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Modelling the effects of electronic excitations in ionic-covalent materials

D.M. Duffy [*], S.L. Daraszewicz, J. Mulroue

Department of Physics and Astronomy and the London Centre for Nanotechnology, University College London, Gower Street, London WC1E 6BT, United Kingdom

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ABSTRACT

High energy radiation events in ionic and covalent materials can lead to highly excited electronic configurations which, over time, relax to the ground state, either radiatively by emitting photons, or non-radiatively. Non-radiative relaxation involves the transfer of energy to the lattice and this can result in lattice heating, defect formation or even phase changes. The effects of the relaxation mechanisms on the atomic configuration are challenging to model accurately by standard methods. The situation is further complicated by interactions between electronic excitations and pre-existing defects, possibly created by other radiation events. In this paper we describe a range of mechanisms by which the electronic energy is transferred to the lattice and the resulting effects on the atomic configuration, along with the different techniques that are used to model these effects.

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1. Introduction

The modification of the microstructure of materials by electronic excitations has become an increasingly important topic since the publication by Itoh and Stoneham of a seminal book on the topic in 2001 [1]. Electronic effects are important in a range of technologies, including surface modification by lasers and ions, nanostructuring of surfaces and materials, structural effects of high energy electron microscopy, radioactive waste immobilisation [2] and radiation damage in fission and fusion [3] technology. The design of radiation tolerant materials and the control of material modification would both benefit from a comprehensive understanding of the processes that occur at an atomistic level and the development of reliable simulations techniques for predictive modelling.

Radiation comes in many forms and it has a wide variety of effects on materials. Low energy ion irradiation primarily interacts with the atomic nuclei and, above an energy threshold, atoms are displaced from their equilibrium sites and Frenkel defect pairs are created. Ionising radiation, on the other hand, interacts primarily with the electrons in the material causing electronically excited states. Photons, high energy electrons and very energetic ions all fall into this category. Ions with intermediate energies deposit energy to both the atomic nuclei and the electrons and the synergy between the two types of radiation damage can result in complex behaviour. High energy neutrons from fusion reactions can result in displacement ions with energies in this range, as can fission products and recoil atoms from radioactive decay.

All types of ionising radiation result in non-equilibrium electron distributions, although the details of the energy distribution vary from case to case. In a band gap (non-metallic) material this implies that there is an excess number of electrons in the conduction band and a corresponding increase in valence band holes. Over time, the energy stored by these excitations will be dissipated, either by photon emission or by energy transfer to the atoms of the material. Energy transferred to the lattice will result in lattice heating, defect production or even a phase change in the material. The resulting atomic rearrangements are sensitive to the type and intensity of radiation, the band gap of the material and the strength of the electron–lattice interactions.

The aim of this paper is to discuss the mechanisms for energy transfer from the excited electrons to the lattice in a range of materials and to demonstrate how modelling techniques may be used to enhance our understanding of these mechanisms and how they modify the material. In the next section we describe the different mechanisms and modifications to the atomic configurations that can result from the energy transfer. In Section 3 we discuss the modelling techniques that are currently used to investigate the effects of electronic excitations on non-metallic materials and give a representative sample of results obtained using these models. In the final section we discuss how these techniques may be combined and developed to move towards a more predictive role for modelling and simulation.

2. Mechanisms and effects

Ionising radiation results in a non-equilibrium electron distribution in ionic and covalent materials, with an excess of electrons in the conduction band and an excess of holes in the valence band. The energy stored by this non-equilibrium distribution will

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[*] Corresponding author.
E-mail address: d.duffy@ucl.ac.uk (D.M. Duffy).

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eventually be dissipated, either by photon emission or by transfer to the lattice where it will result in phonon or defect creation, or possibly a phase change. The dominating mechanisms and the distribution of energy to the different lattice modes are strongly dependent on the material and radiation type. Broadly speaking, the deposited energy can either be transported away from the deposition location, before being transferred to the lattice or lost by radiative transitions, or it can be localised and transferred to the lattice near the deposition location. We discuss the mechanisms for both these scenarios in more detail in the following sub-sections.

2.1. Energy transport and redistribution

Electrons excited to the conduction band in band gap materials become mobile and they can, therefore, transport energy away from the excited region of the material. The excited electrons leave holes in the valence band, which are also mobile, albeit with a different mobility than the electrons. For highly excited systems the time between electron–electron collisions is short ($\sim$few fs) therefore the carriers rapidly exchange energy and establish a local temperature, but this temperature is not necessarily the same for the electrons and the holes. After a certain time period, which will strongly depend on the material, quasi-charge neutrality will be established and the local density of electrons and holes will become approximately equal. Ambipolar diffusion will reduce the local concentration of electrons and holes (carriers) and transport the carriers and the energy away from the site of the original excitation. During diffusion the mobile carriers may undergo a range of interactions, depending on the carrier energy and density. These interactions are illustrated schematically in Fig. 1 and described below.

2.1.1. Electron–phonon interactions

The carriers can exchange energy with the lattice by emitting and absorbing phonons (Fig. 1a) and, as the local temperature established by the excited carriers will not generally equal the lattice temperature, these electron–phonon scattering events gradually bring the carriers and the lattice into equilibrium with each other. Lattice distortions, and hence phonons, change the band structure and electron energies, which results in electron–phonon scattering. The rate of energy exchange between the phonons and the lattice depends on the type of phonon (acoustic or optic), the relevant (acoustic or optic) deformation potential and other parameters such as the effective mass, the carrier temperature and the lattice temperature [4]. The cooling dynamics for photoexcited carriers in silicon has been studied by optical pump and terahertz probe spectroscopy and the data points fit well to the theoretical models, with no adjustable parameters [5]. There is a rapid decrease in carrier temperature due to intervalley scattering of electrons and optical phonon scattering of holes. The cooling time was found to depend on the lattice temperature, but for a lattice temperature of 60 K the lattice and carriers reach equilibrium in about 100 ps. This time would be reduced for a room temperature lattice.

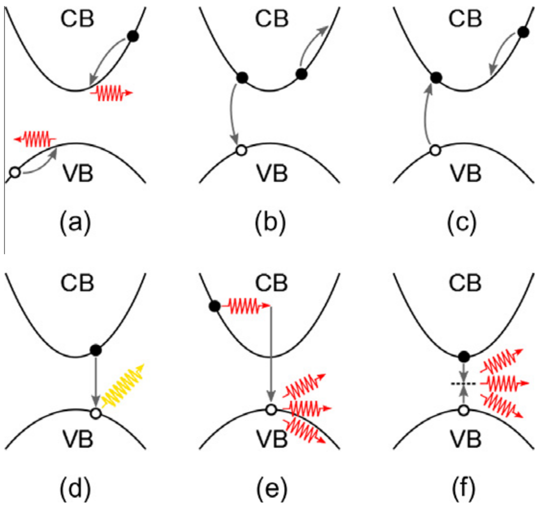

Fig. 1. Schematic representation of various carrier and lattice processes in band-gap materials following electronic excitation (after [17]). VB and CB stand for valence band and conduction band, respectively. (a) Carrier de-excitation by phonon emission (b) Direct Auger recombination, (c) Impact ionisation, (d) Radiative recombination, (e) Indirect non-radiative recombination, (f) Shockley–Read–Hall recombination.

2.1.2. Auger recombination

Auger recombination occurs when an electron and hole recombine and the energy released by the recombination is transferred to a second electron in the conduction band (Fig. 1b). Because Auger recombination involves two electrons and one hole its rate is proportional to $n_e^2\, n_h$, (n_e is the free electron density and n_h is the hole density). For high carrier density in Si ($n_e = n_p = 10^{27}$ m^{-3}) the Auger recombination time (defined as $n_e/(dn_e/dt)$) is approximately 6 ps [6]. Auger recombination decreases the number of carriers but the total energy of the carriers is conserved, resulting in an increase in the average kinetic energy of carriers.

2.1.3. Impact ionisation

Impact ionisation (Fig. 1c) can be viewed as the inverse process to Auger recombination and its rate is proportional to the number of free electrons (n_e). An energetic electron excites a valence band electron and creates an electron–hole pair. Impact ionisation results in an increase in the carrier density but, as with Auger recombination, the carrier energy is conserved therefore the average carrier kinetic energy decreases.

2.1.4. Trapping and self trapping

Excited electrons and holes in a deformable crystal distort and polarise the surrounding lattice and the combination of the carrier (electron or hole) and its associated lattice distortion is known as a polaron. Landau [7] noted that there are two distinct types of polaron, one in which the carrier moves freely through the lattice, albeit with an increased effective mass, and the other in which the coupling between the lattice and the carriers is so strong that the carrier can effectively become trapped by the distortion it creates. The latter case is referred to as a self-trapped polaron or small polaron. A defining characteristic of a small polaron is that its mobility increases with temperature, signalling a “hopping” transport mechanism. Electrons, holes and bound electron–hole pairs (excitons) can become self-trapped in a range of materials. Their mobilities are generally several orders of magnitude lower than those of free carriers, typically (0.1–1 cm^2 s^{-1}) with activation barriers of the order of a few tenths of an eV [1]. Excitons can become self-trapped in halides and oxides, particularly quartz [8–10]. In alkali halides and alkaline earth fluorites self trapped holes form molecular ions with the formX_2^- (where X is the halide ion) [9]. Both holes and electrons can be self trapped in oxides in which cations exist in a range of charge states such as manganese, iron and nickel oxides [1]. Electron self trapping is unusual in halide crystals because of the wide conduction band but it has been observed in one halide (PbCl$_2$) [11]. Carrier self trapping is not observed in III–V or group IV semiconductors.

The atomic rearrangement associated with exciton self-trapping results in the emission of several phonons, which transfers part of the stored electronic energy to the lattice. Self trapped excitons can decay radiatively, emitting a photon, or non-radiatively, which in some materials can create lattice defects directly. The creation of a neutral Frenkel pair in an alkali halide is an example of such a mechanism. The halide molecular ion migrates along a close packed direction in the lattice by a replacement collision sequence, leaving the electron from the exciton trapped in the resulting halide vacancy. The energy required to transform a self trapped exciton into a neutral Frenkel pair is generally small (less than 0.1 eV) [12,13]. This is an important source of radiation damage in some alkali halides.

Self trapping of carriers is observed in a limited number of materials but a much broader range of materials is susceptible to trapping by defects or inhomogeneities in the lattice. Inhomogeneities include point defects (vacancies, interstitials and impurities), extended defects (surfaces, grain boundaries, dislocations) and structural fluctuations in amorphous materials [14]. One example is a positively charged hole polaron in an ionic crystal which interacts strongly with negatively charged cation vacancies. Such trapped excitations reduce the number of mobile carriers and modify the properties (net charge, relaxed structure and migration energy) of the pre-existing defect. Trapped carriers also enhance electron hole recombination as discussed in the following section.

2.1.5. Electron–hole recombination

Electron–hole pairs can recombine either radiatively, by photon emission (Fig. 1d), or non-radiatively by the simultaneous emission of several phonons (Fig. 1e). The probability of non-radiative decay is generally low but it increases by several orders of magnitude in the presence of defects or impurities (traps) which have electronic states near the middle of the band gap (Fig. 1f). Recombination via localised energy levels is known as Shockley–Read–Hall recombination [15,16] and the excess energy is transferred to the lattice. The rate of energy transfer to the lattice is, therefore, enhanced by the presence of certain lattice defects, which may have been created by earlier radiation events.

2.2. Energy localisation

Damage or modification to the lattice is enhanced in situations where the energy of the electronic excitations is localised in a nanometre scale region of space for a sufficient time for the energy to be transferred to the lattice. In such a situation the energy density in the crystal can be high enough to induce a phase change, such as melting, in a localised region of the crystal. A number of mechanisms for such energy localisation are discussed below.

2.2.1. Self trapped excitons

The self trapped excitons discussed in Section 2.1.4 represent a possible mechanism for localising energy deposited to electronic excitations. The timescale associated with self-trapping varies between materials [17] but if it is short, compared with the diffusion time, then instead of diffusing away, the excitons become trapped close to the initial deposition site. The atomic rearrangement during the process of self trapping results in the emission of several phonons therefore some energy is transferred to the lattice in the vicinity of the excitation. Self trapped excitons can decay either radiatively, emitting a photon, or non-radiatively by the creation of lattice defects. Klaumünzer [17] has suggested that the formation of self trapped excitons is the primary mechanism for the decay in the number of mobile carriers, following a high energy excitation event, in silica and the formation of ion tracks in some materials has been attributed to the generation of a high density of self trapped excitons [18].

2.2.2. Coulomb explosion

Localisation of electronic energy can also be attributed to strong repulsive Coulombic interactions, due to a local charge imbalance occurring transiently after strong electronic excitation. The Coulomb explosion was initially suggested as an explanation for the appearance of ion tracks in minerals [19]. It was argued that the tracks, or elongated regions of damage, were formed by ionisation of the atoms along the path of an energetic ion, which created a narrow cylinder filled with positive ions and the resulting repulsive force ejected ions into adjacent interstitial positions. However, with the exception of polymers, where experimental evidence supports Coulomb explosion predictions [20], the neutralisation time is too short for the Coulomb forces to displace atoms. The Coulomb explosion mechanism could be more relevant to intense radiation events at surfaces, where multi-charged ions are seen to be ejected [21].

2.2.3. Lattice destabilisation

An additional mechanism for localising energy deposited in the electronic system is the change in the interatomic interactions between atoms in which electrons have been excited from bonding to anti-bonding states [22]. The shape of the potential energy surface is a function of the density of excitations, therefore atoms sitting at minima of the potential before excitation will be not be at the minima of the potential in the excited state and they will, therefore, experience a force (Fig. 2). The atoms will move from their relaxed positions and gain kinetic energy. As the excitations decay or diffuse, the potential energy surface reverts back to its original configuration but the atoms have been displaced therefore they again experience a force and a kinetic energy increase. The amount of energy imparted to the lattice by this mechanism depends on the lifetime of the excitations and the degree to which the potential energy surface is modified by the excitations. If the excitations have sufficiently long lifetimes lattice destabilization can be an efficient mechanism for transferring energy from the excited electrons to lattice close to the excitation location.

Particular examples of this effect are photo-induced phase transitions which have recently been comprehensively reviewed by Bennemann [23]. The potential energy surfaces of two phases

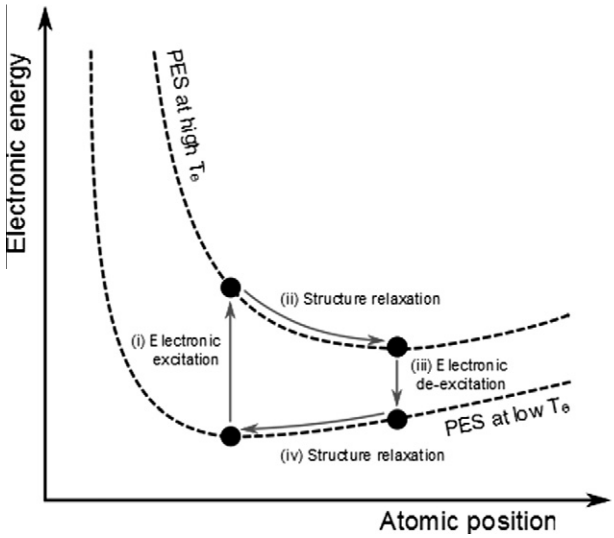

Fig. 2. Schematic illustration of the lattice relaxation model (after [22]). The shape of potential energy surface (PES) changes following an electronic excitation (i). The atoms are no longer in equilibrium and therefore relax to a new PES minimum (ii). As de-excitation occurs (iii) the PES reverts to the equilibrium form and the atoms relax to their original equilibrium positions (iv).

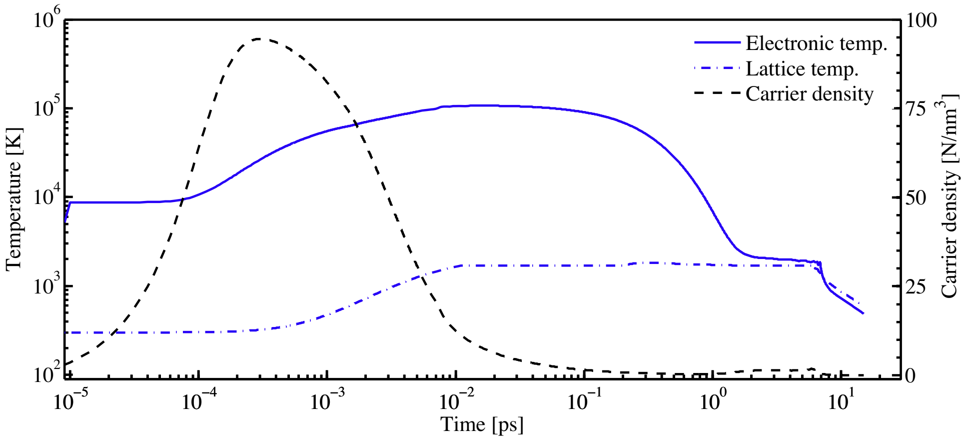

Fig. 3. The time evolution of the lattice temperature (dot-dashed line), the electronic temperature (solid line) and the carrier density (dashed line) at the centre of a 50 keV/nm ion track in Si. Carrier confinement is responsible for the carrier density peak at ~2 ps.

and the energy barrier for transforming between phases are changed by electronic excitation. If the lifetime of the excitations is sufficiently long and the barrier sufficiently small, then the excitations may induce a phase change. Photo induced transitions from bonding to anti-bonding states can cause diamond to graphite transitions, ultrafast melting, surface ablation and even the production of graphene from graphite [24] (Fig. 2).

2.2.4. Carrier confinement

The energy gap between the valence and the conduction bands in semiconductors decreases as the lattice temperature increases, due to the increase in the lattice parameter and the resulting decrease in the potential seen by the electrons. Localised lattice heating will, therefore, induce a spatial variation in the band gap (E_g). The carrier current (J) depends on the gradient of the band gap via the following relationship:

$$J = -D\left(\nabla N + \frac{2N}{k_B T_e}\nabla E_g + \frac{N}{2T_e}\nabla T_e\right);$$

where N is the carrier density, T_e is the electronic temperature and D is the ambipolar diffusivity. Consequently, a high negative gradient in the band gap will effectively reduce the carrier current. In the situation where the lattice has been heated by a high density of electronic excitations, carrier diffusion away from the excited region may be inhibited by band gap gradients and carrier confinement can occur [25]. Whether or not this effect has a significant influence on carrier mobility depends on the relative timescales for lattice heating and carrier diffusion.

A high density of free carriers will also result in a reduction in the band gap due to exchange and correlation effects. This band gap renormalisation may also cause carrier confinement in situations where the gradient in the carrier concentration is very high, which could contribute to energy localisation [26].

3. Modelling

The mechanisms discussed in the previous section have all been investigated, in various degrees of detail, by theory, modelling or experiment, but the complex nature of real radiation scenarios, and the number of unknown parameters in the models, means that many gaps remain in the picture. In this section we summarise the techniques that have been used to model the various processes and knowledge gained from these.

3.1. Transport and redistribution

The fact that the excited carriers should rapidly establish an equilibrium temperature, and that this temperature is different from the lattice temperature, has been used to model energy diffusion and transfer to the lattice. The model, sometimes referred to as the inelastic spike model, is based on the two temperature model (2TM) first discussed by Kaganov et al. [27].

Two thermal diffusion equations (1) and (2), one for the lattice (T_l) and one for the electronic temperature (T_e), are coupled by a term that exchanges energy between the two systems at a rate that is proportional to the electron–phonon coupling constant (g).

$$C_e\frac{\partial T_e}{\partial t} = \nabla\kappa_e\nabla T_e - g(T_e - T_l) + A(r,t), \quad (1)$$

$$C_l\frac{\partial T_l}{\partial t} = \nabla\kappa_l\nabla T_l + g(T_e - T_l). \quad (2)$$

Here C_e and C_l are the electronic and lattice heat capacities and κ_e and κ_l are the electronic and lattice thermal conductivities, respectively. In the inelastic thermal spike model the energy is deposited as a source term in the electronic system ($A(r,t)$) and the temperatures are evolved by numerical solution of the coupled equations. The volume of the material that exceeds the melting temperature is assumed to transform to an amorphous structure or result in a high density of defects. The model has been reasonably successful in explaining material dependent properties of damage formation (tracks) due to swift heavy ions [28,29] but the number of parameters that are required that are known only approximately restricts the predictive power of the model.

The inelastic thermal spike model was originally developed for metallic materials but in recent years it has also been applied to insulating [30,31] and semiconducting [32] materials. The rationale for this is that the properties of electrons excited to the conduction band have similar properties to conduction electrons in metals. However it has been noted [17,33] that there is a fundamental difference between the two types of material in that the number of conduction electrons varies in space and time in a band gap material whereas it is constant in a metal. In a metal the electronic energy diffuses but in a band gap material the excited carriers diffuse and recombine. This effect can be included by introducing an additional conservation equation to the two temperature model used in the inelastic thermal spike model [33] following earlier models for semiconductors [34]. This model assumes charge neutrality, therefore the local concentrations of electrons and holes are equal. It would be possible to extend the model to non-neutral conditions by considering separate conservation equations for electrons and solving Poisson's equation [17]. The non-neutral conditions have been implemented [35] and used to model the Coulomb explosion that results from near-infrared laser irradiation.

The extended inelastic thermal spike model has a natural mechanism for including processes such as Auger recombination and impact ionisation and these have been found to affect the results. Fig. 3 shows the time evolution of the temperatures and carrier density at the centre of a 50 keV nm^{-1} ion track in Si, calculated using the method discussed in [33]. Note the carrier density increase at $\sim$2 ps caused by the carrier confinement process discussed in Section 2.2.4. The extensive research that has been performed on technologically important semiconductors, such as Si, has resulted in reliable parameter sets for such materials.

The thermal spike models are based on numerical solutions to the conservation equations and the output from the model is the lattice temperature as a function of time. This can be used to calculate the volume of material that has exceeded the melting temperature of the material, which is assumed to result in damaged material or tracks. However this method neglects fact that phase changes require a certain nucleation time therefore the material needs to exceed the melting temperature for a minimum time before melting is achieved [17]. Other issues related to the continuum description of the lattice are discussed in [17]. Sound waves, resulting from the rapid lattice expansion, may carry away a substantial fraction of the energy. High lattice temperatures gradients may render the application of Fourier's law invalid and the definition of an equilibrium lattice temperature at timescales shorter than a typical phonon frequency is subject to criticism.

Some of these issues can be addressed by coupling thermal transport models for the electrons to molecular dynamics (MD) models for the lattice [36–39]. Indeed such combined 2TM-MD models for swift heavy ion irradiation in Fe [40] demonstrated the superheating effect, as it found that the lattice temperature could exceed the melting temperature without any disorder or defects being created. It was also established that electronic effects could affect defect creation in the low energy regime as, depending on the strength of the electron–phonon coupling, the number of residual defects could either be increased or decreased by coupling to the electronic system [41]. A methodology that will couple the continuum model for ionic-covalent [33] materials to classical MD is currently under development.

The thermal spike model has been extended to include the effects of self-trapped excitons in $\mathrm{LiNbO_3}$, in order to explain the super linear relationship between damage and stopping power during swift heavy ion irradiation [42]. The initial lattice temperature distribution is similar to that of the thermal spike model and it evolved via heat diffusion. The initial distribution of self-trapped excitons is related to the energy deposited in the electrons by the ion. The excitons are assumed to decay both radiatively and non-radiatively, the latter resulting in the creation of Frenkel pairs. The non-radiative decay rate is dependent on the lattice temperature due to the presence of an energy barrier. The quantitative microscopic model accounts for all the features observed experimentally [43].

3.2. Trapping and self-trapping

In order to model energy localisation by self trapping it is necessary to calculate the response of a lattice to electronic excitations. This is challenging because most electronic structure calculations employ the adiabatic approximation, where the electrons are in the ground state for a given configuration of the atomic nuclei. Generally theory is only able to confirm that self-trapped small polarons have a stable form and it is unable to predict whether self trapping will occur, as it is not possible to calculate the defect formation energies directly [44]. The defect formation energy of the self trapped hole in NaCl, for example, relies on the calculated energy of the vacancy, the formation energy of the $\mathrm{Cl_2}^-$ molecule, the $\mathrm{Cl_2}^-$ interstitial energy and the lattice relaxation energy, which are all dependent on the reference state used in the calculations [45].

Accurate quantum chemistry methods are required for non-biased predictive modelling of the properties of polarons, as Hartree–Fock (HF) based methods will favour self trapping (small polarons), due to the overestimation of the localisation, while density functional theory (DFT) will favour large polarons, as it tends to underestimate the localisation [14]. Small polarons have, however, been modelled successfully in a number of materials using HF and DFT. HF methods have been used to accurately reproduce the optical energies and spin resonance data for the self-trapped exciton in α-quartz [46,47] and the V^- defect in MgO [44] The results from α-quartz are consistent with the higher level quantum chemistry calculations [48]. The description of localisation in DFT can be improved by hybrid functionals which effectively mix HF and DFT methods by including a percentage of exact exchange in the functional. The hybrid density functional B3LYP [49] has been used to study self trapped hole and electron polarons in $\mathrm{HfO_2}$ and self trapped holes in amorphous $\mathrm{SiO_2}$. The results for monoclinic $\mathrm{HfO_2}$ show that both electron and hole polarons can co-exist, which is rare in insulating materials [14]. The trapping of holes in $\mathrm{SiO_2}$ required altering the amount of exact exchange in order to reproduce the spectroscopic data. Some insight into trapping can also be obtained using the Mott–Littleton method with classical shell model description of the ions [44].

Trapping and self-trapping are modelled using two common methodologies, periodic and embedding. In the periodic method a supercell with periodic boundary conditions is modelled and this inevitably includes undesirable interactions between the periodic defect images, particularly for charged defects. A number of methods have been devised to correct for this effect [50]. The issue of interactions between defect images can be avoided by employing embedding methods in which the defect and surrounding volume are modelled by a quantum cluster and the environment is modelled by the classical shell model [51]. The small size of the quantum cluster allows for high level quantum cluster calculations, such as configuration interaction and coupled cluster calculations, to be used if necessary. The main disadvantage of embedding methodologies is that there is currently no systematic approach for constructing the embedding potential for complex systems.

Trapping of holes or electrons on point defects within a crystal changes the structure [52], chemistry [53] and conductivity [14] of the defect. DFT calculations have shown that the localisation of holes on the O^{2-} interstitial in MgO has a significant effect on the relaxed configuration and, consequently, the migration barrier [54]. The minimum energy conformation of the O^{2-} interstitial is located in the centre of a cube of ions however the O^- and O^0 interstitials both favour dumbbell configurations, with the O^- dumbbell oriented along a $\langle 1\,1\,0\rangle$ direction and the O^0 dumbbell oriented along a $\langle 1\,1\,1\rangle$ direction (Fig. 4). Table 1 shows the migration barriers for the O interstitials and vacancies in several charge states calculated using periodic DFT [54,55] and semi-empirical methods [56,57]. Note the exceptionally low migration barrier for the O^- interstitial, which implies that trapping a hole at an O^{2-} interstitial will dramatically increase the mobility of the interstitial. A highly mobile oxygen interstitial has been observed in experiments at temperatures as low 5 K but the charge state of the mobile interstitial is not known [58–60]. This is in strong contrast to the calculated migration energies for O vacancies in MgO, which show that trapped electrons increase migration barriers.

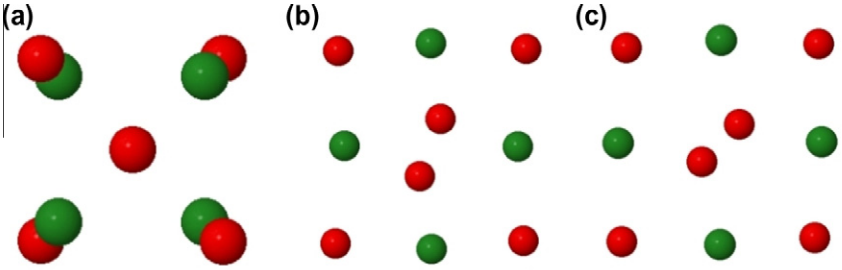

Fig. 4. The relaxed conformations of the (a) O^{2-}, (b) O^{-} and (c) O^{0} interstitials in MgO (after [54]).

Table 1
Calculated migration barriers for the O defects in MgO in different charge states.

Defect charge state	Interstitial migration barrier (eV)	Vacancy migration barrier (eV)
Neutral	1.04[a], 1.45[c]	4.81[a], 4.2[b], 3.1[d]
Singly charged	0.06[a]	3.68[a], 2.7[d]
Doubly charged	0.33[a], 0.54[c]	2.38[a], 2.5[d],

Results are taken from:
[a] [54].
[b] [55].
[c] [56].
[d] [57].

3.3. Modified interatomic interactions

3.3.1. Interatomic potentials

One approach to modelling the modified interatomic interactions induced by electronic excitation is to develop interatomic potentials for excited atoms and use classical MD to model the time evolution of the material. In band gap materials a high level of electronic excitations leads to the transfer of valence electrons into conduction band, anti-bonding. The modified potential is repulsive, therefore the simplest modelling approach removes the attractive part of the full interaction potential, leaving only the repulsive (anti-bonding) part between the excited atoms. This approach has been used to model laser induced excitation of Si surfaces with a Tersoff potential [61], a Stillinger–Weber potential [62] and a hybrid Tersoff–Stillinger–Weber potential [63].

High level quantum chemistry (coupled-cluster) computations of pair interactions of ground and excited states have been used to fit interatomic potentials for LiF [64]. The interaction energies between the Li^0, Li^{+1}, F^0 and F^{-1} ion pairs were calculated at a range of interatomic separations and the resulting interatomic potential curves were used in classical molecular dynamics simulations of the inelastic sputtering process due to slow highly charged ions.

In order to utilise the interatomic potential for non-equilibrium simulations, such as swift heavy ion damage and laser ablation, one needs to construct a potential with electronic temperature as a variable parameter. High temperature DFT has been used to derive embedded atom type interatomic potentials for a limited number of materials at high electronic temperatures. In the case of Au [65] only one electronic temperature (T_e) was considered ($k_BT_e = 6.5$ eV) and the potential, which was derived by fitting to the calculated equations of state of different crystals structures, was used to calculate the phonon dispersion curve and melting temperature of the excited crystal. Interestingly the elastic constants and the melting temperature both increase at high electronic temperatures. High temperature DFT calculations have been used to derive potentials for a range of T_e for W [66] and Si [67]. In these cases the lattice enthalpy was calculated for a range of lattice spacings and the electronic entropy contribution included to obtain the free energy as a function of the lattice parameter. The results were fitted to a series of Finnis Sinclair [66] or Tersoff [67] type potentials. The advantage of electronic temperature dependant interatomic potentials is that they can be used with 2TM-MD type simulations, in which the interatomic potential selected for a particular atom will depend on the calculated local electronic temperature at each timestep.

3.3.2. Tight binding

Electronic degrees of freedom can also be taken into account by employing a self-consistent tight-binding molecular dynamics approach [22,24,68,69]. A tight binding Hamiltonian was used to construct an excited state potential energy surface for a particular atomic configuration and to calculate the resulting forces on the atoms. The atoms are displaced in an MD timestep with the atomistic equations of motion derived from the Euler–Lagrange formalism. An updated Hamiltonian is constructed for the new configuration and the process iterated for the required number of timesteps. The method was applied to a study of ultrafast ablation of graphite films and diamond to graphite transitions [24].

A more sophisticated time dependent tight binding model has recently been developed to study the fundamental processes involved in radiation damage [70,71]. The method is computationally expensive therefore it has only been applied to a model metal to date. Nevertheless it has elucidated interesting mechanisms that could not have been observed by traditional simulation methods.

4. Future developments

Whilst enormous progress has been made in modelling the effects of electronic excitations in ionic and covalent materials in recent years, the understanding of the mechanisms and effects in many materials is far from complete. The overall goal is the development of predictive models for the structural modifications that result from radiation events ranging from high intensity laser and swift heavy ion irradiation to low energy electron irradiation. Isolated excitations create damage only on a very limited class of materials but the interaction between these excitations and defects, either intrinsic or created by other radiation events, may affect electronic properties or microstructure evolution. Examples included photo induced desorption, where excitations which would have minimal effect in bulk crystals result in ions being ejected from surfaces [72] and reduced or enhanced diffusion due to excitations trapped at point defects [54].

In order to model such effects successfully a range of coupled methodologies will be necessary. A range of ab initio techniques can be used to model isolated excitations in detail, to calculate binding energies and migration energies or to derive interatomic potentials for excited atoms. The calculated data could be used in methodologies for modelling. For example, MD atomistic simulations with electronic temperature dependent interatomic potentials, coupled to a coarse grained model for the time evolution of the electronic temperature, would be able to model the structural modifications resulting from intense laser or swift heavy ions.

Lower intensity energy radiation events could be modelled by kinetic Monte Carlo (kMC) techniques with energies for the events calculated using ab initio techniques. For example, the microstructure evolution of a material in which radiation events create both knock-on damage and electron hole pairs could be modelled by object kMC in which the objects are point defects and the events include electron and hole charge trapping and defect hopping. The energies associated with the events (ie the migration energies) would be different for defects with and without trapped excitations and these energies would be calculated using DFT or other ab initio techniques.

In summary, in order to reach the goal of predictive modelling of structural modifications of ionic-covalent materials by electronic excitations, a range of techniques must be employed and validated against experiment where possible. The different techniques will need to be coupled in innovative ways to take full advantage of the strengths of each modelling methodology. Successful developments would impact technologies ranging from nanotechnology and microelectronics to nuclear technology.

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