Energetics of Defects and Diffusion Mechanisms in Graphite

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Extensive first-principles calculations are presented for the formation energies and migration barriers of elementary defects in graphite, as well as for the activation energy of atomic exchange. The calculations show that the long-held view that atomic diffusion in graphite occurs via the direct-exchange mechanism is incorrect, although more complicated exchange processes have not been ruled out. We find that diffusion in graphite is most likely mediated by vacancies with an activation energy which is lower than that of the interstitial and the direct-exchange mechanisms, and is in reasonable agreement with experiment.

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The process of atomic diffusion, despite its technological importance, is still very poorly understood. Even the most basic question, what is the microscopic mechanism responsible for atomic diffusion, has not been answered in most cases of interest. Diffusion mechanics are generally divided in two broad categories: the exchange mechanism, in which atoms directly interchange positions and thereby migrate in the crystalline lattice, and the defect mechanism, in which the motion of a lattice defect (most commonly a vacancy or an interstitial) mediates the atomic migration. Naively, the exchange mechanism may appear to be advantageous since it does not depend on the creation of defects which is an energetically costly process. It has been found, however, that the activation energy of atomic exchange is in most cases very high. This is because during an exchange event large distortions are induced in the lattice.[1,2] Defects on the other hand, once they have been created, can move through the lattice at a considerably smaller energy cost, and thus defect mechanisms are believed to dominate the diffusion process in most solids.

The single exception among covalent solids for which a non–defect mechanism is generally accepted to dominate diffusion is the case of graphite.[3-7] This is based on comparison of diffusion data with theoretical calculations for graphite.[3,8] However, these theoretical calculations are empirical and subject to numerous uncertainties. For example, different assumptions about the orbital configurations of a vacancy change the formation energy dramatically.[8] Furthermore, a critical comparison of different diffusion mechanisms to experimental results did not lead to definite conclusions.[7] Thus, in order to establish the dominant diffusion mechanism first-principles calculations are needed. This is particularly true since experimental information alone cannot identify the diffusion process. An unambiguous identification of the diffusion process would also require the calculation of dynamical factors (such as entropy and attempt frequency) which is beyond the scope of the present work. Here we shall concentrate on activation energies, which are well obtained by static zero-temperature calculations, and will prove adequate for comparing the

various mechanisms that have been proposed in the literature. If atomic exchange turns out to be the dominant mechanism, graphite will represent an intriguing special case for the study of microscopic diffusion mechanisms which do not depend on the presence of defects. Recently, it was shown that an exchange mechanism (the concerted exchange) may be operative in Si (Ref. 9) although the exchange was not previously considered as a likely mechanism for the diamond lattice which has different bonding topology than graphite. The issue of non–defect diffusion mechanisms is of great theoretical and practical importance, since it has serious implications for the stability of doped materials and interfaces.

In this paper we report the first realistic, first-principles calculations for the energetics of the exchange mechanism and the defect mechanisms, vacancy and interstitial, in graphite. Given the extensive computational effort required for such calculations, we have limited the scope of our study to in-plane processes only. For the same reason, we have not investigated exchange mechanisms more complicated than the direct exchange, which might have low activation energy. The results of our calculations lead to conclusions contrary to the widely held view about atomic exchange in graphite. Namely, the direct-exchange mechanism has an activation energy higher than previously calculated (10.4 eV instead of 3.9 eV, Ref. 3), and considerably larger than than experimental values (7–8 eV, Ref. 7). Moreover, the vacancy mechanism, which has an activation energy of at most 9.2 eV, is energetically preferred over the direct-exchange mechanism in graphite.

Our first-principles calculations employ norm-conserving pseudopotentials[10] in the framework of local-density-functional theory.[11] This scheme allows for a fully self-consistent treatment of the electronic wave functions. The use of an appropriately large basis of plane waves and of a set of eight points in the Brillouin zone (which correspond to twelve points in the irreducible Brillouin zone of bulk graphite) to perform reciprocal-space averages gives realistic estimates for the energy cost involved in the various distortions, including the breaking of bonds. Convergence tests as a function

of plane-wave cutoff were performed up to an energy of 32 Ry. In a typical example, we find that the activation energy of the direct-exchange mechanism changes by 0.06 eV as the plane-wave cutoff is increased from 24 to 28 Ry. The large number of reciprocal-space sampling points and the large energy cutoff of the plane-wave basis, which are comparable to those used for high-accuracy bulk calculations in graphite,[12] give a small error bar for the calculated energy differences. This error bar is estimated from the convergence studies to be less than 0.5 eV. The model on which the calculations were performed consists of a supercell geometry with eighteen atoms in each plane of graphite in the rhombohedral form (... ABCABC... stacking).[13] The reason for choosing the rhombohedral rather than the more common hexagonal form of graphite (... ABAB... stacking)[13] is that the former possesses inversion symmetry which greatly facilitates the computations. We have verified that the results in hexagonal graphite, with defects in alternate planes, are the same as in rhombohedral graphite to better than 0.1 eV.

We shall consider first the direct-exchange mechanism on a plane of graphite, which consists of rotating two atoms by an angle θ around their bond center. During a complete exchange θ varies from $0°$ to $180°$. The ideal configuration ($\theta=0°$ or $180°$) and the configuration corresponding to half-rotation ($\theta=90°$) are shown in Figs. 1(a) and 1(b), respectively. In Fig. 2 we show the total energy of the system for $0° \leq \theta \leq 180°$, that is, for a complete in-plane direct exchange. From symmetry

considerations the $\theta=90°$ configuration is an extremum of the total energy, but as seen from Fig. 2, it is a local minimum and not the maximum of the energy curve. The activation energy is determined by the highest of the energy maxima which must be crossed during the exchange process. Therefore, if this process is restricted to take place on the plane, the activation energy is not determined by the $\theta=90°$ configuration, but rather by the $\theta=55°$ or $125°$ configuration, and is 13.7 eV.

The energy of the $\theta=55°$ or $125°$ configuration is high because at these in-plane configurations there is large bond compression. However, this compression can be relieved by out-of-plane motion of the exchanging atoms. The $\theta=90°$ configuration on the other hand, involves bond stretching rather than bond compression, and its energy cannot be lowered by out-of-plane displacements. Instead, if the exchanging atoms are forced out of the plane at $\theta=90°$, the energy increases. Thus, the energy of the $\theta=90°$ configuration is a *lower bound* for the activation energy of the more general direct-exchange mechanism which includes out-of-plane displacements. In the following, since other mechanisms with lower activation energy will be encountered, it will suffice to identify the energy of the $\theta=90°$ configuration as the *minimum activation energy* of the direct-exchange mechanism. This energy is 11.4 eV before allowing for atomic relaxation (the exchanging atoms are at a relative distance equal to the ideal bond length of graphite, 1.42 Å).

We discuss next the effect of relaxation on the activation energy. On account of the extensive nature of the computations we have allowed only relaxation of the exchange-pair atoms relative to their bond center and symmetric relaxation of their four neighbors relative to the same reference point, as indicated in Fig. 1(b). The
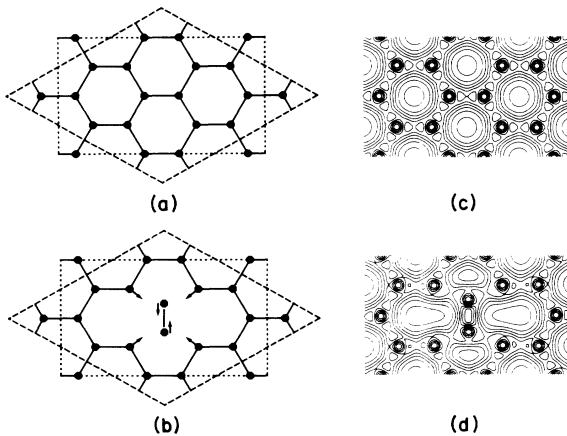

FIG. 1. (a) An ideal plane of graphite. The dashed lines outline the supercell used in the calculations. The dotted lines outline the area for which a valence-charge-density contour plot is shown in panel (c). (b) The $\theta=90°$ configuration (half-rotation) of the direct-exchange path, which corresponds to the saddle point. Arrows indicate the direction of relaxation (not actual displacements). The dashed and dotted lines have the same meaning as in (a). (c) Contour plot of the valence charge density for the ideal configuration. The spacing of contours is 0.05 a.u. (d) Same as in (c) for the saddle-point configuration.
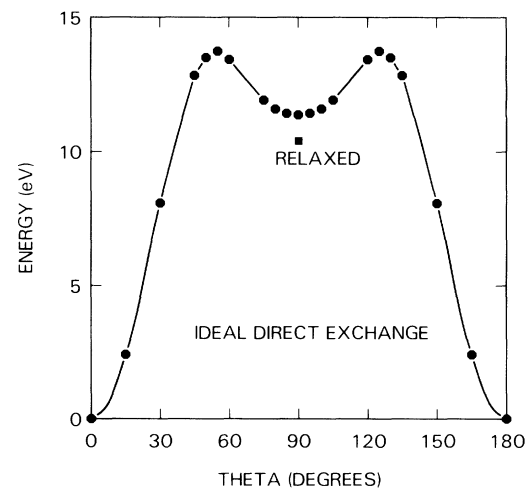

FIG. 2. The total energy vs rotation angle θ for the in-plane direct-exchange path. The dots are calculated energies; the line is a spline fit. The square gives the energy of the relaxed saddle-point configuration.

relaxation of the exchange atoms relative to each other gives an energy gain of 0.8 eV and the relaxation of their four nearest neighbors gives a gain of 0.2 eV. Thus the activation energy for the direct-exchange mechanism including relaxation is 10.4 eV. For comparison, empirical studies, including the relaxation of the exchange atoms relative to each other only, give an activation energy of 3.9 eV,[3] almost a factor of 3 too small.

The fully relaxed saddle-point configuration shows some interesting features of carbon bonding. At this configuration, the two atoms of the exchange pair move closer to each other, to a relative distance of 1.28 Å. This lies between a double and a triple bond in carbon, which have bond lengths 1.33 and 1.20 Å, respectively.[14] The back bonds of the nearest neighbors are slightly stretched (one at 1.45 and the other at 1.43 Å), and the bond length between an exchange-pair atom and one of its neighbors is 1.50 Å. Thus, the two atoms of the exchange pair are effectively fourfold bonded, by a strong double bond to each other and by weaker single bonds to their neighbors. This bonding arrangement is illustrated in Fig. 1, where valence-charge-density contour plots for the ideal and the saddle-point configurations are compared in panels 1(c) and 1(d). The bond between the exchange atoms at the saddle-point configuration [Fig. 1(d)] is different from other bonds: It lacks the double-hump feature of the normal graphite bonds and has considerably higher charge density. The weak bonds of the exchange atoms to their neighbors are also evident, containing a smaller amount of charge than normal bonds.

In the case of defect mechanisms, the activation energy is the sum of the formation energy and the migration barrier, that is, the energy to create a defect in the ideal lattice and the barrier to move it to a different site. We investigate first the interstitial mechanism. Since the present study is limited to in-plane diffusion only, the interplane interstitial, which might be important for atomic migration between planes, will not be considered in the following discussion. In the same vein, relaxations or migration paths which involve out-of-plane motion of an interstitial atom will not be considered here. This motion would lead to interplanar interstitial atoms which are known experimentally[7] to diffuse rapidly at temperatures an order of magnitude lower (200 °C) than those required for in-plane diffusion (2000 °C). The only physically reasonable position for the in-plane interstitial atom is the center of an open hexagon.

We find that the formation energy of the ideal in-plane interstitial is 19.5 eV. Empirical calculations also give a high formation energy for the interstitial, close to our result (18.1 eV, Ref. 3). The high formation energy leads us to conclude that the total activation energy of the in-plane interstitial will be higher than the activation energy of the direct exchange by many eV. This is due to the fact that the *migration* energy alone for the in-plane interstitial should be roughly of the same magnitude (10 eV) as the *activation* energy of the exchange,

since both processes involve atomic interchanges. In fact the interchange in the interstitial mechanism takes place in a severely constrained environment because of the presence of the extra atom, and is probably a higher-energy process than the direct exchange. If one adds to the migration energy of the interstitial the formation energy (even lowered by a factor of 2 to 10 eV as a result of relaxation, which is an extremely favorable and unlikely situation) the activation energy becomes at least 20 eV, making further study of the in-plane interstitial unnecessary.

We consider next the energetics of the vacancy mechanism. Our calculations give a formation energy of 7.8 eV for the ideal vacancy, which suggests the possibility of a low activation energy. To calculate the migration barrier, we need the energy of the saddle-point configuration relative to the equilibrium vacancy configuration. The vacancy in its equilibrium and saddle-point configurations is shown in Figs. 3(a) and 3(b), respectively. The energy of the unrelaxed saddle point is 1.9 eV with respect to the ideal equilibrium vacancy configuration, giving an activation energy of 7.8+1.9=9.7 eV. Even without considering atomic relaxation, our calculated value for the vacancy activation energy is lower than the activation energy of the fully relaxed exchange mechanism (10.4 eV). This already casts doubt on the feasibility of the exchange mechanism in graphite. For comparison, the formation energy and the migration barrier of the vacancy as obtained by empirical calculations, without any relaxation, are 5.2 and 3.1 eV, respectively, giving an activation energy of 8.3 eV (Ref. 3).

The atomic relaxation of the vacancy is complicated because of the possibility of symmetry-breaking Jahn-Teller deformations. An elaborate treatment of this possibility has been given by Coulson *et al.*[8] in the context of empirical molecular-orbital theory. The formation en-
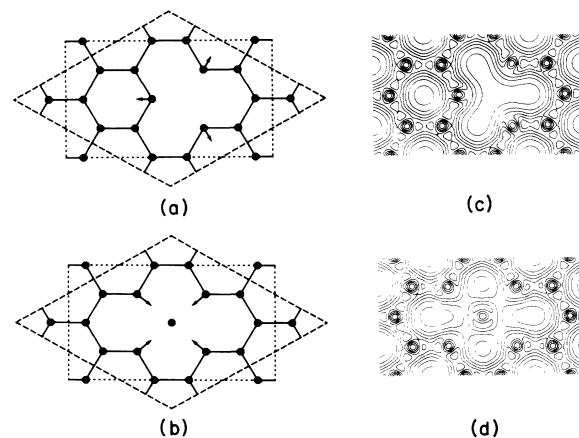

FIG. 3. (a),(c) The equilibrium vacancy configuration. (b),(d) The saddle-point vacancy configuration. Symbols are the same as in Fig. 1.

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ergy of the relaxed vacancy was estimated by these au-
thors to be 10.7 eV, a factor of 2 larger than the empiri-
cal result of Dienes (5.2 eV, Ref. 3). Even the result of
Ref. 8, however, is uncertain since a different orbital
configuration could change the formation energy dra-
matically. Within our first-principles approach, because
of technical reasons, we have been able to consider only
the symmetric relaxation of the nearest neighbors of the
vacancy for the equilibrium and the saddle-point
configurations, as indicated in Figs. 3(a) and 3(b). In
the equilibrium configuration, the three atoms adjacent
to the vacancy site move radially away from it, thereby
strengthening their back bonds. In the saddle-point con-
figuration, the four nearest neighbors to the migrating
atom move toward it, thus forming four weak bonds to it.
These bonding arrangements are illustrated by valence-
charge-density contour plots shown in Figs. 3(c) and
3(d), for the equilibrium and the saddle-point
configurations, respectively. The formation energy and
migration barrier of the relaxed vacancy configurations
are 7.6 and 1.6 eV. Thus, the activation energy of the
vacancy including the relaxation described above is
$7.6 + 1.6 = 9.2$ eV, considerably lower than the relaxed
direct-exchange mechanism (10.4 eV) but still higher
than the experimentally observed activation energy 7–8
eV (Ref. 7).

Our calculated activation energy for the vacancy is
only an upper bound because we have not been able to
consider more general relaxations, which require great
computational effort as a result of the lower symmetry.
The full relaxation of the vacancy may bring the activa-
tion energy closer to the experimental results and even
lower than the direct-exchange activation energy. On
the other hand, refinement of the relaxation for the
direct-exchange mechanism is not expected to lower the
energy significantly, since the first-neighbor relaxation
energy (0.2 eV) is already 4 times smaller than that of
the exchange-pair atoms (0.8 eV). Thus, the exchange
mechanism considered above seems an unlikely process
for diffusion in graphite, and the vacancy mechanism is
energetically preferred. The possibility of a more com-
plicated exchange path of lower energy cannot be ruled
out, however. A search for such paths of low activation
energy by means of the first-principles scheme employed
in this work is not feasible at present.

In conclusion, we have shown that the most favorable
in-plane diffusion mechanism in graphite is the vacancy
mechanism with an upper bound for the activation ener-
gy of 9.2 eV. This value may become lower and in better
agreement with experimental results of 7–8 eV by allow-
ing further relaxations which are outside the computa-
tional scope of the present work. The direct-atomic-
exchange mechanism on the other hand has an activation
energy considerably higher (10.4 eV). These results are
in sharp contrast to previous empirical calculations
which estimated the activation energies of the direct-
exchange and the vacancy mechanisms to be 3.9 and 8.3
eV, respectively.[3] It remains to be established whether a
more complicated exchange path of lower activation en-
ergy exists, which can compete with the vacancy mecha-
nism.

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