

## Models of electronic defects and self-trapped excitons in $\text{Li}_2\text{O}$

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

1990 J. Phys.: Condens. Matter 2 4119

(<http://iopscience.iop.org/0953-8984/2/18/008>)

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

Download details:

IP Address: 171.66.16.96

The article was downloaded on 10/05/2010 at 22:07

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

## Models of electronic defects and self-trapped excitons in Li<sub>2</sub>O

Alexander Shluger<sup>†</sup> and Noriaki Itoh

Department of Physics, Faculty of Science, Nagoya University, Furocho, Nagoya 464-01, Japan

Received 12 December 1989

**Abstract.** The semi-empirical INDO method and the embedded-molecular-cluster model have been applied to calculate the atomic structures and electronic transition energies of the F<sup>+</sup>, F and F<sub>2</sub> centres in Li<sub>2</sub>O and to simulate the self-trapping process of a triplet exciton. Using the parameters of the Slater-type floating orbitals adjusted to the experimental transition energy (4.13 eV) and hyperfine splitting parameters of the F<sup>+</sup> centre, the transition energies of the F and F<sub>2</sub> centres were obtained to be 4.82 eV and 3.31 eV, respectively. The lattice relaxation accompanied by formation of a triplet exciton and by two neighbouring triplet excitons are also simulated. The results indicate that a triplet exciton is self-trapped by a shift of an oxygen ion by 0.34 Å along a ⟨100⟩ direction, while defect formation as a consequence of the relaxation of a triplet exciton is very improbable. We found that two excitons at the nearest neighbour relax into a more stable relaxed state including an O<sub>2</sub><sup>-</sup> bond, and further to a vacancy–interstitial pair. The results of the simulation were compared with experimental observation of the effects of neutron irradiation and of heavy-ion irradiation of Li<sub>2</sub>O.

### 1. Introduction

Lithium oxide is one of the candidates for blanket materials of fusion reactors and studies are needed to understand its behaviour under irradiation. It has been shown that neutron irradiation of Li<sub>2</sub>O produces the F<sup>+</sup> centres [1], which have been studied using electron paramagnetic resonance (EPR) [2, 3] and optical absorption [1]. Besides the F<sup>+</sup> centres, some unspecified optical absorption bands are produced at 375 and 570 nm. Lithium colloids or aggregates of F centres are also produced by high-temperature irradiation with neutrons [4], indicating decomposition of the materials under heavy irradiation. It appears that irradiation with γ- and x-rays of Li<sub>2</sub>O does not produce any permanent defects. However, it has been shown recently that the yield of the F<sup>+</sup> centres by heavy ions increases as the stopping power increases and the result has been ascribed to the effects of dense electronic excitation [5].

Studies of radiation damage of Li<sub>2</sub>O are of fundamental interest; a comparison of radiation damage of this material with that of several oxides such as the MgO-type crystals, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, may give further insight into the characteristics and the nature of defects and the process of radiation damage, and in particular on the effects of the difference in the valence of cations and of the ionicity. Comparing information available

<sup>†</sup> Permanent address: Latvian State University, Rainis Boulevard 19, 226098 Riga, USSR.

on radiation damage for MgO and Al<sub>2</sub>O<sub>3</sub>, that for Li<sub>2</sub>O is rather fragmented. For example, no F-centre formation by neutron irradiation has yet been reported and hence it is not yet known whether an anion vacancy in Li<sub>2</sub>O can trap two electrons, although it is established that both F and F<sup>+</sup> centres are produced in MgO [6] and Al<sub>2</sub>O<sub>3</sub> [7]. Furthermore no information on the F complex centres is available although some of the optical absorption bands have been ascribed to these centres.

It is also known that electronic excitation produces Frenkel pairs in the bulk of some of inorganic solids [8] and that self-trapping of excitons, which results from strong electron–lattice coupling, is a crucial step for defect production by electronic excitation [9]. In some solids such as alkali halides, excitons are known to relax either to self-trapped excitons or to defect pairs while, in others such as crystalline SiO<sub>2</sub>, self-trapping of excitons does not lead to defect formation [10]. Nevertheless defect generation occurs in the latter class of solids when self-trapped excitons are produced densely [11]. No information is yet available on the self-trapping of excitons in Li<sub>2</sub>O, although it is known that heavy-ion irradiation of LiO<sub>2</sub> produces defects by electronic encounters.

The purpose of the present paper is to report theoretical studies of defects and self-trapped excitons and defect-pair formation in Li<sub>2</sub>O. Up to now there are only a few theoretical papers on F<sup>+</sup> centres [12, 13] but no theoretical studies on F or F aggregate centres have been published. The present study clarifies the properties of F<sup>+</sup>, F and F aggregate centres and the self-trapping process of excitons and gives a useful clue to understanding the radiation damage processes in this material.

## 2. Methods of calculation

In this work, defects in Li<sub>2</sub>O were simulated based on the embedded-molecular-cluster model [14] and self-consistent semi-empirical INDO-type calculation scheme [15]. The basis set includes the 2s functions of lithium ions, and 2s and 2p functions of oxygen ions. The parametrisation scheme and values of the INDO parameters have been described in a previous paper [16]. The cluster, which includes valence electrons and cores, was placed in the Coulomb field of the infinite non-point ion lattice of the rest of the crystal [16, 17]. The relaxation of the lattice surrounding a defect was calculated so that the total energy of the embedded molecular cluster was a minimum [17].

The electronic structures and the lattice constant of the perfect crystal were calculated using the large-unit-cell (LUC) method [18, 19]. The band gap obtained in our calculation using the restricted configuration interaction method was 9.9 eV and corresponds to direct  $\Gamma$ – $\Gamma$  transition. The Lowdin population analysis was used to calculate the effective charge; the result obtained for an oxygen ion in the perfect lattice was  $-1.67e$ . The electronic structure of the valence band and the absolute energy at the top of it are in good agreement with *ab initio* band-structure calculations [20]. The optimised lattice constant of the perfect crystal was 4.6 Å, in good agreement with experimental results. The electronic density distribution obtained for the perfect crystal with the LUC method was used to calculate the Coulomb field of the rest of the crystal in the cluster calculations of defects.

## 3. Results of calculation

### 3.1. F-type centres

The molecular clusters used for studying the defects in Li<sub>2</sub>O are shown in table 1. All of them include two spheres of nearest-neighbour cations and anions surrounding an

**Table 1.** Distortion of ions surrounding several types of defect in  $\text{Li}_2\text{O}$  and energies of optical transitions. The displacement is given in the units of the lattice constant  $a = 4.6 \text{ \AA}$  and a + sign corresponds to outward shift. An optical absorption band has been obtained at 3.31 eV [1] but not yet assigned.

Defect	Molecular cluster	Displacement		Optical transition energy (eV)	
		Lithium	Oxygen	Theory	Experiment
$\text{V}_a^{2+}$	$[\text{Li}_{26}\text{O}_{12}]^{2+}$	0.06	-0.028		
$\text{F}^+$	$[\text{Li}_{26}\text{O}_{12}]^+$	0.017	-0.021	3.93	4.13 [1]
$\text{F}$	$[\text{Li}_{26}\text{O}_{12}]$	-0.034	-0.015	4.82	
$\text{F}_2$	$[\text{Li}_{36}\text{O}_{16}]$	-0.031	-0.017	3.5	3.31

oxygen site in which an F-type centre was going to be placed. Before any defect is introduced, the equilibrium positions of all ions in the cluster simulating the perfect lattice were obtained by minimising the total energy of the cluster interacting with the rest of the crystal. The shift of each ion was inwards and less than 0.5% of the lattice constant. This shows that the embedded-molecular-cluster model [14] represents well the interaction between the cluster and the rest of the crystal.

Now, removing the oxygen ion at the centre of the cluster, the relaxation of the surrounding ions was obtained and the results are shown in the row for  $\text{V}_a^{2+}$  in table 1. The relaxation of anions is inwards and that of cations is outwards, as usually observed in ionic crystals. To deal with the F-type centres, we extended our basis set to include 2s and 2p Slater-type atomic orbitals (AOs) centred at the vacancy. Usually, the basis set should include a 1s function for the ground state and 2p functions for the next excited state reached by an allowed electronic transition [21]. We found it more convenient to use a nodeless 2s function instead of a 1s function. The exponent of the functions was optimised to fit to experimentally observed optical absorption energy and EPR isotropic hyperfine interaction with neighbouring cations. The values of the exponents were obtained to be  $1.24 \mu_B^{-1}$  for the 2s AO and  $1.15 \mu_B^{-1}$  for the 2p AO where  $\mu_B$  is the Bohr radius. The relaxation of the surrounding ions for an  $\text{F}^+$  centre is smaller than that for a vacancy, as shown in table 1. The difference in the self-consistently calculated total energy of the system in the ground and excited states represents the optical transition energy, and the calculated and experimental results are compared in table 1. The wavefunction of the ground state is localised within a vacancy but that of the excited state was delocalised onto the nearest-neighbour cations. The spin density on the nucleus of the surrounding cations was evaluated to be  $1 \times 10^{-3}e$ , in good agreement with the experimental data [3] and also with the results of the previous calculation [12].

The same basis set was used to calculate the electronic structure and optical transition energies of the F and  $\text{F}_2$  centres. The distortion around these centres is shown in table 1. When an electron is added to an  $\text{F}^+$  centre at its equilibrium configuration, we found that the wavefunction of the lowest singlet state is delocalised. Now, by allowing relaxation of the neighbouring cations, their inward displacement makes the electronic density distribution more localised and the total energy of the system is reduced to a value lower than that of the  $\text{F}^+$  centre. This process can be regarded as a negative- $U$  interaction. In this relaxed configuration the wavefunction of the excited state of the F centre becomes delocalised. The transition energy was calculated using the restricted configuration interaction method to be 4.82 eV, which is even larger than that of the  $\text{F}^+$

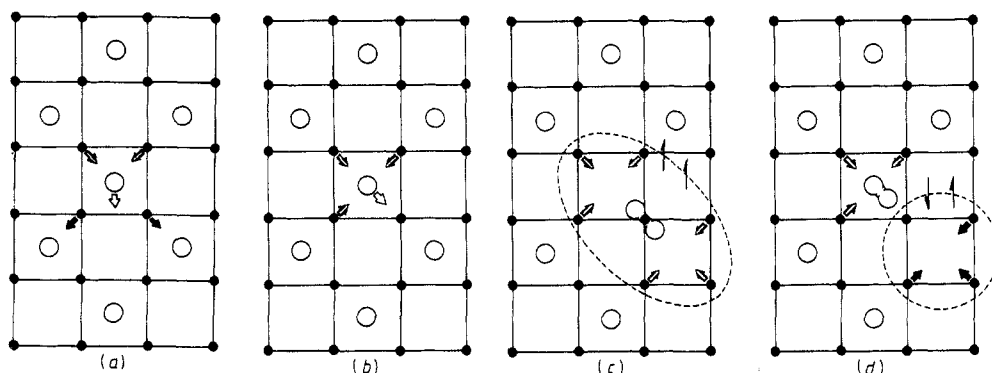
centre. We found that the relaxation of ions surrounding an  $F_2$  centre is close to that of an F centre, while the energy of the lowest allowed transition is smaller than that of the F centre, because of the interaction of two F-centre orbitals.

### 3.2. Self-trapping of excitons

Up to now the correlation between the self-trapping of triplet excitons and defect formation has been established for alkali halides [10] and amorphous silicon dioxide [22, 23]. Therefore the self-trapping process of a triplet exciton was simulated, using a symmetrical cluster containing 54 ions ( $Li_{36}O_{18}$ ). In order to simulate the electron density distribution in a distorted lattice at a triplet excited state, the wavefunctions should be flexible. Therefore we introduced six 1s floating Slater-type wavefunctions centred at several off-site positions and orthogonalised to other basis functions. The exponent of these wavefunctions was assumed to be the same and optimised to  $0.77 \mu_B^{-1}$  so that the calculated singlet–triplet transition energy in the cluster simulating the perfect lattice is very close to the singlet–singlet transition energy obtained using LUC. The wavefunctions of the electron and hole in the triplet excited state for the perfect lattice are completely delocalised within the cluster area.

In order to find the possible lattice distortion by self-trapping of an exciton, we calculated the total energy of the triplet excited state of the cluster, in which one or two oxygen ions were shifted along various directions. We found that the total energy is reduced and the electron and hole of an exciton are localised when an oxygen was shifted along either a  $\langle 100 \rangle$  or a  $\langle 110 \rangle$  direction. The configurations which give the minimum total energies for both cases are shown in figures 1(a) and 1(b). The distortion of each of the surrounding ions is shown in the figure caption. At the minimum, the hole is completely localised on the displaced oxygen, while the electron is widely distributed on the lithium ions that are shifted to the centre (see figures 1(a) and 1(b)) and on the floating orbital located on the axis along which the oxygen atom was displaced. The energy gain by the distortion to the configuration of figure 1(a) was 0.7 eV and that to the configuration of figure 1(b) was 0.2 eV. We calculated also the energy increase of the singlet ground state by the distortion and obtained 0.9 eV for figure 1(a) and 0.4 eV for figure 1(b). Thus the self-trapped state shown in figure 1(a) is more preferable and we expect a Stokes shift for the exciton luminescence to be 1.6 eV.

A further shift of the oxygen ion from the configurations shown in figures 1(a) and 1(b) increases the total energy very rapidly (0.5 eV for a shift of 0.2 Å from the equilibrium position) because of the Coulomb repulsion between oxygen ions. It turns out that the total energy continues to increase to a value of about 2 eV, and hence no defect formation from self-trapped exciton can be expected in this material. The situation may be different if another exciton is self-trapped at one of the neighbouring sites; the Coulomb repulsion between the oxygen ions will be reduced and even a bond formation between them may be expected. We tried to simulate this situation by exciting another electron in a cluster containing a self-trapped exciton of the configuration in figure 1(b), for which the nearest oxygen–oxygen distance is the shortest. The energy needed to excite the second electron was smaller than that for the first electron by about 2 eV. A shift of the second oxygen ion towards the first oxygen ion immediately traps the hole on it, reducing the ionic charge. Further relaxation brings the two oxygen ions close to each other and reduces the total energy. The configuration at which the total energy takes a minimum is shown in figure 1(c). The distance between the two displaced oxygen ions is 1.24 Å, which is close to the equilibrium distance (1.26 Å) of an  $O_2^-$  molecular



**Figure 1.** The configurations at which the total energy of the lowest triplet excited state of  $\text{Li}_2\text{O}$  takes minima ( $\circ$ , oxygen ions;  $\bullet$ , lithium ions): (a) configuration when the oxygen ion with an arrow is displaced along a  $\langle 100 \rangle$  direction; (b) configuration when the oxygen ion with an arrow is displaced along a  $\langle 110 \rangle$  direction; (c), (d) lattice relaxation followed by the formation of two triplet excitons at the nearest neighbours (two connected circles,  $\text{O}_2^-$  molecular ions;  $\circ$ , electron and spin density distributions in triplet bi-exciton and nearest-defect-pair cases (schematically)).

Figure	Ions	Arrows	Displacement ( $\text{\AA}$ )
1(a)	Oxygen	Open	0.34
	Lithium	Open	0.04
		Full	0.16
1(b)	Oxygen	Open	0.16
	Lithium	Open	0.04
		Full	0.07
1(c)	Lithium	Open	0.04
		<sup>a</sup>	0.37
		Full	0.16
1(d)	Lithium	Open	0.08
		Full	0.16
		<sup>a</sup>	0.35

<sup>a</sup> Lithium ions located on the planes above and beneath the plane shown in the figures.

ion. The total energy after the relaxation is even lower than the total energy of a single self-trapped exciton, which is ascribed to the bond formation between the oxygen ions and energy gain due to the strong localisation of the two electrons on the two half-vacancies formed by the displacement of the oxygen ions. The optical absorption energy of the hole component of this bi-self-trapped exciton, due to the bonding-to-antibonding electron transition of the oxygen quasimolecular ion, was evaluated to be 1.9 eV.

The configuration shown in figure 1(c) is similar to that of the on-centre self-trapped exciton in alkali halides, which consists of a halogen molecular ion and an electron [5]. It is established that for alkali halides the displacement of the halogen molecular ion leads to a vacancy–interstitial pair, in which the electron is localised in the vacancy formed by this displacement [10]. A completely analogous situation may occur in the case of bi-self-trapped exciton. Thus we adiabatically shifted the oxygen molecular ion along a  $\langle 110 \rangle$  direction and calculated the total energy and wavefunctions of the system along the path of its motion. We found that the total energy takes a minimum at the

configuration shown in figure 1(d). In this configuration the oxygen molecular ion is displaced onto an oxygen site and two electrons are localised on the vacancy, forming a Frenkel pair. To convert from the configuration in figure 1(c) to that in figure 1(d) there is an energy barrier of 1 eV.

#### 4. Discussion

Neutron irradiation of  $\text{Li}_2\text{O}$  produces optical absorption bands at 4.13, 3.31 and 2.18 eV [1]. Among these, the 4.13 eV band has been assigned to the  $\text{F}^+$  centre, as discussed already. The present calculation shows that the optical absorption bands of the F centres is at 4.8 eV and that of the  $\text{F}_2$  centre is at 3.5 eV. Since the optical absorption at around 4.5 eV of unirradiated crystals is relatively high [1], the optical absorption due to the F centres, even if they are produced, cannot be measured. We presume that F centres are also generated by neutron irradiation as in MgO and  $\text{Al}_2\text{O}_3$  [6, 7], but that they are not observed by optical spectroscopy. We suggest also that the 3.31 eV band is that of the  $\text{F}_2$  centres because of the proximity of the transition energy to the theoretical value.

The present calculation indicates that self-trapping of an exciton does occur in  $\text{Li}_2\text{O}$ . Among oxides, self-trapping of excitons has been well established for  $\text{SiO}_2$  [22, 24–26]. Recent theoretical studies for  $\text{SiO}_2$  have shown that even a small shift of an oxygen ion towards an interstitial position localises the hole of an exciton on the oxygen and the electron on one of Si ions surrounding it [27]. According to the present calculation the self-trapping of an exciton in  $\text{Li}_2\text{O}$  results from a symmetry-breaking displacement of an oxygen ion along a  $\langle 100 \rangle$  or  $\langle 110 \rangle$  direction, accompanied with subsequent displacements of surrounding cations. We found that the displacement of an oxygen ion along a  $\langle 100 \rangle$  direction is energetically more favourable. As in  $\text{SiO}_2$ , the hole is trapped by displaced oxygen and the electron is localised near the site from where the oxygen ion is displaced.

We note that the self-trapping processes of excitons in  $\text{SiO}_2$  and  $\text{Li}_2\text{O}$  have common features, although the crystalline structures and the ionicities are different. Apparently there are two factors that govern the self-trapping of excitons in ionic-covalent solids: the crystalline field and free volume for displacement of an anion. The role of the crystalline field is twofold: to localise the hole of an exciton on the displaced anion and to attract the electron on the site of the displaced anion. The ease of the anion displacement is governed by the free volume for anion motion. Clearly the concept described above can explain why the oxygen is displaced along a  $\langle 100 \rangle$  direction in the self-trapped exciton in  $\text{Li}_2\text{O}$ . Comparing the self-trapping processes in these two crystals, one may note that, even though the ionicity in  $\text{SiO}_2$  is smaller than that in  $\text{Li}_2\text{O}$ , the cation charge in the former is larger, making the magnitude of the crystalline field in the two crystals close to each other. In fact the values of the matrix elements of the crystalline field on the atomic orbitals of an oxygen ion at the site position are typically  $-21$  eV in  $\text{SiO}_2$  and  $-20$  eV in  $\text{Li}_2\text{O}$ . In both of these crystals, there is an open space for displacement of an oxygen ion: in  $\text{SiO}_2$  in the direction perpendicular to the Si–O bond and in  $\text{Li}_2\text{O}$  along a  $\langle 100 \rangle$  direction. The larger free volume for  $\text{SiO}_2$  may explain why the amount of the shift of oxygen ( $0.4 \text{ \AA}$  in  $\text{SiO}_2$ ) and hence the Stokes shift in  $\text{SiO}_2$  is larger than in  $\text{Li}_2\text{O}$ .

We now compare the exciton relaxation in  $\text{Li}_2\text{O}$ , MgO and  $\text{Al}_2\text{O}_3$ ; in MgO, the presence of a sharp resonance-type luminescence [28] suggests that there is no self-trapping of an exciton while, in  $\text{Al}_2\text{O}_3$ , it is not yet clear whether excitons are self-trapped. Using the same conjecture, we can argue that, even though the value of the

matrix elements of the crystalline field for  $\text{MgO}$  is larger than that for  $\text{Li}_2\text{O}$ , the free volume for oxygen displacement is extremely small in  $\text{MgO}$ . Similarly, we may expect that the 'intrinsic' luminescence at 7.5 eV in  $\text{Al}_2\text{O}_3$  [29] is due to the self-trapping of excitons with qualitatively the same structure as those in  $\text{SiO}_2$  and  $\text{Li}_2\text{O}$ ; the small Stokes shift may be ascribed to the rather small free volume available for oxygen displacement.

A relatively high energy is needed to convert a self-trapped exciton to a Frenkel pair in  $\text{Li}_2\text{O}$ . The situation is very different for bi-self-trapped excitons. Experimentally it has been observed that the yield of F centres is higher when a specimen is bombarded with ions having a larger stopping power [5]. Presumably ions with a higher stopping power produce dense electronic excitation along their tracks, resulting in a higher yield of bi-self-trapped excitons and hence of defects. The phenomena is generally known as registration of heavy-ion tracks in insulating solids; the tracks of heavy ions are often etchable by etchants because of the heavy radiation damage [30].

## References

- [1] Uchida K, Noda K, Tanifuji T, Nasu K, Kirihara T and Kikuchi A 1980 *Phys. Status Solidi a* **58** 557
- [2] Noda K, Uchida K, Tanifuji T and Nasu K 1980 *Phys. Rev. B* **91** 234
- [3] Noda K, Uchida K, Tanifuji T and Nasu K 1981 *Phys. Rev. B* **24** 3736
- [4] Noda K, Ishii Y, Matsui H and Watanabe H 1986 *Radiat. Eff.* **97** 297
- [5] Noda K, Ishii Y, Matsui H, Ohno H, Hirano S and Watanabe H 1988 *J. Nucl. Mater.* **155-7** 568
- [6] Hughes A E and Henderson B 1972 *Point Defects in Solids* ed J H Crawford and L M Slifkin (New York: Plenum) p 381
- [7] Crawford J H Jr 1984 *Nucl. Instrum. Methods B* **1** 159
- [8] Itoh N and Tanimura K 1986 *Radiat. Eff.* **98** 435
- [9] Toyozawa Y 1983 *Physica B+C* **117-8** 23
- [10] Rashba R I *Excitons* ed R I Rashba and M D Sturge (Amsterdam: North Holland) p 543
- [10] Itoh N 1982 *Adv. Phys.* **31** 491
- Williams R T 1978 *Semicond. Insul.* **3** 251
- [11] Pascucci M R, Hutchison J L and Hobbs L W 1983 *Radiat. Eff.* **74** 219
- [12] Kassim H A 1986 *Phys. Status Solidi b* **137** 199
- [13] Ong C K 1985 *J. Phys. C: Solid State Phys.* **16** 4081
- [14] Shluger A L, Kotomin E A and Kantorovich L N 1986 *J. Phys. C: Solid State Phys.* **19** 4183
- [15] Shluger A L 1985 *Theor. Chim. Acta* **66** 355
- [16] Stefanovich E, Shidlovskaya E, Shluger A L and Zakharov M 1989 *Phys. Status Solidi b* at press
- [17] Shidlovskaya E, Stefanovich E and Shluger A L 1988 *Zh. Fiz. Khim.* **2** 1352 (in Russian)
- [18] Evarestov R A and Lovchikov V A 1977 *Phys. Status Solidi b* **80** 743
- [19] Evarestov R A 1982 *Quantum-Chemical Methods of Solid State Theory* (Leningrad: Leningrad State University Publishing House)
- [20] Dovesi R 1985 *Solid State Commun.* **54** 183
- [21] Shluger A L and Kotomin E A 1981 *Phys. Status Solidi b* **136** 673
- [22] Griscom D L 1979 *Proc. 33rd Frequency Control Symp.* (Washington, DC: Electronic Industries Association) p 98
- [23] Itoh C, Suzuki T and Itoh N 1990 *Phys. Rev. B* **41** 3794
- [24] Trukhin A N and Plaudis A E 1979 *Sov. Phys.-Solid State* **24** 644
- [25] Trukhin A N 1980 *Phys. Status Solidi b* **98** 541
- [26] Tanaka T, Eshita T, Tanimura K and Itoh N 1985 *Cryst. Lett. Defects Amorph. Mater.* **11** 221
- [27] Shluger A L 1988 *J. Phys. C: Solid State Phys.* **21** L431
- [28] Rachko Z A and Valbis J A 1979 *Phys. Status Solidi b* **93** 161
- [29] Runcimen W A 1968 *Solid State Commun.* **6** 537
- Kuznetsov A I, Jyessaar T E, Namozov B R and Uibo T V 1982 *Opt. Spectrosc. (USSR)* **52** 438
- [30] Dooryhee E, Langevin Y, Boag J, Duraud J P and Balanzat E 1988 *Nucl. Instrum. Methods B* **32** 264
- Itoh N 1989 *Radiat. Eff. Defects Solids* **110** 19