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Theoretical status of diamond and its defects, excited states and atomic motion

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Abstract

The key technical problems for diamond concern control: controlled growth (quality, composition, shape and texture), controlled doping (lasing species, electrically active species, redistribution and anneal of implanted species) and controlled interfaces (contacts, passivation, adhesion and friction). Theory has contributed to all these. Here I shall concentrate on electronic and motional aspects of defects. Several key phenomena involve features of the excited states, and I emphasize what can be obtained from the wealth of optical data. For diamond, optical data—involving a bound excited state—are especially fruitful; one feature to emerge is the strength and nature of the Jahn–Teller effect, which is both observed and measured through the satellite lines that it produces, so that the neutral vacancy is one of the best-understood Jahn–Teller centres. Three further features follow from examination of other properties. The first is the role of electron–electron correlation. The second is the question of whether all asymmetric defects are indeed examples of the Jahn–Teller effect. Isolated nitrogen is a key case, because of the families of nitrogen-related defects in diamond, and the important recent results of the Exeter group conclude, probably rightly, that wholly different mechanisms are involved. Thirdly, the nature and contributions to the energy in diamond and in ZnSe can be usefully contrasted, with again different reasons for the asymmetry of the singly charged cation vacancy.

I shall also comment on some of the more general aspects of defect phenomena, including diffusion and reorientation behaviour. In particular, the motion of hydrogen and the muon studies need special comment, since it is likely that the diffusion mechanism is not simple classical diffusion (although this cannot yet be ruled out; further, other classical diffusion channels are available) and is perhaps closer to mechanisms now accepted for diffusion in of hydrogen in metals and indeed to reorientation of the V^- centre in ZnSe.

1. Introduction

The key technical problems for diamond concern control: controlled growth (quality, composition, shape and texture), controlled doping (lasing species, electrically active species, redistribution and anneal of implanted species) and controlled interfaces (contacts, passivation, adhesion and friction). In all these areas, there have been contributions from theory, ranging from predictions of coefficients of friction, through the differences between diamond-like carbons and diamond itself, to detailed calculations for specific defects [1]. I have discussed most of these aspects in a review [2]; in the present paper I shall concentrate on electronic and motional aspects of defects.

Several of the key phenomena for the practical use of diamond involve features of the excited states, and my paper comments on the understanding which can be obtained from the wealth of optical data. There is an immediate and enormous contrast to studies of defects in silicon; there it is ground-state spin resonance which has provided most insight, and optical data for intrinsic defects are of far less importance, although the deep level transient spectroscopies can offer special insight. For diamond, optical data—involving a bound excited state—are fruitful in special ways not always clear to those whose background has been silicon. One of the features to emerge is the strength and nature of the Jahn–Teller effect, which is both observed and measured through the satellite lines it produces.

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As a result, the neutral vacancy is one of the best-understood Jahn–Teller centres. Three other features follow from examination of other properties. The first is the role of electron–electron correlation; this, which was controversial two decades ago, has been the key to understanding the gallium vacancy in GaP and—with the Jahn–Teller effect—may provide the explanation of the extraordinary narrow photoconducting GR2–GR8 lines. The second is the question of whether all asymmetric defects are indeed examples of the Jahn–Teller effect. Isolated nitrogen is a key case, because of the families of nitrogen-related defects in diamond, and the important recent results of the Exeter group conclude, probably rightly, that wholly different mechanisms are involved. This can have implications for other compact donors and acceptors in wide-gap fourfold-coordinated hosts. Thirdly, the nature and contributions to the energy in diamond and in ZnSe can be usefully contrasted, with again different reasons for the asymmetry of the singly charged cation vacancy.

I shall also comment on some of the more general aspects of defect phenomena, including diffusion behaviour. In particular, the motion of hydrogen and the muon studies need special comment, since it is likely that the diffusion mechanism is not simple classical diffusion (although this cannot yet be ruled out) and is perhaps closer to mechanisms now accepted for diffusion in of hydrogen in metals. The central theoretical problem concerns vibrations both at and away from the equilibrium configuration. This, in turn, raises the question of interatomic forces and their representation as interatomic potentials.

2. The vacancy in diamond

From the earliest days, it was believed that the GR1 band, produced by many types of irradiation, was the signal of a vacancy. The case for the interstitial was harder to rule out, but the evolution towards a consensus contained some important points. First, pioneering calculations of the ground state [3] found that (in addition to agreement with experiment which, given the means available, can only be described as fortuitously good) (i) there were several possible ground states, all not too different in energy, and with different multiplicities, (ii) electron–electron correlation was crucial, not because it was unusually large [3–5] but because of the similarity of energies of states of the same symmetry, (iii) vibronic effects were substantial (spectroscopically), and indeed the optical spectra could be analysed to give an exceptionally clear picture of the Jahn–Teller behaviour [6–8] and (iv) the important excited states could not usefully be described in a one-electron picture; not only do some excited states remain not understood to this day, but even the basic GR1 transition appears to be a transition from t^2 to t^2, *i.e.* between states which are identical in the simplest one-electron picture.

Experimental progress clarified several of these features. The vacancy picture of the GR1 centre was verified by uniaxial stress, confirming its cubic symmetry and that the line was an A-to-T transition, in line with early theory [3]. Zeeman data confirmed spin zero, as expected for the neutral vacancy (spin resonance is, of course, impossible, as for the neutral vacancy in silicon). Separate studies indicated that the ND1 band was that of another charge state, the negative vacancy [9]. Further work investigated the optical fine structure. Again, early theory was confirmed; the satellite lines close to the main zero-phonon line of the GR1 band had been predicted to be the consequence of a dynamic Jahn–Teller effect [6]; 10 years later, once full uniaxial stress data were available, this could be confirmed, and accurate estimates made of the ground-state and excited-state Jahn–Teller energies [9–12]. These led to further attempts to predict the Jahn–Teller energies, with some success [13]. However, experiment had further puzzles, in the sharp GR2–GR8 lines. A full explanation is still lacking, and a possible model will be given later.

Most of the early theory emphasized spectroscopy, or results available therefrom. Formation energies attracted less attention, partly because there were technical problems, and partly because simple estimates suggested there was no real possibility of thermal production under laboratory conditions (*i.e.* equilibrating and avoiding graphitization); so there could be little practical interest. The simple arguments are based on tabulated C–C bond energies; there is a spread of such energies from about 3 to 5 eV, depending on what other radicals are attached to the carbon atoms, and the most naive vacancy formation energy would be twice this bond energy, *i.e.* 6–10 eV. Some early results found just this [5, 14], perhaps fortuitously; recent local density functional work by Bernholc *et al.* [15] found a value of 7.2 eV, confirming the simple picture.

2.1. Electron-electron correlation

For the neutral vacancy in diamond, early calculations suggested there were three states likely to be low in energy, and that whether one got a single E state, a triplet T state or a quintet A state depended on a balance between energies in which electron-electron interaction (usually called the configuration admixture, from the approach adopted) was significant [5]. For the vacancies in silicon, Watkins' [16] seminal spin resonance work was interpreted wholly differently, through the negative vacancy (for which a mixed trigonal and tetragonal distortion appears incompatible with simple Jahn-Teller theory; this still seems not to be predicted by modern approaches); spin resonance again seems to demand a configuration admixture. The issue slipped from attention, returning dramatically when the observed gallium vacancy in GaP required that there was different filling of the one-electron levels from that conventional wisdom had accepted, and that this difference was entirely parallel with the features that Coulson and Kearsley had argued for diamond three decades before [17].

2.2. The dynamic Jahn-Teller effect and its consequences

The GR1 transition is from a singlet E state to a singlet T state. Both have electronic degeneracy, and both should show a Jahn-Teller effect. Since the stress response shows the centre to be cubic, the effect is presumably dynamic. This was the view of Lannoo and Stoneham [6] who first attempted to predict the extent of vibronic coupling and its effects on optical absorption. The results showed rather good agreement with experiment, despite the simple means available, including the differences between Huang-Rhys factors from different approaches to analysis of experiment. What was perhaps more interesting was their explanation of the satellite line, which arises from a state some 8 meV above the ground state. This was proposed to be the A2 state arising from the standard dynamic Jahn-Teller prediction for an E state coupled to E modes. Later work confirmed the symmetry but left undecided the issue of whether the state was a distinct electronic state (near degeneracy) or vibronic (from a single electronic state plus electron-lattice coupling). This was settled later, when both intralevel and interlevel stress coupling coefficients became available [7]; the ratio should lie within tight bounds if vibronic, whereas it should be well outside these if another electronic state were involved. Later works [8] refined these calculations, although with some simplifications (basically, the issue is what one assumes about the local force constants at the vacancy in relating macroscopic and microscopic strain, and whether or not one interprets the conspicuous side band on the GR1 line as the effective frequency for the Jahn-Teller mode). The analysis—however done—gives Jahn-Teller energies and displacements, barriers to reorientation, and also the prediction—later confirmed—that there should be a detectable higher vibronic state. At much the same time, the first self-consistent cluster calculations were being done, and the Jahn-Teller properties were again predicted consistently. It would be interesting to carry out those calculations again with current methods.

The conclusion is that the Jahn-Teller effect for the neutral vacancy in diamond is certainly present, very well understood qualitatively and respectably so quantitatively.

2.3. The GR2-GR8 lines

The GR1 spectrum is itself complex and informative [18]. Yet at higher energies there are still other sharp line [19], the GR2-GR8 lines (the nomenclature has been confused by the fact that some diamonds have internal strains and other complications suggesting extra weak lines; I shall refer to them collectively as GR*N*). The GR2-GR4 lines are certainly from the vacancy (they have the same ground state, as is verified by uniaxial stress), and probably the GR5-GR8 lines are from the same neutral vacancy. There are three central puzzles. First, why do they give p-type photoconductivity? Common intuition (a very poor guide) is said to suggest n type; perhaps the main issue is why one rather than the other. Secondly, why are the lines so narrow? They are only a few millielectronvolts wide, far less than the "sharp" features seen in photoionization of other deep centres (like the L bands of anion vacancy F centres in alkali halides), which are hundreds of millielectronvolts wide. For the GR*N* lines, the widths seem to be limited by strain and lifetime only. The loss of a hole from the positive divacancy in silicon has a peak only

40 meV wide, and its behaviour may be similar to GRN. Thirdly, why are there so many lines? There are at least 13 resolved, and all have threefold orbital symmetry.

The explanations have been of several types. The simplest suggests the excited states are one-electron levels at a band edge. This explanation, however given, fails on two criteria. First, the widths and their trends with energy disagree grossly with predictions for such a model [20]. Secondly, most electronic structure models agree about the orders and symmetries of excited states, and none predicts so many threefold-degenerate states. I discuss here another possibility [21], which makes use of the two ideas noted above: the importance of electron–electron correlation, and the Jahn–Teller effect. The components of the model are conventional but not common in defect studies.

The first basic assumption is that the large number of lines comes from a few distinct electronic excited states (one or two) plus vibronic coupling; the mechanisms which yield the satellite structure of the GR1 line are doing the same for GRN, a view consistent with the fact that the GR2–GR8 lines are confined to an energy less than the maximum phonon energy for diamond. I would not rule out the possibility that some lines are the result of degeneracy removal by a nearby defect. The second basic assumption is that, to ensure such narrow lines, only bound–bound transitions can be considered. The third assumption is that photoconductivity and bound–bound transitions can be reconciled provided that the optical absorption is a two-electron transition and not a one-electron transition.

Consider a two-electron system (the two electrons could be the t^2 electrons of the neutral vacancy). The ground state can be written as the Slater determinant $\det\|ab\|$ in terms of the one-electron orbitals. In a one-electron excitation, the excited state might be $\det\|xb\|$, with energy close to the one-electron energy difference $x-a$. In a two-electron transition, the electron–electron interaction allows excitation instead to $\det\|xy\|$, with energy similar to the sum of the one-electron energy differences $x-a$ and $y-b$. Even if both x and y correspond to bound states, the double excitation may be able to decay to give one electron in its initial state and one as a free carrier (it is, of course, easier to speak of electrons rather than holes, but the argument is symmetrical). This is known in atomic physics as autoionization but should not be confused with simple one-electron excitation into a resonance, for which the same term is sometimes used.

The model has several interesting consequences, one being that no GRN luminescence is expected, nor is it observed; instead, consistent with the model, one sees instead the GR1 luminescence. Secondly, there may be another simple absorption in the 1–1.5 eV range, corresponding to the excitation component which is distinct from the GR1. Selection rules could forbid it, but a closer look at what is involved is needed. There are several other checks from g factors and lifetimes, all needing a fuller theory than given here.

3. Isolated substitutional nitrogen in diamond

In diamond, nitrogen is the pervasive impurity, which is present in many forms from isolated substitution through simple aggregates to platelets (an even more extensive class of nitrogen-based defects than oxygen-based defects in silicon exists), and with the state of aggregation giving information about diffusion mechanisms on geological time scales [22].

It has long been asserted that the trigonal spin resonance spectrum of nitrogen in diamond has its low symmetry because of the Jahn–Teller effect [23]. This view was reinforced, qualitatively at least, when thermal reorientation was seen, so that estimates of the Jahn–Teller energy could be deduced. Yet it was realized early on that the order of the energy levels was not obviously right to yield a degenerate ground state, and self-consistent calculations for the symmetric (unrelaxed) geometry suggested the contrary [24]. Explanations based on accidental degeneracy or otherwise were possible but still remain to be convincing. Recently, work by Briddon *et al.* [25] appears to have solved the problem. They use local density functional theory, combining it where necessary with a valence force fit to their density function analysis. They confirm that for the symmetric unrelaxed state there is only an A state in the gap (and so not degenerate); there is an orbital triplet in the conduction band, and a hyperdeep A state in the valence band. The conclusion is that the ⟨111⟩ symmetry cannot be Jahn–Teller in origin. A simple description is this. Suppose that we concentrate only on the nitrogen atom and one of its carbon neighbours. We may form bonding and antibonding combinations of the sp^3 hybrids. The lower (bonding) state will be doubly occupied, and the upper antibonding state singly occupied. It is this bonding–antibonding occupancy which is the source of a distortion which moves the carbon and the nitrogen atoms from each other, each moving some 0.2 Å. There are some parallels with the oxygen vacancy centre in quartz. The relaxed state then has two gap states, one largely based on the nitrogen atom and doubly occupied, and the other mainly based on the carbon atom and singly occupied. How well this fits the spin resonance data remains to be seen, but the two gap states do explain the optical spectra qualitatively, and the model neatly explains a previous problem for vibrational spectra. The difficulty was that a sharp resonance associated with nitrogen showed no nitrogen isotope effect. The explanation is that the mode is primarily associated with the carbon atom, which has moved closer to the plane of its three carbon neighbours.

Clearly, much remains to be done to understand fully the excited states of nitrogen-related centres, especially those which show laser action. The GR1, N–V (W-15), H3 and H4 centres all appear to be vacancy or vacancy–nitrogen complexes [26]; Lowther [27] has suggested the interesting view of these centres as vacancies to which the nitrogen atom adds a source of electrons and asymmetry. One outstanding issue concerns the prediction of laser action and the efficient means of generating lasing centres by choice of growth mechanism or subsequent treatment.

4. Relation to other excited states

A meeting devoted to wide-gap materials should consider the parallels between diamond and other hosts. I note two examples here, namely the zinc vacancy in ZnSe, and the compact donors seen in various II–VI compounds. The compact donor issue is closely related to the shallow donor issue, which is crucial if useful n-type diamond is to be prepared. It has yet to be demonstrated that there is any simple shallow donor in diamond (most claims seem to be based on radiation damage complexes or what may be graphite intercalates).

4.1. The compact donors

Nitrogen in diamond is a good example of a compact donor, where the wavefunction is confined to a few sites, not remotely like the shallow donors in silicon. It is useful to realize that this case is not unique. In ZnS, for instance, aluminium, gallium and indium (all at the zinc site) and fluorine at the sulphur site all give compact centres but keep the site symmetry. The similar centres in CdS (gallium at the cadmium site, and chlorine, bromine or iodine at the sulphur site) are all diffuse; boron in diamond is similar. Yet in BeO, the donors are compact and asymmetric (aluminium or boron at the beryllium site, and fluorine at the oxygen site), partly because of the wurtzite structure. The central cell problem is still fairly unsatisfactory, with many incompatible claims of success (for those up to 1975 see ref. 5).

4.2. The zinc vacancy in ZnSe

This system shows two important features: the variety of ways that asymmetry can arise, and the variety of consistent descriptions which are possible [5], here the wholly ionic (where zinc has a 2+ charge and selenium a 2− charge) to the wholly covalent (where the hybridized form gives zinc a 2− charge and selenium a 2+ charge).

The vacancy in question must be defined operationally by the removal of Zn^+. The ionic picture has a 2+ ion removed, and a further electron too (equivalent to adding a hole); the added hole localizes on a single selenium ion, just as in many other small-polaron systems, and polarization drives the ⟨111⟩ distortion. The covalent picture has a 2− ion removed, but three electrons replaced into the molecular orbitals built from the selenium hybrids; the Jahn–Teller effect then drives the ⟨111⟩ distortion. These views are conceptually far apart, and yet the qualitative picture is similar; either can be used provided that this is done consistently.

Since my earlier examples are all from the covalent end, one may ask how well one can do quantitatively in the ionic model. The answers prove remarkably good. The optical excitation is essentially charge transfer, *i.e.* the hole, originally localized on one specific selenium atom, is excited at constant nuclear positions (but with electronic polarization changes; the electronic polarization is essential if even qualitative consistency is needed) to the other three selenium atoms, where it is shared until relaxation localizes the hole again. No luminescence is expected in this model. The key energies are dominated by the ionic and electronic polarization of the host, and this can be modelled by the very-well-tested techniques developed to exploit the shell model

[28]. The predictions are in excellent accord for energies in which the net number of ions is constant (the ionic model is too simplistic otherwise, with energies other than polarization important). Thus the stability of the state localized on one selenium atom is shown, the centroid of the optical bands is predicted as 0.6 eV (0.8 eV is the value observed), and most other values are sensible; one exception is the predicted stress coupling, but this is probably related to poor modelling of the piezoelectric coupling in this early calculation. What is significant is that calculations for complex defects are practical and cheap, provided that the key energy is polarization dominated.

5. Reorientation

The reorientation mechanisms of nitrogen in diamond and of the V centre in ZnSe raise interesting questions. In particular, there is no motion of an atom from one crystal lattice site to another. There is, to be sure, a substantial change in displacement for several atoms, but only an electronic carrier moves from one site to another. One cannot use a classical adiabatic energy surface (with the heavy host ions following the electron adiabatically, precisely opposite to the Born–Oppenheimer approximation) and the usual "over-the-barrier" description on such a surface. The motion of a carrier, localized by the deformation that it drives, from one position to another is given instead by small-polaron theory [29, 30]. The deformation must suffice to lead to incoherent hopping, but that is another issue.

A simple description is this. Suppose that the carrier is at site A, in a sensibly localized wavefunction a. For the equilibrium distortion, the equivalent sensibly localized state b will have a higher energy (the energy would only be the same after lattice relaxation with the carrier on site B). In the course of thermal fluctuations, a geometry will be reached (the "coincidence" configuration, with strain energy ε relative to equilibrium) when a and b have the same energy. For this configuration, tunnelling can occur with characteristic frequency given by the difference in energy between the bonding $(a+b)$ and antibonding $(a-b)$ states. The jump rate will show activated behaviour (at least in certain regimes) with characteristic energy ε. This description needs substantial generalization for accurate calculations [31], but it has been used with success for small-polaron motion in I–VII and in both fourfold- and sixfold-coordinated II–VI compounds.

There is a corollary: one can relate the hopping to the optical absorption; charge transfer transitions correspond to going at constant nuclear positions (the Franck–Condon principle) from the energy surface corresponding to a to that corresponding to b. Further, the "relaxed" excited state is degenerate with the initial state (*i.e.* b is degenerate with a) and luminescence is not expected unless some other class of electronic states is involved (for the V centre in MgO, for instance, both intrasite oxygen excitation and intersite charge transfer appear to occur).

What about nitrogen in diamond? The small-polaron picture would seem to apply, just as for the V centre in ZnSe. Qualitatively, one expects Arrhenius-like behaviour, and this will be related to the asymmetric relaxation energy; the relation will not, however, be quite the same as in previous discussions based on the Jahn–Teller effect (where degeneracy and the coupling of T states to e as well as t modes are involved). Indeed, the nitrogen reorientation problem has more in common with the quantum diffusion approach developed initially in refs. 32 and 33.

6. Quantum diffusion: small-polaron or classical motion?

Diffusion in silicon is still controversial, even after many careful experiments. Why should the situation be any better in diamond? One reason is that consistency of geological data and the proportions of nitrogen aggregates put bounds on nitrogen diffusion [22]. However, laboratory experiments frequently suffer from uncertainty as to what is moving (although a vacancy may accompany an impurity in many cases) and as to what its charge state is. In wide-gap materials, one cannot be sure that the Fermi level is well defined, *i.e.* whether equilibrium carrier distributions are recovered in times corresponding to experiments (a clear example is the range of charge states of transition metals observable in some oxides). The understanding needed to control doping is incomplete, although progress is being made for both SiC and diamond [15]. Hydrogen is a special case, for several reasons. One is that hydrogen can passivate electrically active species; another reason is that some synthesis routes incorporate large amounts of hydrogen into diamond-like carbons, and there are reports of significant amounts of hydrogen even in natural diamonds (see the references in ref. 34). A further reason is that extensive muon studies point to limitations of our knowledge, but one other reason for discussing hydrogen diffusion is that the mechanism may well be different from the classical picture usually considered, and closer to small-polaron motion, as discussed above. The issues do not depend greatly on whether the form of hydrogen is atomic, molecular or paired in some other way, nor which precise site hydrogen prefers. There is an important issue as to whether the zero-point energy is so large as to prevent localization of hydrogen (or, more critically, the muon) in a particular interstice.

Classical diffusion [35] is usually predicted on the basis of an argument such as this. In thermal equilibrium, for each region of phase space (in which particles have specific positions and momenta) one can assign a probability. The probability that the diffusing particle is at the saddle point (relative to the probability that it is at the equilibrium position) involves an Arrhenius expression with characteristic enthalpy (at constant pressure), and that enthalpy is often closely similar to the internal energy obtained from static relaxed-lattice calculations with the defect at its initial and saddle point positions. An adiabatic energy surface (in which the host atoms follow the diffuser fully) suffices, and good predictions of both energies and absolute rates exist for suitable systems. For hydrogen diffusion, however, the situation is different, and a distinct route is needed to predict energies and rates. In particular, the zero-point energy, and indeed its change with host lattice atom position, cannot be ignored. This is true even if one is attempting a classical calculation (for Si:B,H the experimental—or theoretical—adiabatic barriers to hydrogen motion about boron are of the same order as the zero-point energy for the hydrogen local mode [36]. The host atoms move sluggishly compared with the hydrogen atom (still more so for the muon) and, because Planck's constant is finite, new diffusion channels are available, just as for the electronic carriers discussed above. The consequences of alternative diffusion channels are (1) that deviations from Arrhenius behaviour will be expected at low temperatures (for diamond, this could be quite hot!), (2) altered isotope effects and (3) a need for different calculations when linking theory and experiment.

The basic ideas were set out in ref. 32 and have since been generalized substantially [37]. The mechanism which competes with the "over-the-barrier" mechanism has a "coincidence site" rather than a saddle point. When the hydrogen is at site A, its zero-point motion and electronic effects lead to lattice relaxation about that site. If the lattice were fixed at this geometry, the hydrogen would have a higher energy at neighbouring site B. Since the hydrogen moves too fast for relaxation to occur as it moves, the jump can only occur when there is a thermal fluctuation of the host geometry such that the hydrogen atom would have the same energy at the two sites. This is the basis of both small-polaron behaviour and of the more general Flynn–Stoneham approach [32, 33, 37].

The hydrogen motion in the coincidence configuration may be quantal (tunnelling, but thermally activated because of the energy to get this configuration) or classical (*i.e.* a small—or zero—additional energy barrier, thermally overcome). One can see what looks like the latter behaviour in recent work with the Car–Parrinello method (where the ionic motions of both hydrogen and silicon are purely classical, even though the electrons are modelled quantally). Indeed, the classical (near-melting) behaviour for hydrogen in silicon can be described very similarly; unlike masses exchange energy very inefficiently, and so the fast-moving hydrogen atom can only move to a neighbouring site when both the barrier is low and, additionally, the diffusing particle at the final site requires neither gain nor loss of energy [38].

One further diffusion channel should be noted; one normally assumes that jumps are short, typically between nearest neighbours. However, for light diffusers, such as hydrogen, and for high temperatures (which diamond is well able to sustain) there can be a significant proportion of light interstitials in states higher in energy than the normal barriers [39]. These can lead to very fast diffusion (for hydrogen in liquid iron, for instance, the diffusion rate is about a factor of 100 above that set by normal limits).

Finally, I remark that, even though quantum effects are the key to some of this behaviour, most of the energies of interest are calculable using classical interatomic potentials. There are many such potentials (a tabulation is given in refs. 40 and 41; see also ref. 42 for some comparisons) depending on whether information for more than one coordination is used, and the input of electronic structure calculations is improving these.

7. Concluding remarks

The behaviour of diamond defects and other similar defect species in wide-gap materials includes striking effects from the Jahn–Teller effect through to small-polaron behaviour and similar consequences of the electron–phonon coupling. Yet, in addition, electron–electron correlation appears essential for understanding some features, and it is necessary for these to go beyond simple local treatments. Whilst these aspects of diamond are complicated, they are not unique to diamond, and they may often be modelled by simpler means, such as the use of suitable interatomic potentials. There remains a large gap between the current state of the art theory and predictions of laser action or of the effects of lasers on diamond surfaces (*e.g.* etching and graphitization) and whether or not laser anneal of radiation damage is possible.

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