

Lattice defect creation induced by exciton self-trapping in solid Ne

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 9785

(<http://iopscience.iop.org/0953-8984/9/45/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.209

The article was downloaded on 14/05/2010 at 11:00

Please note that [terms and conditions apply](#).

Lattice defect creation induced by exciton self-trapping in solid Ne

Chun-rong Fu and K S Song

Physics Department, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

Received 27 May 1997, in final form 18 August 1997

Abstract. We have performed theoretical studies of the possible evolution of the self-trapped exciton (STE) into stable lattice defects in solid neon. The species considered include the STE bubble with symmetric elastic relaxation of the surrounding atoms and the STE bubble which has induced several plastic deformations containing one or more Frenkel-type defect pairs (interstitial–vacancy pair). We also determined the potential energy surfaces connecting the original STE bubble to the various Frenkel pairs. Some of the species studied may lead to stable lattice defects (Frenkel pairs) after the exciton has recombined. We have also evaluated the emission energy changes between the pure STE bubble and those accompanied by one or two extra vacancies. The latter bands occur at energies smaller by about 30–66 meV than the regular STE bubble and compare reasonably well with the experimental data. The excited Ar atom in solid Ne is also investigated.

1. Introduction

When self-trapping of an exciton occurs spontaneously in an otherwise perfect crystal, an energy package of several electron volts becomes concentrated within a volume of the order of a unit cell. Depending on the bonding nature and lattice structure of the crystal, the concentrated electronic excitation energy can induce various large-scale atomic motions. These include permanent lattice defect creation and desorption of atoms and molecules from the surface. There are also other spectroscopic changes such as a more or less substantial Stokes shift in the emission energy.

Rare gas solids (RGS) constitute a group apart from other insulators, such as the halides and oxides. The energy of cohesion is a few orders of magnitude smaller than in the ionic solids, yet has one of the largest electronic band gap energies. A considerable amount of studies have been made on the spectroscopy of electronic excitations. They show strong correlation to atomic and molecular excitation spectra with interesting matrix effects. There are also specifically surface related properties of excitations. As in other insulators electronic excitation of the RGS induces a host of interesting and sometimes novel phenomena [1, 2, 3]. A conduction electron can be self-trapped by creating a cavity in the lattice in solid Ne. This is directly related to the electron affinity being negative in s-Ne ($E = -1.2$ eV; and -0.5 eV in s-Ar) as has been determined experimentally [2]. An excited electron interacts with a large number of ground state Ne atoms. Due to Pauli's principle, the wavefunction of such an electron should be orthogonal to those of all the occupied orbitals of the surrounding Ne atoms. This introduces a short-range repulsive potential, which is stronger than the attractive interaction terms such as the screened Coulomb, exchange and polarization. In lighter RGSs, the net effect is a repulsive short-range interaction [4]. There is also the

covalent bond formation which is generally possible between a pair of rare gas atoms after a p electron has been removed. These factors make possible the creation of several forms of localized excited states in RGS: the electron bubble; the atomic type self-trapped exciton (a-STE); the molecular type STE (m-STE).

In s-Ne the strongest luminescence bands are associated with the a-STE [5, 6]. Formation of a cavity (bubble) around an a-STE (an excited Ne atom) or an excited impurity rare gas atom in solid Ne was well studied earlier [5]. Both the earliest qualitative theory as well as later more elaborate calculations based on several approaches predicted a bubble of about 4 Å radius which surrounds an a-STE. The time dependent shift of the transient absorption energy corresponding to 3s–3p transition at 19 K has been interpreted as being due to the capture of thermal vacancies [3]. Recent experiments show that under electron beam excitation a second UV luminescence band, attributed to a lattice defect created during the exciton self-trapping, grows beside the intrinsic emission band [7]. The new band is about 60 meV lower in energy than the intrinsic band. The intensity of the new band starts from a non-zero value initially and grows linearly with time until it reaches a saturation at about 20 minutes irradiation at 6 K. During the same irradiation, the intrinsic band intensity remains constant. These data are interpreted in terms of radiation induced defects which accumulate in the sample until a saturation concentration is reached [7]. From the presence of the new band at the beginning of irradiation, it is considered to be possibly vacancy associated defects which existed in the sample prior to excitation [7].

We have performed theoretical studies of the possible evolution of the STE bubble into stable lattice defects. The method used was developed earlier in the studies of the STE in ionic crystals [5, 8], and relies on a few-electron (excited electron) Hartree–Fock approach in combination with pair potentials to represent the lattice. This method is similar to that employed in recent series of works on metallization of ionic halide clusters [9]. They used the norm conserving pseudopotential in combination with classical pair potentials to study the clusters of NaF in various degrees of metallization containing one or more excess electrons. The species considered in the present study include: the STE bubble with symmetric elastic relaxation of the surrounding atoms; the STE bubble which has induced several forms of plastic deformation containing one or more Frenkel type defect pairs (interstitial–vacancy pairs); a split electron bubble and Ne⁺ system. We also determined the potential energy surfaces connecting the original STE bubble to the various defect associated STEs.

We found that some of the STE bubbles accompanied by a plastic deformation are at lower energies than a pure STE bubble. The lowest-energy species are found to be those with two vacancies in the first atomic shell. Some of the vacancy–interstitial pairs (Frenkel pairs) remained stable in the recombined electronic ground state, thereby creating stable lattice defects. On the other hand some others relaxed back to the perfect lattice after recombination. We therefore have strong indications that in solid Ne exciton self-trapping can lead to permanent defects which survive recombination. Earlier, Ratner and Fugol [10] discussed the possibility of plastic deformation beyond the elastic bubble creation around an excited Ne atom. They proposed that in the expanded first atomic shell, more Ne atoms could be inserted. This would correspond to the creation of a Frenkel pair with the interstitial Ne atom close to the excited Ne atom. We found such systems only at higher energies compared to the elastic STE bubble or vacancy associated STE bubble.

We have also evaluated the emission energy changes between the various STE bubbles with and without the plastic deformation associated. The emission energies become smaller with more vacancies attached. For example, the energy changed by about 30–66 meV and this is in fair agreement with the data of [7]. As an example of impurity atom excitation,

we have also studied the excited Ar atom in solid Ne. The results are very similar to that in the pure Ne.

In section 2 will be presented a brief description of the method used, followed by the results on the structures and energetics of various species studied in section 3. A brief conclusion is in section 4.

2. Method of calculation

We have developed earlier a package of methods to determine the structure and energetics of defects in insulating crystals containing one or two excess electrons. The excited (or excess) electron wavefunctions are directly orthogonalized to the wavefunctions of all occupied electron states. Short-range interaction terms in the Hartree–Fock operator for the excited electron are directly evaluated. In the course of the total-energy minimization, these terms are evaluated a very large number of times. This was made practical by the exclusive use of the floating spherically symmetrical Gaussians ($\exp(-\alpha(r - R_i)^2)$) as the basis functions. The above-mentioned short-range interaction terms have been evaluated and interpolated into a set of simple formulae for each ion or atom. One of the basic assumptions is that the occupied electron wavefunctions are not modified in the presence of a few excess electrons. The Ne atom and Ne^+ wavefunctions are taken from the tables of Clementi and Roetti [11]. An excited Ne atom can be in spin singlet or triplet states. In this work, we calculated the exchange terms corresponding to a spin triplet state.

The remainder of the system is treated using classical pair potentials and the point polarizable dipole approximation [12]. The Ne–Ne pair potential is of (6–12) type as given by Kittel [13], while Ne^+ –Ne was assumed to be the same as for Ne–Ne. Our earlier studies [12] on the a-STE bubble in s-Ne showed that because of the dominant repulsive interaction of the excited electron and Ne atoms, the details of interaction of Ne^+ –Ne mattered little. As for the Ar^+ –Ne pair potential we used the scaled parameters of Ar and Ne according to Prigogine [14]. The parameters of pair potentials used are given in table 1. The electronic polarizabilities are as found in [13].

Table 1. Parameters of (6–12) pair potentials for Ne (Ne^+)–Ne and Ar^+ –Ne: $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$.

Coefficient	Ne (Ne^+)–Ne	Ar^+ –Ne
ϵ (10^{-4} eV)	21.207	57.033
σ (Å)	2.740	3.070

To determine the equilibrium configuration of the electronically excited state of the crystal, we need to minimize the total energy with respect to individual atom positions. In practice we calculate the direction and magnitude of the gradient of the energy surface for each relaxing atom. The atom is then moved one small step along the direction of the energy gradient at a time. We re-evaluate the energy with the atom at its new position and compare it with the other energies that have been calculated in the course of minimization, and the atom is placed at the position that gives the lowest energy. The same process is carried out in sequence over all atoms allowed to relax. The whole procedure is repeated until the total energy converges to within some pre-determined threshold (0.003 eV in this work).

To investigate the possible evolution of the regular STE bubble into a stable defect, we

need to calculate the potential energy surfaces (barrier work) connecting the STE bubble to the various Frenkel pairs. In this case, one particular neon atom in the first shell is specified and moved step by step along a designated path toward the interstitial site. Usually the formation of a Frenkel pair is a fast process. The atom can surmount the potential energy barrier presented by its neighbouring atoms and quickly reach the interstitial site once it has acquired enough thermal activating energy. In the present work, this atom is held at a designated position and all other atoms are allowed to move in a single minimization cycle.

The present approach is based on a combination of quantum mechanical treatment of the excited electron and classical treatment of the remainder of the crystal. In particular the interaction between other electrons in the crystal is not directly addressed, except in semiempirical terms through the polarization and short-range pair potentials. An alternative approach would be the *ab initio* (either all-electron or in conjunction with pseudopotentials) approach. The density functional approach within the local density approximation has been very successful in the study of the ground state properties, but generally not indicated for the excited states. The Hartree–Fock approaches in conjunction with the embedded cluster are often used in studying excited systems. They are more complex and expensive. It is desirable to try a semi-empirical approach in the studies of excited defect systems, when a suitable method is available, before undertaking a full scale *ab initio* work [15].

In the present system we have the following factors which justify the approach used. The very large bandgap in Ne, more than 20 eV, indicates that the excited electron is well distinguished from the other occupied states. Also, the polarization is quite weak and can adequately be represented by the classical approach. The converging results regarding the bubble size based on diverse methods of calculation [5] seems to indicate that the empirical pair potentials used are quite acceptable. There are some obvious drawbacks in the present method. For example, it is not possible to evaluate the luminescence energy directly, as the occupied electron states are not part of the electronic subsystem energy. It is, however, possible to estimate the changes in the recombination energies between related systems. One advantage of the present and other similar approaches is that because of the transparency of the various energy terms, it is quite straightforward to analyse which terms play the key roles in a given process.

3. Results and discussion

We have examined several possible cases of plastic deformation which can be induced during the lifetime of the STE. As has been discussed in earlier papers [5, 12], the formation of an STE bubble is believed to take place within a very short time of the order of a period of the lattice vibration following electronic excitation. This bubble (or cavity) is of cubic symmetry when the excited electron is in the lowest-energy *s*-like state (corresponding to the 3*s* state of a free Ne atom). Such a bubble collapses once the electronic subsystem returns to the ground state. For this reason, it will be called an elastic deformation in this paper. We designate the lattice deformations of lower symmetry which survive annihilation of the electronic excitation as plastic. Simpler forms of such deformations would include Frenkel pairs in the Ne lattice. In the absence of *a priori* knowledge on the structure of stable Frenkel pairs accompanying an STE, we have considered a number of possible ‘pre-existing’ Frenkel pairs in the immediate neighbourhood of an STE bubble. For a Frenkel pair adjoining an excited neon atom Ne*, there can be two possibilities: one with the vacancy close to Ne* (see figures 1(a)–(d)); and the other with the interstitial Ne close to Ne* (figure 1(e)). The first one will be named the ‘vacancy associated STE’ and the second the ‘interstitial associated STE’. The equilibrium structure of these defect associated

STEs have first been determined. Next we determined the stability of each of them in the recombined electronic ground state by further relaxing the lattice in the absence of the excited electron. As will be shown below, some of the defect associated STEs lead to permanent Frenkel pairs in the ground state, while others are found to collapse and the perfect lattice is restored.

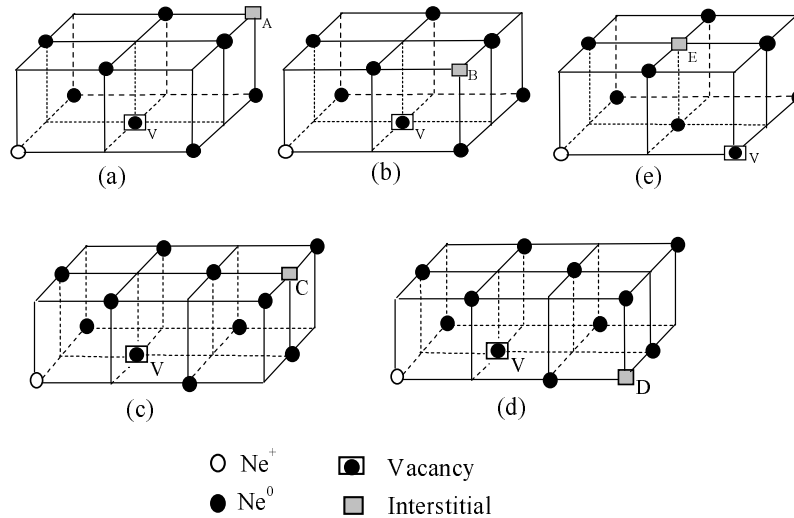


Figure 1. Sketches of models used for the representation of the vacancy–interstitial pairs. V is vacancy, A–E are interstitials. The interstitial is originally at the vacancy position. (a)–(d) are the vacancy associated STEs, while (e) the interstitial associated one. (a), (b) and (e) are the second-neighbour Frenkel pairs, (c) and (d) the third ones.

3.1. The regular STE bubble

In solid neon, the lattice expands around the STE immediately upon its creation in response to the repulsive interaction of the excited electron and the surrounding Ne atoms. The cavity radius is about 4 Å, according to the earlier work [12]. We have determined the equilibrium positions of the first 15 shells (321 atoms) in this work. The calculation shows that the displacements experienced by the shells along the $\langle 110 \rangle$ axes are the most important due to the close-packed nature of the lattice. The first shell (110) is displaced by about 1.06 Å, the fourth shell (220) by 0.66 Å, and the ninth shell (330) by 0.30 Å. The last shell (the 15th) included in our work experienced no shift. The electronic energy and the total system energy are -4.595 eV and -4.425 eV, respectively. These data are close to those of [12]

3.2. Frenkel pairs (vacancy–interstitial pairs) induced by STE

We have considered several possible arrangements of Frenkel pairs formed near a STE–bubble. The solid Ne has a face centred cubic lattice and the interstitial site can be found by moving half a lattice constant along a cubic edge. Therefore, a neon atom has six first-neighbour interstitial sites, eight second and 12 third ones. For the sake of convenience, (l, m, n) designates an interstitial site, while (l, m, n) designates a lattice site. Our preliminary work clearly showed that a Frenkel pair with a first-neighbour interstitial

is unstable in both the excited and recombined states. This is the reason why they are not included in this work. The second- and third-neighbour Frenkel pairs are shown in figure 1. Before studying the dynamic evolution of the regular STE bubble into one of the species enumerated above, we investigated the behaviour of STEs associated with 'pre-existing' pairs. Without loss of generality, we choose the Ne^+ site as the origin, and Ne^0 at site (1,1,0) as the atom to move into an interstitial position. In this work the lattice constant is taken as 2.23 Å and a unit of half a lattice constant is used to represent a lattice site.

After the formation of the STE bubble, the $\text{Ne}^0(1,1,0)$ is much closer to some of its second- and third-neighbour interstitial sites. Besides, the lattice surrounding the exciton has become much more dilated compared to the perfect one. Thus the Ne atoms could be removed from the first shell and fitted into the second or third shells where space can be made by a modest rearrangement of the nearer neighbours. It is unlikely for $\text{Ne}^0(1,1,0)$ to occupy an interstitial site close to the origin due to the strong repulsive interaction of the electron. Considering the significant displacement of $\text{Ne}^0(1,1,0)$ along the [110] axis, we only list those interstitial sites which can be most possibly occupied by $\text{Ne}^0(1,1,0)$. In figure 1, A, B and E are second-neighbour interstitial sites, C and D are third ones. We shall first focus our attention on the 'pre-existing' Frenkel pairs and discuss the barrier work latter.

Table 2. Characteristic data of Frenkel pairs. The vacancy is at site (1,1,0). The lattice constant is $a = 2.23$ Å and the site coordinates are in unit of $a/2$. The rep., elec. and total represent the interatomic repulsive potential, the electronic energy and the total system energy, respectively.

Type	Interstitials		Energy terms (eV)		
	Sites	Final position (Å)	rep.	elec.	total
A	(2,2,1)	(4.22, 4.09, 2.08)	0.201	-4.628	-4.427
B	(2,0,1)	(4.53, -0.06, 2.02)	0.197	-4.624	-4.427
C	(3,1,1)	(6.40, 2.12, 2.09)	0.211	-4.623	-4.413
D	(3,0,0)	(6.72, -0.01, 0.10)	0.206	-4.620	-4.415
**	Regular bubble		0.170	-4.595	-4.425

Results obtained with one vacancy at site (1,1,0) are shown in table 2 which includes the interstitial sites, the final positions of $\text{Ne}^0(1,1,0)$, the lattice energies, the electronic energies and the total system energies. One can see that $\text{Ne}^0(1,1,0)$ is always stuck close to the interstitial sites and leaves the vacancy in the first shell. It is also found the sites A and B are at slightly lower energies than the pure STE bubble, while sites C and D are at higher energies. Therefore it is energetically more favourable for $\text{Ne}^0(1,1,0)$ to occupy site A or B than to occupy C and D. The different behaviour of the sites A, B and C, D is largely due to their difference in geometry. Every interstitial has six neighbouring atoms. For A and B, there is always one atom lying in the $\langle 110 \rangle$ axes, which is $\text{Ne}^0(2,2,0)$ for A, (1,0,1) for B. The atoms in the $\langle 110 \rangle$ axes play the most important role in the formation of the STE bubble. The large displacement experienced by atoms (2,2,0) or (1,0,1) destroys the cubic symmetry of the local lattice surrounding the interstitial A or B. The additional repulsive interaction of the interstitial further strengthens the local lattice distortion which will result in a significant rearrangement. The influence of the interstitial extends over more shells. This is confirmed by the calculated lattice distortion field. However, the cases for C and D are quite different: no neighbouring atoms are of the special status as described above, and the local lattice does not expand significantly. Some typical data for the expansion around interstitials A–D are listed in table 3. The distances between the interstitial and its

neighbouring atoms in table 3 indicate that the cavity around A (or B) is indeed larger than those around C and D. The resulting lattice repulsive energy and electronic energy in site A (or B) are therefore respectively smaller than those in sites C and D.

Table 3. The maximal and minimal distances (Å) between the interstitial atom and its six neighbours corresponding to the four vacancy associated STEs listed.

Type	Maximum	Site	Minimum	Site
A	2.75	(2,1,1)	2.66	(3,2,1)
B	2.78	(1,0,1)	2.62	(3,0,1)
C	2.68	(3,0,1)	2.58	(4,1,1)
D	2.72	(3,0, $\bar{1}$)	2.57	(4,0,0)

In their experimental work on the STE bubble in s-Ne, Savchenko and collaborators [7] have observed that the local deformations appearing around an excited centre in the regular Ne lattice under the action of the STE lead to structural defects which persist even after the annihilation of the excitation. We have performed the calculations for several types of vacancy–interstitial pair formed in the lattice. Whether these deformations can lead to stable defects is an interesting question. To test the stability of the above ‘pre-existing’ Frenkel pairs, we remove the excited electron from the system (i.e. replace Ne^+ at (000) with Ne^0) and let all atoms relax starting from the vacancy–interstitial state (A, B, C and D). After a sufficient number of iterations of the minimizing cycle, Frenkel pairs C and D collapse, but A and B remain in the lattice. We schematically exhibit the recombination process of Frenkel pairs C and D in figure 2. This is a two-step process. In figure 2(a), one can see that while $\text{Ne}^0(2,0,0)$ moves step by step to the vacancy position (1,1,0), the interstitial D simultaneously moves to occupy the site (2,0,0). At last the whole lattice recovers perfectly with two atoms (2,0,0) and (1,1,0) exchanging their positions. We have tested all Frenkel pairs formed by removing one Ne^0 from the first shell to its second- and third-nearest-neighbouring interstitial sites. It is found that the third-nearest-neighbouring vacancy–interstitial pairs always collapse in the ground state, while the second-nearest-neighbouring ones can persist in the lattice and create permanent defects.

In view of the completely different behaviour of the two types of Frenkel pair, one may question why the second-nearest-neighbouring pairs are stable and the third-nearest ones unstable. The reason is associated with the interstitial positions. The vacancy and its second-nearest-neighbouring interstitial are at the two ends of the cubic diagonal, while the vacancy and its third-nearest-neighbouring interstitial lie in the same plane (see figure 1). When $\text{Ne}^0(1,1,0)$ is brought into the interstitial site A (or B), all neighbouring atoms around A (or B) will be pushed away from the vacancy. Quite a different situation happens to the interstitial C (or D): the neighbour atom $\text{Ne}^0(2,0,0)$ of the interstitial D (or $\text{Ne}^0(2,1,1)$ of C) will be pushed by the interstitial toward the vacancy. It is the $\text{Ne}^0(2,0,0)$ (or $\text{Ne}^0(2,1,1)$) that will occupy the vacancy site (1,1,0) after the annihilation of the exciton. Every third-nearest-neighbouring interstitial site has such a special neighbouring atom which is ready to relax toward the vacancy position. The repulsion of the electron prevents this ‘special atom’ from moving to the vacancy when the exciton is present in the system. Once the electron has recombined to the hole, there is no potential energy barrier to prevent the recombination of the Frenkel pair. However, the significant rearrangement of the lattice around the interstitial A (or B) presents a barrier in the vacancy region, and no atom can freely move toward the vacancy. Therefore the second-nearest-neighbouring vacancy–interstitial pairs can survive the recombined electronic ground state and create the permanent lattice defect.

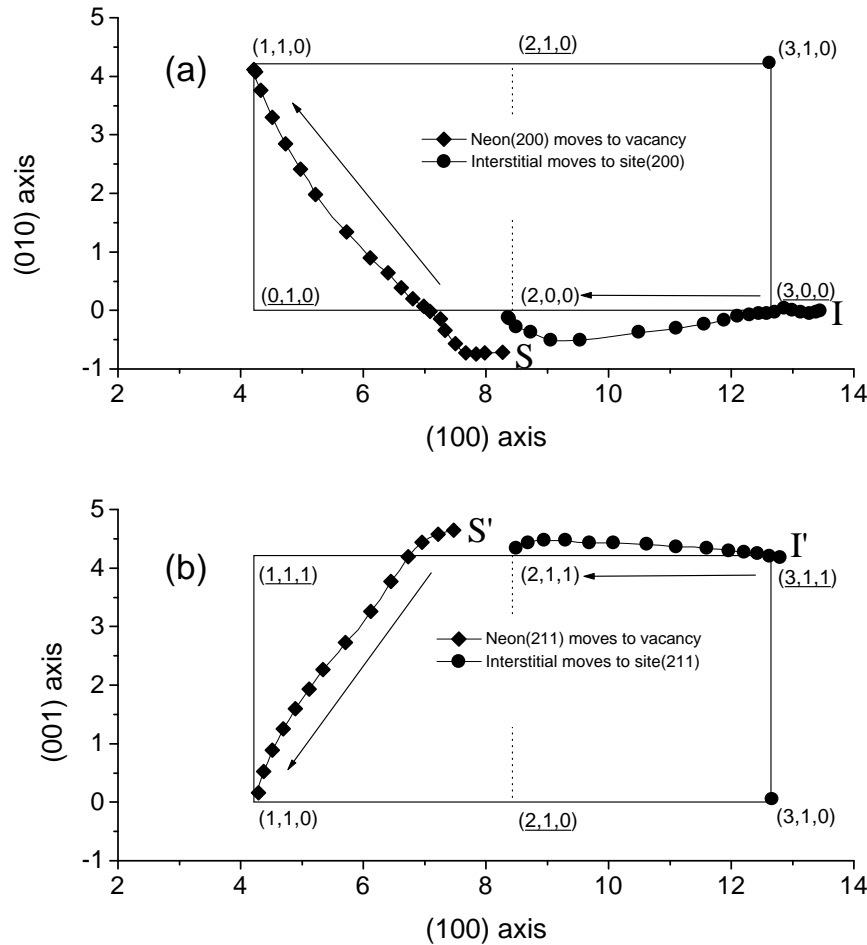


Figure 2. Two-step recombination process of Frenkel pairs. (a) Neon (2,0,0) is initially at position S (near (2,0,0)), and then moves step by step towards the site (1,1,0). Interstitial neon (1,1,0) simultaneously starts from position I (near interstitial site (3,0,0)) relaxing to the site (2,0,0). (b) Neon (2,1,1) and interstitial neon (1,1,0) perform a similar process to (a).

In an earlier work, Ratner and Fugol [10] have discussed the possibility of plastic deformation associated with the STE bubble. They proposed that the first shell could accommodate more atoms due to the large expansion around the excited atom. This would correspond to the creation of an ‘interstitial associated STE’ by inserting the interstitial Ne in the expanded first atomic shell. Figure 1(e) displays an example of this type of Frenkel pair. After the system has reached equilibrium, the $\text{Ne}^0(2,0,0)$ is found stuck at (2.50, 2.42, 2.50) (Å), and the total system energy is -4.395 eV, the highest among all states discussed. It is energetically unfavourable for $\text{Ne}^0(2,0,0)$ to enter the first shell because both the electronic energy and lattice energy increase during the course of deformation. But, once this type of Frenkel pair had been created in the lattice, they would remain stable after the annihilation of the exciton; this is in agreement with the conclusion that the second-nearest-neighbouring vacancy–interstitial pair can evolve into a permanent defect.

3.3. Barrier work

We have studied the evolution of the regular STE bubble into various Frenkel pairs in the following way. Starting from the lattice configuration of the regular STE bubble, a designated Ne atom is moved in small steps along a designated path until the desired defect STE system is realized. For each step 321 neon atoms were relaxed to new equilibrium positions along the direction of the energy gradient. One atom is moved at a time, and only one minimization cycle is performed at each step, as described in section 2.

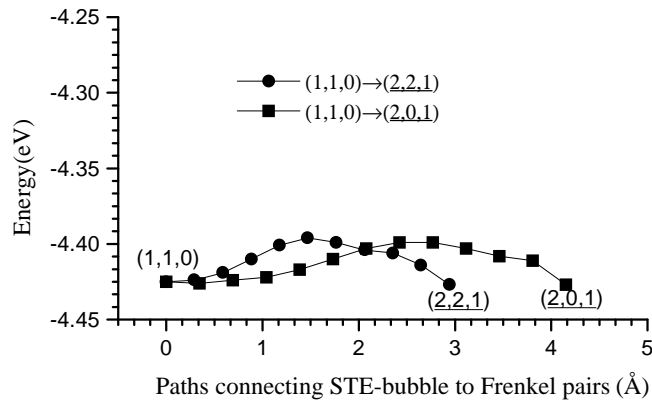


Figure 3. Potential energies connecting the regular STE bubble to the Frenkel pairs. The energies are flat for paths $(1,1,0) \rightarrow (2,2,1)$ and $(1,1,0) \rightarrow (2,0,1)$.

The potential energy leading from the regular STE bubble to the second-neighbour Frenkel pairs (the stable pairs) is given in figure 3. The barrier heights for the paths $(1,1,0) \rightarrow (2,2,1)$ and $(1,1,0) \rightarrow (2,0,1)$ are about 20 meV. The creation of the third-neighbour Frenkel pairs (the unstable pairs) is investigated in two different ways. In the first one, starting from the regular STE bubble the Ne atom $(1,1,0)$ was taken directly to one of the third-neighbour interstitial sites, e.g., $(3,0,0)$ or $(3,1,1)$, in discrete steps. The barrier heights leading to these two interstitial sites are both more than 200 meV! The significant difference in the potential barriers between the two types of Frenkel pair is completely due to the different densities of their corresponding local lattices. As we have discussed previously, the local lattices around the interstitial sites C and D are much denser than those around A and B. When the designated neon $(1,1,0)$ moves along the path $(1,1,0) \rightarrow (3,0,0)$ or $(1,1,0) \rightarrow (3,1,1)$, the repulsive interaction between it and the atoms surrounding the path strengthens rapidly, which increases the interatomic potential greatly. In this case, the gain of electron energy is far from sufficient to offset the rise of the interatomic potential. On the other hand, for the paths $(1,1,0) \rightarrow (2,2,1)$ and $(1,1,0) \rightarrow (2,0,1)$, the local lattices are much dilated due to the large radial displacements of the first and second shells. Therefore the gain of the electron energy when the neon $(1,1,0)$ moves along the path $(1,1,0) \rightarrow (2,2,1)$ or $(1,1,0) \rightarrow (2,0,1)$ can compensate the expense of energy to deform the lattice locally. It is obvious therefore that the neon $(1,1,0)$ will not reach the third-neighbour interstitial site in a single-step process. The second approach we took is via a two-step process. Starting from the second-nearest-neighbouring Frenkel pair, for which the neon $(1,1,0)$ has already moved to the interstitial site $(2,0,1)$, it may then diffuse to one of its nearest-neighbouring interstitial sites. Calculation shows that the potential energies are very flat for the paths $(2,0,1) \rightarrow (3,0,0)$ and $(2,0,1) \rightarrow (3,1,1)$.

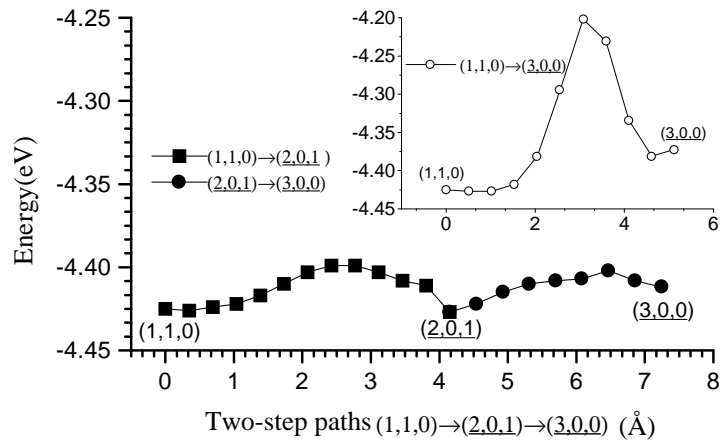


Figure 4. Potential energies of the two-step process: $(1,1,0) \rightarrow (2,0,1) \rightarrow (3,0,0)$. The inset presents the potential energy for the single-step process $(1,1,0) \rightarrow (3,0,0)$.

Figure 4 presents the combined results of the two-step process: $(1,1,0) \rightarrow (2,0,1) \rightarrow (3,0,0)$. The other case corresponding to $(1,1,0) \rightarrow (2,0,1) \rightarrow (3,1,1)$ is similar and not produced here. In the inset of figure 4, we have presented the single-step process for $(1,1,0) \rightarrow (3,0,0)$ described above. Thus, it is reasonable that the third-neighbour Frenkel pairs could be formed by a two-step process rather than a direct one. It is an interesting result that the formation and recombination of the third-nearest-neighbouring Frenkel pair are both via a two-step process. Of course, it is the excited electron that plays the most important role in the two-step formation of the third-nearest-neighbouring Frenkel pair because the first four atomic shells around the exciton have been dilated significantly due to its strong repulsion of the surrounding neon atoms. Considering that the lattice far from the Ne^* centre has been compressed, it is unlikely for the interstitial to diffuse away to a very distant interstitial site.

3.4. Emission energies of the defect associated STE band

As reported in [7], a second UV luminescence band (denoted as the component '1') grows beside the intrinsic emission (component '2'). The origin of this band was thought to be connected to the defect formation. The observed dose dependence of the component '1' points towards the long life of the emerging defects. We have found the STE bubble could induce some stable Frenkel pairs which are at lower energies than the regular bubble. It is also possible to create more vacancies in the first shell because of the decreases in the electron energy. The results are given in table 4. It is found that the STE bubble accompanied by two non-adjacent vacancies in the first shell is at the lowest energy. The system energy begins to rise with more than two vacancies in the first shell. This suggests the number of extra vacancies at equilibrium would be small, somewhere between two and three. In fact, the number of vacancies captured in equilibrium depends also on the kinetics of vacancy diffusion. If there were many Frenkel pairs created in the lattice, the local concentrations of vacancies and interstitials would be high. The number of vacancies in the first atomic shell could fluctuate around the optimum value of two we found here.

We have determined the equilibrium configurations of the regular STE bubble and the ones with Frenkel pairs. The electronic energies of those states can then be used to estimate the luminescence energy difference as in [12]. Assuming the hole state energy is the same

Table 4. The geometries of STEs with multi-vacancies in the first atomic shell and the corresponding energies.

Geometries of Frenkel pairs			Energy terms (eV)		
No of vacancies	Vacancies	Interstitials	rep.	elec.	total
two	(1,1,0) → (2,0,1)		0.214	−4.651	−4.437
	(1,1̄,0) → (0,2̄,1)				
two	(1,1,0) → (2,0,1)		0.215	−4.649	−4.434
	(1̄,0,1) → (2̄,1,0)				
two	(1,1,0) → (2,0,1)		0.210	−4.661	−4.451
	(1̄,1,0) → (2̄,0,1)				
three	(1,1,0) → (2,0,1)		0.229	−4.678	−4.449
	(1̄,1,0) → (2̄,0,1)				
	(1,1̄,0) → (0,2̄,1)				

for the various lattice configurations in s-Ne, the luminescence energy difference between the regular STE bubble and those with defects is in a range 30–66 meV, as can be seen from tables 2 and 4. If we consider only the STE bubbles accompanied by two vacancies, the corresponding luminescence bands would occur at energies smaller by about 54–66 meV than the regular STE bubble, which is in good agreement with the experimental value of 60 meV in [7].

Table 5. Geometries and energy terms of Ar* centre STEs.

Type	Energy terms (eV)		
	rep.	elec.	total
Regular bubble	0.201	−3.764	−3.563
One Frenkel pair (1,1,0)→(2,2,1)	0.230	−3.810	−3.580
One Frenkel pair (1,1,0)→(2,0,1)	0.226	−3.800	−3.574
Two Frenkel pairs (1,1,0)→(2,0,1) (1̄,1,0)→(2̄,0,1)	0.244	−3.869	−3.625

3.5. Ar* centre in solid neon

As an example of an excited rare gas impurity in solid Ne, we studied the case of the excited argon atom in solid neon. The situation regarding the Frenkel pairs associated with Ar* in solid Ne is quite similar to that in pure solid Ne. The results are listed in table 5. In this case, the first shell of atoms is displaced radially by about 1.18 Å. The geometries of the Frenkel pairs induced by the Ar*-centre STE are the same as those by Ne* centre. The luminescence band difference is in the range 36–105 meV. Similarly, the two-vacancy state gives the band energy 105 meV lower than the regular STE bubble, which compares well with the experimental result of 100 meV in [7].

3.6. Split electron–hole system

In many ionic halide crystal lattice defects, Frenkel defect pairs of the anion sublattice are created efficiently at low temperature as the result of exciton self-trapping [5]. In these materials, the excited electron and hole localize separately in the lattice, the so called off-centre STE, and may eventually lead to well separated Frenkel pairs, as seen in KBr [16]. The driving force of this process is in the strong localization of the excited electron at an anion vacancy. The electron in fact becomes an F centre, while the hole which is localized on a pair of halogen ions as in Br_2^- is expelled along the $\langle 110 \rangle$ axes and becomes an H centre. The binding between the electron and hole of an exciton is mediated by the ionic lattice.

In solid neon the driving force is the repulsive interaction of the excited electron with the ground state Ne atoms. On the other hand the binding between the electron and hole is the straight Coulomb attraction. It is therefore interesting to examine if a split structure of the STE is possible in solid neon. Indeed, the excited electron localizes on its own as an electron bubble [4] and an Ne^+ ion can relax separately by polarizing the surrounding lattice atoms. We found that the strong attraction of the electron on Ne^+ and the softness of the lattice makes such split STE very unstable. From as far as six times the lattice constant, the Ne^+ ion migrates toward the site of the electron. The end product is a regular STE bubble. This conclusively shows that a split (an off-centre) STE is unlikely to form in solid neon.

4. Conclusion

We have studied the possible evolution of the STE into stable lattice defects in solid Ne using the extended-ion method to describe the excited electron and the classical approach to represent the rest of the crystal. The STE bubble accompanied by a second-nearest-neighbouring vacancy–interstitial pair is found to have lower energy than a regular STE bubble. The potential energy surface connecting the regular STE bubble to the second-nearest-neighbouring vacancy–interstitial pair is very flat. The lowest-energy configuration is found to be the STE bubble with two non-adjacent vacancies in the first atomic shell, and the corresponding luminescence band occurs at energy smaller by about 66 meV than the regular STE bubble, which compares reasonably well with the experimental value of 60 meV. The results for the Ar^* -centre STE are very similar to that for the Ne^* -centre STE and also in good agreement with the experimental data.

Acknowledgment

We would like to thank Professor E Savchenko for her interest in this work.

References

- [1] Fugol I 1978 *Adv. Phys.* **27** 1
- [2] Schwentner N, Koch E E and Jortner J 1985 *Electronic Excitation in Condensed Rare Gases (Springer Tracts in Modern Physics 107)* (Berlin: Springer)
- [3] Ueta M, Kanzaki H, Kobayashi K, Toyozawa Y and Hanamura E 1986 *Excitonic Processes in Solids (Springer Series in Solid-State Science 60)* (Berlin: Springer) ch 5
- [4] Emery L and Song K S 1986 *J. Phys. C: Solid State Physics* **19** 2469
- [5] Song K S and Williams R T 1996 *Self-Trapped Excitons* 2nd edn (Berlin: Springer) ch 3
- [6] Zimmerer G 1994 *Nucl. Instrum. Methods B* **91** 601

- [7] Savchenko E, Rybalko Y I and Fugol I 1988 *Sov. J. Low Temp. Phys.* **14** 220
- [8] Song K S, Leung C H and Williams R T 1989 *J. Phys.: Condens. Matter* **1** 683
- [9] Rajagopal G, Barnett R N and Landman U 1991 *Phys. Rev. Lett.* **67** 727
- [10] Ratner A M and Fugol I 1987 *Low Temp. Phys.* **13** 90
- [11] Clementi E and Roetti C 1974 *At. Data Nucl. Data Tables* **14** 177
- [12] Leung C H, Emery L and Song K S 1983 *Phys. Rev. B* **28** 3474
- [13] Kittel C 1976 *Introduction to Solid State Physics* (New York: Wiley)
- [14] Prigogine I 1957 *The Molecular Theory of Solutions* (Amsterdam: North-Holland) ch 2
- [15] Song K S 1996 *Curr. Opinion Solid State Mater. Sci.* **1** 834
- [16] Meise W, Rogulis U, Koschnick F K, Song K S and Spaeth J M 1994 *J. Phys.: Condens. Matter* **6** 1815