecular dynamics (MD) is used to determine the TDE's along different crystallographic directions for Si and C atoms in SiC, also allowing for irradiation temperature effects, and to study in detail the mechanisms of atomic displacement production in this material. For this purpose, the widely tested Tersoff potential, implemented in a MD code optimized to study the interaction of high-energy ions with crystals, is used to describe the interatomic forces in SiC. It is found that it is difficult to define a single threshold for this material. Instead, the introduction of two thresholds, *upper* and *lower*, becomes necessary. These two thresholds delimit an *uncertainty band*, within which the displacement may or may not be produced, because the Frenkel pairs generated in such a transferred-kinetic-energy range are metastable. The Arrhenius law expressing the lifetime of one of these metastable defects has also been deduced from the simulation. Finally, on the basis of the results of the simulation, possible values for the recombination distance and the average threshold energy ($E_{d, Si}$ and $E_{d, C}$) in SiC are proposed and discussed.

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I. INTRODUCTION

Silicon carbide (SiC), a low- Z ceramic material, exhibits several outstanding properties, such as low-activation after prolonged irradiation, resistance to high temperature, and excellent chemical compatibility. For this reason it has long been considered for performing structural and protective functions in the first wall and blanket of future nuclear fusion reactors,¹ especially in the form of SiC-fiber/SiC-matrix composite.² Moreover, thanks to the broad variation of its band gap, which depends on the polytype it crystallizes in, SiC is also a material of choice for electronic devices of superior characteristics (high speed, high power, high temperature).³ However, as to the former application, its capability of withstanding prolonged neutron irradiation, without experiencing prohibitive deleterious changes in its microscopic and macroscopic properties, is of concern.⁴ And, regarding the latter, the doping of this material appears to be complicated, because of the high temperature necessary for dopant diffusion, therefore making ion implantation and annealing the only valid alternative technique for such a purpose.⁵ For both applications, a detailed knowledge of the effects of irradiation in SiC is of fundamental importance and, thanks to the ever-growing power of modern computers, the computational simulation of the microscopic changes induced by radiation in materials is nowadays a powerful tool to gain such knowledge.⁶

Probably the most important physical parameter for describing radiation damage in a material is the threshold displacement energy (TDE), which is simply the minimum amount of kinetic energy transferred by an impinging particle to a lattice atom that results in the formation of one stable Frenkel pair. Despite the considerable work carried out

by many different authors, there still exists great uncertainty about the most adequate value of this parameter in SiC, particularly regarding Si atoms (see exhaustive review in Ref. 7).

In this paper, a thorough computational molecular-dynamics (MD) study of the TDE's along different crystallographic directions for Si and C atoms in SiC—also allowing for possible irradiation temperature effects—is reported. However, the present work tries to go further than just determining the numerical value of the TDE's in SiC. For either type of hit atom (Si or C) and for each direction in which it was pushed, much wider transferred-kinetic-energy intervals have been considered than was strictly necessary to identify the TDE's. This was done in order to examine in detail the mechanisms of production of atomic displacements in this material. In particular, in each case the defect formed after the simulated collision was duly recorded and studied. This procedure permitted the identification of metastable defects (Frenkel pairs) which are formed, for either type of struck atom and for each direction, when the transferred kinetic energy lies within a certain band of values. The lifetime of one particular case of metastable Frenkel pairs as a function of temperature (Arrhenius law) was also deduced by simulation.

The existence of metastable defects makes it difficult to define a single TDE value for each crystallographic direction, leading to the necessity of introducing the concepts of *lower* and *upper* thresholds.⁸ Within these two thresholds an *uncertainty band* is contained, in which the atomic displacement may or may not be produced because, when the kinetic energy transmitted to the atom lies in such an uncertainty interval, only metastable Frenkel pairs can be generated. These can temporarily survive thanks to the existence of *energy barriers* which, at low enough temperature, prevent the

recombination of the interstitial atom with the nearby vacancy, for this reason called *recombination barriers* [the existence of such barriers has also been reported in Si (Ref. 9)]. However, within the uncertainty band, any small perturbation intervening during the displacement process (e.g., due to high lattice distortion, or to a low-energy collision with another atom, or to thermal agitation at high temperature) is sufficient to enable the displaced atom to overcome the recombination barrier, thereby causing the prompt disappearance of the defect, or preventing its formation. Only kinetic energy transfers *above* the *upper* threshold always lead to the production of a stable defect, whereas *below* the *lower* threshold no defect whatsoever is ever generated. Defects formed above the *upper* threshold will only have a chance of disappearing by means of diffusion mechanisms (defect migration), i.e., at high enough temperature and over time scales much longer than the MD technique can reach (\gg ns).

The paper is organized as follows: in Sec. II, details about how the simulation was conducted are given; in Sec. III, the results of the detailed analysis carried out at 300 K are described (Sec. III A), together with those obtained in one particular case at different temperatures (Sec. III B); finally, in Sec. IV, on the basis of the results presented, the basic mechanisms of atomic displacement production in SiC are discussed and possible average values for TDE's and recombination distances in this material are proposed.

II. COMPUTATIONAL PROCEDURE

In a MD computer simulation the classical equations of motion of an ensemble of particles are solved numerically, for a certain number of time steps, with adequate initial and boundary conditions, so that the velocity and position of each atom or molecule are known at every time step.¹⁰ The heart of the method is the interatomic potential, which has to be able to reproduce correctly the interaction between atoms for the material taken into consideration. By means of this tool, the determination of the TDE for an atom in a material is conceptually very simple. After equilibrating the system (≈ 150 fs simulated time is an adequate duration for this phase in the present case), an atom (Si or C) is selected and given a certain amount of kinetic energy, by pushing it in a certain direction. If the transferred energy is high enough, the recoiling atom will progressively abandon its position to gain a new one. If, after a reasonably long amount of time (≈ 6 ps in the present work), the atom is still occupying the newly reached position, then it is said that an atomic displacement has taken place and hence the energy can be considered higher than the TDE. On the other hand, if the atom regains its position within the observation time, then the energy transferred is lower than the TDE. By sweeping a wide enough energy range by, for example, 1 eV increments, it is therefore possible to establish the position of the threshold in such a range.

All the simulations of recoil production herein reported were carried out with the MD simulation code MDCASK, developed in collaboration between the Lawrence Livermore National Laboratory and the DENIM. In this code, optimized for studying the interaction of high-energy ions with

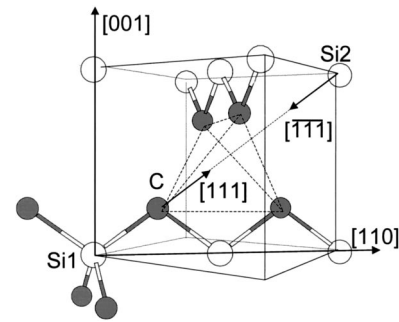


FIG. 1. Schematic representation of the main crystallographic directions in the cubic cell of 3C-SiC. White balls are Si atoms; gray balls are C atoms. Si1 can be identified with the recoiling atom for the [001], [111], and [110] directions; Si2 for the $\overline{[111]}$ direction. Si1 is surrounded by its four C first neighbors. C can be identified with the carbon recoil.

crystals,¹¹ the interatomic forces for SiC are described using the many-body empirical potential proposed by Tersoff,^{12,13} merged with a binary *ab initio* repulsive potential, to adequately treat the atomic collisions in the short-distance range (>0.5 Å).^{14,15} The Tersoff potential has long been demonstrated to allow the performance of reliable MD simulations of the behavior of SiC in a variety of conditions and situations.^{16–18} The MDCASK code is implemented in the Cray-T3E massively parallel supercomputer of the CIEMAT (Madrid, Spain), which can make available up to 32 processors for a single computational task, though only 8 or 16 were used for the present work. The parallel implementation is based on the PVM message-passing library. On 16 processors the code runs at a rate of approximately $8 \mu\text{s}_{(\text{CPU})}/\text{atom}/\text{time step}$.

All simulations were conducted at constant number of particles and constant volume. The temperature was controlled (i.e., maintained approximately constant, though the system was, strictly speaking, out of thermodynamic equilibrium) by employing the velocity rescaling method, applied only to the two outer atomic layers of the simulation box (heat bath). The latter was a $6a_0 \times 6a_0 \times 7a_0$ ($a_0 = 4.36$ Å, lattice parameter) box, which contained 2016 atoms, initially distributed according to the 3C-SiC, or cubic, structure. Though most simulations were performed at 300 K, other temperature regimes, from 150 to 2000 K, were also considered.

For either type of atom (Si and C), at 300 K, the four main crystallographic directions were studied: [001], [110], [111], and $\overline{[111]}$. As a matter of fact, it is well known that the TDE value is very sensitive to the crystallographic direction of motion of the recoil. The crystallographic directions chosen in this work have already been considered in other papers^{20–23} and are the typical low-index directions used to characterize the behavior of materials exhibiting a zincblende structure. The features of these directions, in relation with the cubic SiC crystalline structure, are illustrated in Fig. 1. By considering the multiplicity of each of these directions, it is possible to cover a significant quantity of points of the polar TDE surface and therefore, in principle, deduce a reasonable average value for this magnitude. In order to check

TABLE I. Angles defining geometrical and modified crystallographic directions for the determination of the TDE's.

Direction	θ (deg)	φ (deg)
[001]	0	0
[001 m]	2	44
[110]	90	45
[110 m]	88	44
[111]	55	45
[111 m]	45	44
$\overline{[111]}$	125	-135
$\overline{[111m]}$	135	-134

to what extent small deviations from a certain direction may affect the TDE value, each of the mentioned directions was defined by using two sets of angles: the geometrical ones and a pair of slightly modified angles, denoted by m , as shown in Table I. The choice of these angles was not based on any particular criterion, except that of considering a direction close to, but not coincident with, the four main crystallographic directions. In total, eight directions were considered for either type of atom at 300 K and for each of them the transferred-kinetic-energy range studied was comprised between 10–20 eV and >100 eV, with variations depending on the particular case. In all cases, the increment used to sweep the energy range was 1 eV and for each energy, for better statistics, at least two simulations were performed, with the same recoil pushed in the same direction, but starting at a slightly different time step. The result of the simulation, in each case, was visualized as “stick-and-balls” diagrams with the help of the package called XMOL,¹⁹ and on that basis was analyzed. The effect of irradiation temperature on the TDE values was examined only in the case of a Si atom pushed along the [001] direction.

III. RESULTS

A. Lower and upper thresholds at 300 K

Tables II and III synthesize the results obtained at 300 K for Si and C atoms recoiling along the four main crystallographic directions, both geometrical and modified. It is important to note at once that, along the [111] direction, and the relevant modified direction, the Si atom collides with its first C neighbor (see Fig. 1), so that the TDE values indicated in Table II actually correspond, in that case, to the displacement of a *secondary* C recoil, the *primary* Si recoil always regaining its initial position (in all the energy range investigated, that is, up to ≈ 120 eV). By examining Tables II and III, it can be seen that displacing a C atom is always easier than displacing a Si atom. It can also be seen that the difference between the geometrical and modified direction, in each equivalent case, is normally negligible, perhaps with the exception of Si [110] and Si [110 m], which is a highly packed direction. Therefore the polar TDE surface can be judged reasonably smooth, thereby justifying a calculation of the average TDE by considering only a few representative points

of such surface. Because of this substantial coincidence, no distinction will be made henceforth between the geometrical and the modified direction. Another important observation is that, with the only exception of C [001], in all cases there exist uncertainty bands, which are generally broader for Si atoms, as compared with C atoms. This fact might partly explain the greater difficulty in assigning a value for the TDE of Si atoms in SiC based on experimental observations.⁷

By comparing the results of Tables II and III with analogous results obtained computationally by other authors,^{20–23} it turns out that, with good approximation, the *lower* thresholds of the present work match the threshold values reported by those authors. This is probably a symptom of the fact that the transferred-kinetic-energy ranges considered in previous work were not broad enough to grasp the complexity of the behavior of this material under irradiation.

The main discrepancy concerns the Si [111] case. Some authors proposed for this recoil and direction a threshold value as high as 113 eV.²³ This so-much-higher value stems from the different criterion applied to define the TDE. In the present paper the TDE was considered to be the minimum energy necessary to create *one* Frenkel pair, even when the displaced atom was not the primary knocked-on atom (PKA); i.e., even if the displaced atom was a C atom, pushed by the Si atom to which the energy had been initially transmitted. This choice lies upon the idea that the TDE should be a threshold for the creation of a defect in the material as a whole. On the other hand, other authors consider that the TDE must be intended as the minimum energy necessary to displace the primary recoil, even if this means, like in the Si [111] case, producing at the same time a large number of defects on the other sublattice (small displacement cascade). This criterion implies that the two sublattices should be treated separately. It is difficult to establish which of the two criteria is physically more correct, but it is important to state which criterion has been adopted. The reported value of 113 eV corresponds, according to Devanathan and Weber, to the energy needed to displace *one* Si atom in the [111] direction and, at the same time, a remarkable number of C atoms.

In the remaining part of this subsection, a concise and qualitative description will be given of the defects formed when knocking on the atom both *within* the uncertainty band (either metastable defect formation or else no net atomic displacement) and *above* it (stable defect creation), for each direction and for either type of recoil. Si-recoil cases are schematically described in Fig. 2; C-recoil cases in Fig. 3.²⁴

Si [001]. Along this direction the Si recoil heads towards its *above-lying* Si fourth neighbor (Fig. 1). (i) Within the uncertainty band (35–62 eV) the recoil forms sometimes (i.e., for a few kinetic energy values) a Si₁-Si dumbbell with its neighbor, oriented as the [001] direction. The distance between atoms in the dumbbell is $\approx 0.47a_0$. The formation of this defect is highly probable between 44 and 55 eV, much less probable both above and below. As a matter of fact, below 44 eV the recoil still has little energy and is easily prevented from forming the metastable dumbbell by small perturbations. On the other hand, above 55 eV the recoil succeeds sometimes in replacing temporarily its neighbor,

TABLE II. Summary of TDE values and uncertainty-band widths for Si atoms in SiC. Averages are also indicated.

Si recoils Directions	Multiplicity	Threshold energies (eV)			Uncertainty band (eV)
		Lower	Intermediate	Upper	
[001]	6	35.0	48.5	62.0	27.0
[001 <i>m</i>]		36.0	49.0	62.0	26.0
[111] ^a	4	27.0	35.5	44.0	17.0
[111 <i>m</i>] ^a		28.0	36.0	44.0	16.0
[110]	12	73.0	83.0	93.0	20.0
[110 <i>m</i>]		70.0	85.5	101.0	31.0
[$\bar{1}\bar{1}\bar{1}$]	4	38.0	56.5	75.0	37.0
[$\bar{1}\bar{1}\bar{1}$ <i>m</i>]		36.0	58.0	80.0	44.0
Arithmetical average		48.0±16.6	63.4±15.1	78.8±14.3	30.8±6.8
Weighed average		55.4	69.7	83.9	28.5
Minimum		35.5	48.8	62	25.5

^aDisplacement produced on C sublattice; excluded from the averaging.

but is thereafter pushed back to its initial position by the other atom, which tries to regain its site. When the dumbbell forms, the distance between the recoil and its vacant initial position is $\approx 0.8a_0$. This case is illustrated in Fig. 2(a). (ii) Above the upper threshold (≥ 62 eV), the Si recoil always succeeds in replacing its above-lying neighbor, as in a minimum-possible-length replacement collision sequence, without ever going back to its initial position. In this case, the distance between the interstitial (the *secondary* Si recoil) and the vacancy left behind is $\approx 1.8a_0$ [see Fig. 2(b)].

Si [111]. Along this direction, as already observed, the Si recoil hits its C first neighbor, displaces it, and goes back to its initial position. The displaced C atom heads towards an empty tetrahedron defined by four Si atoms (*TSi*), as shown in Fig. 2(c). (i) Within the uncertainty band (≈ 27 –44 eV) the C atom sometimes (i.e., for a few Si recoil's energy values) finds a metastable location around the center of the *TSi*, thereby getting as far from its vacancy as $\approx 0.5a_0$ – $0.8a_0$. However, in many cases no displacement is produced after 6

ps have elapsed. (ii) Above the upper threshold (>44 eV) the C atom always succeeds in forming a stable defect, generally a C₁-Si dumbbell with one of the Si atoms belonging to the *TSi*, oriented as the [001] direction and with a separation between atoms $\approx 0.38a_0$. In this case, the distance of the C interstitial from its vacancy is $\approx 0.9a_0$ – $1.2a_0$ [see Fig. 2(d)].

Si [110]. Along this direction, the first atom encountered by the Si recoil is its Si second neighbor (Fig. 1). (i) Within the uncertainty band (≈ 70 –101 eV), the Si recoil sometimes forms a dumbbell with its second neighbor. The orientation of this dumbbell is not easy to define and varies from case to case; however, the separation between atoms is always $\approx 0.47a_0$ [see Fig. 2(e)]. Depending on how the dumbbell is created and which atom is considered as interstitial, the distance between the latter and the vacancy left behind is found to vary between $\approx 0.4a_0$ and $\approx a_0$. Nonetheless, in many cases the recoil regains its initial position, without any net atomic displacement being produced. (ii) Above the upper threshold (≥ 101 eV) a short replacement collision sequence

TABLE III. Summary of TDE values and uncertainty-band widths for C atoms in SiC. Averages are also indicated.

C recoils Directions	Multiplicity	Threshold energies (eV)			Uncertainty band (eV)
		Lower	Intermediate	Upper	
[001]	6	30.0	30.0	30.0	0.0
[001 <i>m</i>]		30.0	30.0	30.0	0.0
[111]	4	20.0	25.5	31.0	11.0
[111 <i>m</i>]		19.0	22.5	26.0	7.0
[110]	12	26.0	42.0	58.0	32.0
[110 <i>m</i>]		27.0	44.5	62.0	35.0
[$\bar{1}\bar{1}\bar{1}$]	4	41.0	51.5	62.0	21.0
[$\bar{1}\bar{1}\bar{1}$ <i>m</i>]		47.0	52.5	58.0	11.0
Arithmetical average		30.0±8.9	37.3±11.0	44.6±15.4	14.6±12.3
Weighed average		28.9	38.6	48.2	19.3
Minimum		19.5	24.0	28.5	0.0

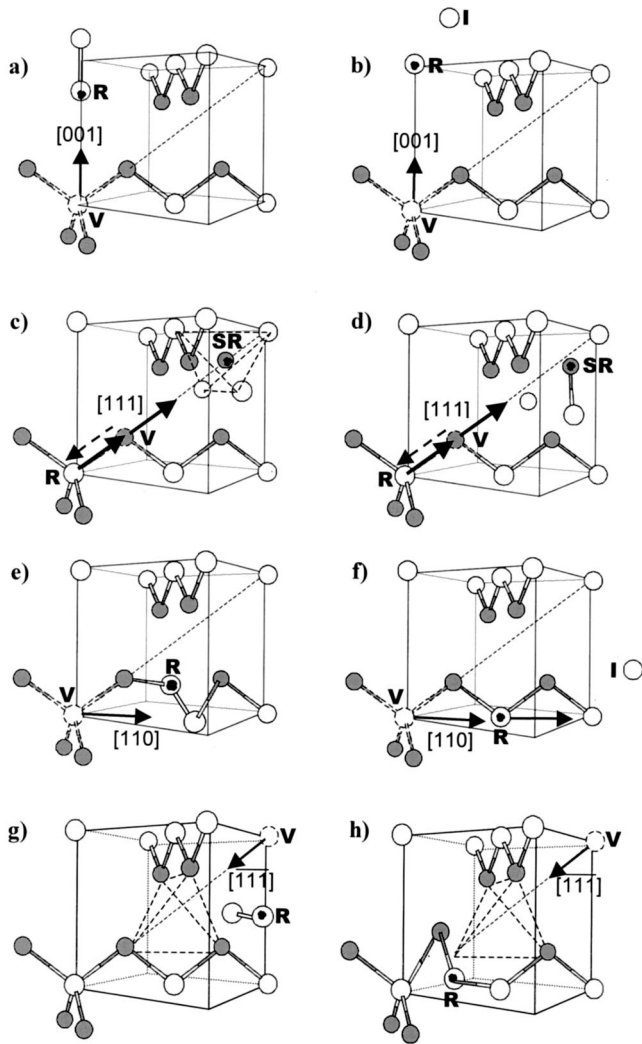


FIG. 2. Schematic representation of the defects generated when a Si atom recoils along the [001] (a) and (b), [111] (c) and (d), [110] (e) and (f), and [111] (g) and (h) directions, within the uncertainty band [left: (a), (c), (e), (g)] and above it [right: (b), (d), (f), (h)]. **R** denotes the recoil (**SR** the secondary recoil); **V** denotes the vacancy; **I** denotes the interstitial (when it does not coincide with the recoil); arrows indicate directions of motion.

takes place: the Si recoil replaces its Si second neighbors, which subsequently replaces the following Si atom along the [110] direction. The last atom becomes an interstitial, situated at a distance $\approx 1.9a_0$ from the vacancy [Fig. 2(f)].

Si [111]. Along this direction, the Si recoil heads towards the tetrahedron defined by four C atoms (*TC*), whose center may as well be considered the center of the cubic cell (see Fig. 1). If the recoil kept moving strictly along the direction in which it has been pushed, the first atom encountered would be the C atom occupying the farthest *TC* vertex from the initial position of the moving atom. (i) Within the uncertainty band ($\approx 36-80$ eV) many different possibilities may occur: either no displacement is produced, or the recoil forms either a Si_1-Si dumbbell with one of the nearby centers of the faces of the cube (distance between atoms $\approx 0.47a_0$), oriented as the $\langle 100 \rangle$ direction [any of the different equiva-

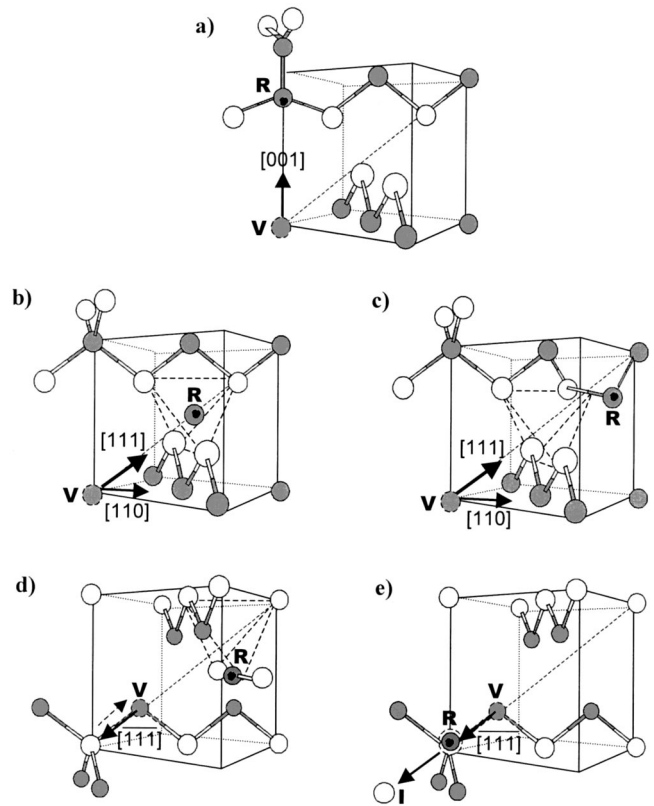


FIG. 3. Schematic representation of the defects generated when a C atom recoils along the [001] (a), [111] and [110] (b) and (c), and [111] (d) and (e) directions, within the uncertainty band [left: (b) and (d)] and above it [right: (c) and (e)]. **R** denotes the recoil; **V** denotes the vacancy; **I** denotes the interstitial (when it does not coincide with the recoil); arrows indicate directions of motion.

lent directions, see, for example, Fig. 2(g)], or else, with much less frequency, a Si_1-C dumbbell with one of the nearby vertices of *TC*, also oriented as the $\langle 100 \rangle$ direction, with separation between atoms $\approx 0.39a_0$. When the Si_1-Si dumbbell is formed, the distance between vacancy and interstitial is $\approx a_0$, whereas in the other case it lowers down to $\approx 0.75a_0$. (ii) Above the upper threshold (≥ 80 eV) the Si recoil succeeds in forming a Si_1-C dumbbell (approximately oriented as [001]) with the farthest *TC* vertex from its initial position, thereby locating itself as far as $\approx 1.1a_0$ from the vacancy [Fig. 2(h)]. In this case, even more clearly than in others, what decides the stability of the Frenkel pair is the separation between interstitial and vacancy.

C [001]. This is the only case in which no uncertainty band is observed. The situation is virtually identical to Si [001]: the C recoil heads towards its *above-lying* C fourth neighbor and a Frenkel pair is created as soon as the transferred energy is high enough (≥ 30 eV) for the two atoms to form a C_1-C dumbbell, oriented as the [001] direction, with a separation between them $\approx 0.33a_0$ [see Fig. 3(a)]. When the dumbbell is generated, the distance between interstitial and vacancy is $\approx 0.85a_0$, that is, only a little different from the equivalent case for the Si recoil. However, this time no metastability can be detected, a symptom of the fact that the re-

combination distance on the C sublattice is shorter than on the Si sublattice, i.e., Si Frenkel pairs recombine more easily.

C [111]. This case is closely related to Si [111], since the same atom currently taken as *primary* recoil was, in the earlier one, the *secondary* recoil. (i) Within the uncertainty band ($\approx 20\text{--}31$ eV) the C recoil may find metastable locations inside the *TSi* [Fig. 3(b)], sometimes forming a C_1 -Si dumbbell ($\langle 100 \rangle$ direction, distance between atoms $\approx 0.38a_0$) with one of the closest vertices of the *TSi*. Depending on the actual configuration produced, the distance from the vacancy left behind may vary between $\approx 0.8a_0$ and $\approx 0.5a_0$. In many cases, though, no net displacement survives. (ii) Above the upper threshold (≥ 31 eV), many possible configurations were observed (C_1 -Si and C_1 -C dumbbells), some of them apparently similar to those occurring within the uncertainty band [C_1 -Si dumbbells, see Fig. 3(c)]. However, the distance between the recoil and its initial position is now always $> 0.8a_0$, namely $\approx 0.9a_0\text{--}1.2a_0$ when forming C_1 -Si dumbbells and $\approx 0.8a_0\text{--}a_0$ when forming the more stable C_1 -C dumbbell.²⁵ In this case therefore the distance separating the two elements of the Frenkel pairs definitely reveals itself as key, in order to determine the stability of the configuration.

C [110]. Though along this direction, by analogy with Si [110], a replacement collision sequence is expected, none ever takes place. In fact, the C recoil is, invariably, strongly deviated from its initial direction of motion towards a $\langle 111 \rangle$ direction. For this reason, this case is qualitatively identical to the previous one [Figs. 3(b) and (c)], except for the greater number of possible events occurring below and above the upper threshold. (i) Within the uncertainty band ($\approx 26\text{--}62$ eV), when a displacement is produced, three possible metastable configurations have been observed: (i) C_1 -Si dumbbell with one of the closest *TSi* vertices to the recoil's initial position (separation between interstitial and vacancy $\approx 0.65a_0$); (ii) C_1 -C dumbbell with a C atom which is never the second neighbor of the recoil (separation $\approx 0.55a_0\text{--}0.7a_0$); (iii) interstitial location around the center of *TSi* [separation $\approx 0.8a_0\text{--}0.9a_0$, see Fig. 3(b)]. It might appear surprising that interstitial sites as far from the corresponding vacancy as $0.9a_0$ are still metastable. However, the peculiarity of this case (C [110]), compared to the previous one (C [111]), is that the recoil's C second neighbor always receives a significant kinetic energy. It is hence displaced, at least temporarily, so as to produce high local lattice distortion, which certainly increases the instability of any defect configuration. Also, it is worth noting that, in a few cases, the effect of the process is that the hit atom (the recoil) and its second neighbor just exchange their positions, without any net defect production. (ii) Above the upper threshold (≥ 62 eV), again, C_1 -C or Si_1 -C dumbbell formation is observed; however, this time the separation between vacancy and interstitial is $\approx 1.1a_0\text{--}1.2a_0$, so that the stability of the Frenkel pair is always guaranteed.

C [111]. This direction is the equivalent, for the C sublattice, of the [111] direction for the Si sublattice: the C recoil encounters at short distance its Si first neighbor, to

which much of the energy is transmitted. This time, nevertheless, due to the difference in mass between the C recoil and the Si target, the situation is quite different from the Si [111] case. (i) Within the uncertainty band ($\approx 41\text{--}62$ eV) the C recoil, after colliding with its Si neighbor, bounces back, failing to displace it, and finds itself in a situation very similar to the C [111] case. The typical metastable configuration thereby produced is a C_1 -Si dumbbell with one of the closest Si atoms delimiting the nearby empty *TSi* [Fig. 3(d)]. In this situation, the interstitial is separated from the vacancy by $\approx 0.55a_0\text{--}0.65a_0$. Still, in many cases, at the end of the process, no net atomic displacement is produced. (ii) Above the upper threshold (≥ 62 eV), on the contrary, the C recoil has enough energy to replace its Si first neighbor definitively, which in turn ends up occupying a stable interstitial position [Fig. 3(e)]. Therefore an antisite (C_{Si}) is formed. Since the Si interstitial is not likely to occupy the C vacancy left behind, there is no point in defining a stability distance, in this case, between the two elements of the Frenkel pair.

In summary: According to the simulations performed, when knocking on an atom in SiC, both within the uncertainty band and above the upper threshold, in most cases the interstitial configuration produced is a dumbbell. What decides the stability of the generated Frenkel pair is fundamentally the separation between interstitial and vacancy. Within the uncertainty band, the separation is small and therefore the production of an atomic displacement cannot be guaranteed. Above the upper threshold the separation is greater and the configuration is stable. Finally, only in very few cases a replacement collision sequence, however short, takes place.

B. Temperature effects

Of all the cases studied at 300 K, by far the simplest one, and still representative of the general trend, is Si [001]. For this reason, this case was used as a paradigm to examine the effect of temperature on the TDE's in SiC. For a number of temperatures between 150 and 2000 K, the interval of possible transferred kinetic energies between 25 and 75 eV was swept, in order to establish the lower and the upper displacement threshold for a Si recoil pushed in the [001] direction. The formation of the Si_1 -Si dumbbell (within the uncertainty band) and the replacement of the neighbor (above the upper threshold), as described above [see Figs. 2(a) and (b)] were used to discriminate between the two energy regimes. Besides, the lifetime of the corresponding metastable configuration (vacancy + Si_1 -Si dumbbell) was determined as a function of temperature, by performing long simulations between 1200 and 2000 K (by increments of 100 K), in which, after equilibrating it, the defect was continuously monitored, until its recombination was observed. In this way, the relevant Arrhenius law was interpolated from the collected data points and it was possible to estimate, for this particular case, the height of the energy barrier, that prevents the Frenkel pair recombination (*recombination barrier*).

Table IV describes quantitatively how the upper and

TABLE IV. Lower and upper thresholds, uncertainty-band width, and intermediate threshold value for a Si recoil along the [001] direction, as a function of temperature.

T (K)	Thresholds (eV)		Uncertainty band (eV)	Intermediate value (eV)
	Lower	Upper		
150	36 ^a	61	25	48.5
300	35	62	27	48.5
600	34	59	25	46.5
800	33	60	27	46.5
1000	31	55	24	43
1300	34	58	24	46
1700	34	52	18	43
2000	30	47	17	38.5 ^a

^aObserve the closeness of these numbers.

lower threshold for a Si recoil in motion along the [001] direction depend on temperature. The values in the table show that the upper threshold tends to diminish, while the lower threshold can be considered constant. As a result, the uncertainty band shrinks. The effect is more patent above 1000 K. Qualitatively, as temperature is raised, within the uncertainty band a larger selection of events becomes possible, as compared to the reference case at 300 K. In particular, between 600 and 1300 K it is no longer feasible to recognize, within the uncertainty band, an energy interval where the formation of the dumbbell is more likely than outside (like 44–55 eV at 300 K). Moreover, the recombination of the interstitial with the vacancy within the 6-ps observation becomes more and more probable, as temperature is increased. At 1700 K anomalous evolutions, leading to an apparently stable defect configuration, have a probability of occurring, even at energies higher than, but very close to, the lower threshold. Finally, at 2000 K, within the uncertainty band it becomes possible, sometimes, to produce a stable configuration (replacement), even though for higher energies no net displacement is produced. Globally, the impression is that the thermal agitation makes it easier, at the same time, both annihilating metastable defects (higher probability of recombination in the uncertainty band) and producing stable defects (smaller upper thresholds, as compared to room temperature and, occasionally, stable defects created also within the uncertainty band), thereby broadening the spectrum of possible evolutions when an atom is pushed out of its site.

In Fig. 4 the lifetime τ of the metastable defect configuration for the case here considered (Si [001]) is plotted using logarithmic scale against temperature (actually $1/kT$, k being the Boltzmann constant). The data points correspond to the results of the simulations and the interpolation was made using the Arrhenius function:

$$\tau = \frac{1}{\nu} \exp\left(\frac{E_b}{kT}\right), \tag{1}$$

where E_b is the energy barrier that has to be overcome in order for the interstitial to recombine with the vacancy and ν is the Debye frequency. The interpolation yielded, for these two magnitudes, the values $E_b = 1.16$ eV and $\nu = 2.5 \times 10^{13}$ Hz, the latter agreeing very well with the experimen-

tal value of the Debye frequency for SiC.²⁶ By extrapolating the curve down to 300 K, with the same value for E_b , a lifetime ≈ 350 h is found. However, already at 500 K τ drops to only a few milliseconds.

IV. DISCUSSION

The results presented in the previous section show that the basic mechanisms of displacement production in SiC reflect what is expected for a predominantly covalent material. In particular, as opposed to metals,²⁷ the replacement collision sequences are not the most favorable mechanism to create a Frenkel pair and, when they do take place, they are very short. The unlikelihood of replacement collision sequences is explained by the high energy required to break chemical bonds in a covalent material, as compared to a metal. At the same time, the localized nature of the bond in a covalent material makes it possible that an interstitial survives at a reasonably small distance from a vacancy, without recombining, contrary to metals, whose recombination distance (equal to the maximum extension of the spontaneous recombination volume) may be as large as many lattice parameters.²⁷

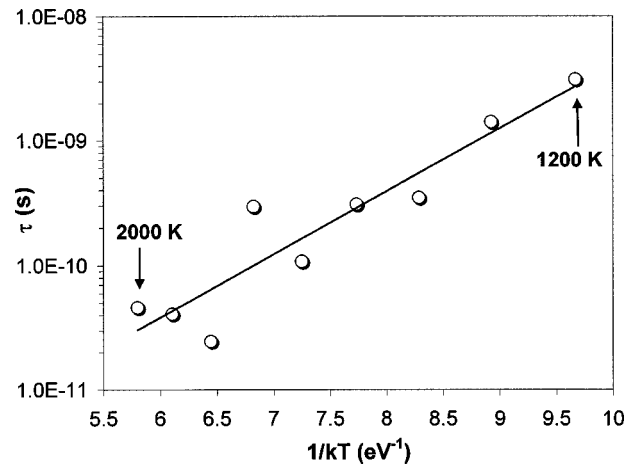


FIG. 4. Lifetime of the metastable Frenkel pair formed when knocking on a Si recoil along the [001] direction within the uncertainty band (Si₁-Si dumbbell+vacancy), as a function of temperature.

TABLE V. Spontaneous and induced recombination distances in SiC (expressed in lattice parameters), as estimated on the basis of the MD simulation.

Recoil and direction	Recombination distance (a_0)	
	Spontaneous	Induced
Si[001]	≈ 0.8	≈ 1.8
Si[111] ^a	≈ 0.5	≈ 0.9
Si[110]	≈ 0.4	≈ 1.9
Si[$\bar{1}\bar{1}\bar{1}$]	≈ 0.7	≈ 1.1
C[001]	//	≈ 0.85
C[111]	≈ 0.5	≈ 0.8
C[110]	≈ 0.55	≈ 1.1
C[$\bar{1}\bar{1}\bar{1}$]	≈ 0.55	//
Average Si	≤ 0.65	≤ 1.6
Average C	≤ 0.5	≤ 0.9

^aValues in this line refer to C sublattice.

As a matter of fact, in SiC, due to the existence of recombination barriers, which allow the formation of metastable Frenkel pairs within the uncertainty band, it seems sensible to introduce *two* different recombination distances: a *spontaneous recombination distance*, r_{SR} , defining the spontaneous recombination volume, and an *induced recombination distance*, r_{IR} , which in turn defines a bigger volume, within which the Frenkel pair may survive without recombining, but will easily annihilate as a result of a small perturbation (very-low-energy collision with another atom, local lattice distortion, local temperature rise, etc.). Based on the results of the previous section it is possible to attempt the estimation of an average upper limit for r_{SR} and r_{IR} , as shown in Table V. Such estimation shows that the recombination distance for the Si sublattice is larger than for the C sublattice, that is, Si interstitials should recombine more easily. This prediction is confirmed by the simulation of displacement cascades in SiC, in which it is seen that the primary damage state in SiC is characterized by a vast majority of C interstitial atoms, most Si displaced atoms ending up occupying vacancies.^{28–30} The values for r_{SR} given in Table V can be compared with the average, global value $r_{\text{SR}} = 0.53a_0$, obtained elsewhere³¹ by simulating by MD the highest possible Frenkel pair concentration in SiC, before turning amorphous. Note that the recombination distance for SiC is clearly much shorter than in metals.

The big question arising from the results presented in this paper is what value should be adopted for the average TDE of Si and C atoms in SiC when, for example, dpa (displacement per atoms) have to be calculated, or other estimations have to be made that require the knowledge of the parameter usually indicated as E_d (displacement energy). As it is, the anisotropy of this magnitude and the existence of *two* thresholds in SiC seem to complicate notably the task of proposing reliable numbers for E_d (actually $E_{d,\text{Si}}$ and $E_{d,\text{C}}$, that is, one value for each sublattice). In Tables II and III, the arithmetical and weighed averaged values, over all the directions, of the lower and the upper thresholds are calculated for, respectively, Si and C atoms. Also the minimum value is indicated.

The weighed average is determined by taking into account the multiplicity of each direction (also specified in the tables), that is, the number of equivalent directions, to which the same threshold energy should correspond. In the same tables, the intermediate value between lower and upper threshold is proposed as possible candidate *global* average value, capable of allowing for the presence of an uncertainty band. The width of such bands is also tabulated. It should be remembered that all these values hold at room temperature.

The question is then which of the average values given in Tables II and III should be chosen as the most meaningful and therefore adopted as $E_{d,\text{Si}}$ and $E_{d,\text{C}}$. If the values recommended by Zinkle and Kinoshita,⁷ based on experimental and computational determinations of the threshold energy in SiC, are taken as a reference, that is, $E_{d,\text{Si}} = 40$ eV and $E_{d,\text{C}} = 20$ eV, then it looks like the *minimum* values of the *lower* thresholds, as determined in this work and presented in Tables II and III, are to be adopted as actual thresholds. The same conclusion is suggested if the values of Tables II and III are compared with threshold energies obtained by applying inversely the Norgett-Robinson-Torrens (NRT) model³² to the number of displacements per cascade as predicted by MD simulations.³⁰ In Ref. 23 similar values (namely $E_{d,\text{Si}} = 35$ eV and $E_{d,\text{C}} = 20$ eV) are proposed too. Therefore it seems that not only does the existence of uncertainty bands not affect the global, macroscopically observable value of the TDE's (at least at room temperature or below), but also that the computational determination of such thresholds overestimates them. It is possible that the explanation to this discrepancy between results obtained in different manners lies in the fact that in the present paper (as well as in earlier ones, by other authors^{20–23}) the TDE's are found by creating a defect in an otherwise perfect crystal. It is likely that within a displacement cascade (and in experiments) the simultaneous production of many defects, and/or the presence of defects prior to the displacement generation, makes it less energetically costly to produce a single atomic displacement in the material. However, this explanation should be checked by performing adequate MD simulations, in which, for example, the TDE's are determined in a previously damaged lattice.

The last, maybe more important, aspect to be discussed is the effect of temperature on the TDE's. In a way, it is not surprising that the presence of barriers to the recombination of metastable Frenkel pairs does not affect at all the TDE values *at room temperature*. The study of the lifetime of these *so-called* metastable Frenkel pairs has shown that at room temperature these defects may survive for up to 300 h. That is, if the disappearance of these metastable defects was due only to thermal activation, then at 150 or 300 K they would never recombine in less than 6 ps and without any doubt the E_d would always coincide with the lower threshold. The simulations herein reported show that, even for those temperature regimes where the metastable defect lifetime should be on the order of hours, there still exists an *uncertainty band* that hampers the definition of a single threshold energy value. This means that, during the very process of displacement production, as long as the defect is

metastable, any small perturbation, due to the temporary distortion of the lattice or to the subthreshold interaction of the recoil with other atoms, can prevent the formation of the defect. In other words, the metastability of these defects is revealed, at low temperature, only by the fact that they are *not always produced*, because within the uncertainty band the *recovery* can be so quick as to be confused with the absence of defect production. But, *when they are created*, at low temperature they can be well considered stable for all practical purposes. Therefore, from the macroscopic point of view, one could say that, at low temperature, when transmitting energies close to the lower threshold to the atoms, a certain probability of producing displacements already exists. Consequently, at low temperature the value of E_d to be used for dpa calculation should be chosen close to the *minimum lower* threshold for both sublattices.

At higher temperature (>500 K) the lifetime of the metastable Frenkel pairs becomes exponentially shorter than milliseconds. Therefore, in such a temperature regime, even in an ideal experimental observation it should become impossible to detect the formation of defects by transferring energies within the *uncertainty band* to the atoms, for example, by means of electron irradiation, because these defects will disappear too quickly to be seen. Only stable defects could be detected in that temperature interval. Hence, as the irradiation temperature increases, the presence of uncertainty bands should become evident and the measurable TDE's ought to get closer and closer to the upper threshold or, at least, to an average value, intermediate between the upper and lower threshold. In other words, at high temperature the value of E_d should be chosen closer to the average upper threshold herein reported, or at least to the intermediate value between lower and upper threshold, for both sublattices.

However, so far the reasoning did not take into account the fact that the temperature rise has an influence not only on the metastable defect recombination rate, but also on the very process of displacement production. The simulation reveals that the width of the uncertainty band shrinks with increasing temperature, particularly for very high temperature (above 1000 K), while the lower threshold remains approximately constant; i.e., the upper threshold becomes smaller (Table IV). Moreover, as mentioned in Sec. III B, at very high temperature the possible events within the uncertainty band become more numerous and it turns impossible to find a regular behavior pattern while the energy transmitted to the atom increases. Sometimes, stable defect configurations (replacement instead of dumbbell in the case of a Si atom hit along the [100] direction) are produced even for energies on the order of the lower threshold. Hence, at *very high* temperature there already exists a certain probability of producing long-lived, observable defects by giving the atoms energies within the uncertainty bands, close to the lower threshold. Quantitatively, this is shown in Table IV by the fact that the intermediate value of the uncertainty band at 2000 K is very close to the lower threshold at 150–300 K. The overall effect is that, at *very high* temperature, the value of E_d should be chosen again very close to the lower thresh-

old at room temperature, as is worked out in Table IV. Though this result was obtained only for the Si sublattice, it seems reasonable to extend it to both sublattices.

In summary, all these arguments suggest that, qualitatively, E_{dSi} and E_{dC} should be well estimated by the *minimum* lower threshold found computationally in this paper, both at room temperature and above 1000 K. However, in the temperature range between, approximately, 500 and 1000 K their value should experience a peak, as a result of the shorter lifetime of the metastable Frenkel pairs formed within the uncertainty band. There is only one experimental work available, in which the TDE's in SiC were measured at high temperature (890 K), performed by Hudson and Sheldon.³³ The fact that these authors found a much higher value than in any other work (all carried out at room temperature or below)⁷ might therefore not be due to experimental errors, but to this MD-predicted TDE peak at intermediate temperature. Finally, it should be noticed that another possible effect of the existence of uncertainty bands could be the wide scattering of experimental data on TDE's in SiC, especially for Si recoils, noted in Ref. 7.

V. CONCLUSIONS

In silicon carbide (SiC) the threshold displacement energies (TDE's) along different directions for both types of recoils (Si and C) appear to be substituted by a whole band of energy values, comprised between a *lower* and an *upper* threshold. Within such *uncertainty band* the atomic displacement may or may not be produced, as the Frenkel pairs therein produced are metastable. Their metastability has been demonstrated in one particular case, by determining the Arrhenius law that expresses their lifetime as a function of temperature.

The uncertainty bands are broader for Si atoms, and this perhaps explains the greater uncertainty in experimentally obtained TDE values for this sublattice. Also, Si atoms are harder to displace than C atoms.

The analysis, by means of MD simulation, of the evolution of an atom pushed out of its site in a bulk SiC sample, both within and above the uncertainty band, at 300 K, reveals that, at least according to the version of the Tersoff potential herein adopted, the interstitial configurations thereby created are almost invariably dumbbells. At any rate, the interstitial thereby generated locates itself always at a small distance from the vacancy, as replacement collision sequences take place very rarely and, when they do take place, they are very short, as opposed to metals. The separation between the interstitial and the vacancy also decides the stability or metastability of the generated Frenkel pairs.

In accordance with the existence of metastable Frenkel pairs, it seems sensible to define two different recombination distances for SiC: a spontaneous-recombination distance ($r_{SR, Si} \leq 0.65a_0$; $r_{SR, C} \leq 0.5a_0$) and an induced-recombination distance ($r_{IR, Si} \leq 1.6a_0$; $r_{IR, C} \leq 0.9a_0$). The values estimated for these recombination distances indicate that Si interstitials recombine more easily than C interstitials. As to threshold energy values of practical usefulness, the discussion proposed leads to accepting the already recommended

values $E_{d, Si} = 35$ (Ref. 23) or 40 (Ref. 7) eV and $E_{d, C} = 20$ (Ref. 7) eV. However, these values appear to be acceptable only for low or very high irradiation temperature, as it is expected that, due to the reported existence of recombination barriers, in the range of approximately 500 to 1000 K, the TDE's should experience a peak, apparently measured also experimentally.

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