

## Photoconversion and dynamic hole recycling process in anion vacancies in neutron-irradiated MgO crystals

M. A. Monge, R. González, J. E. Muñoz Santiuste, and R. Pareja

*Departamento de Física, Escuela Politécnica Superior, Universidad Carlos III, Butarque 15, 28911 Leganés, Madrid, Spain*

Y. Chen

*Division of Materials Sciences, U. S. Department of Energy, Germantown, Maryland 20874-1290*

E. A. Kotomin\*

*Institute for Solid State Physics, University of Latvia, 8 Kengaraga, LV-1064 Riga, Latvia*

A. I. Popov

*Institute for Solid State Physics, University of Latvia, 8 Kengaraga, LV-1064 Riga, Latvia*

*and Departamento de Física, Escuela Politécnica Superior, Universidad Carlos III, Butarque 15, 28911, Leganés, Madrid, Spain*

(Received 12 June 1998)

Optical spectroscopy and theory demonstrate that photon excitation of the positively charged anion vacancies ( $F^+$  centers) at 5.0 eV in neutron-irradiated MgO crystals releases holes that are subsequently trapped at  $V$ -type centers, which are cation vacancies charge compensated by impurities, such as  $Al^{3+}$ ,  $F^-$ , and  $OH^-$  ions. The concentration of trapped-hole centers was found to exceed that of available anion vacancies. The disproportionately large amount of holes produced is attributed to a dynamic recycling process, by which the  $F^+$  center serves to release a hole to the  $V$ -type centers and subsequently trap a hole from an  $Fe^{3+}$  ion. The net effect was the increase of  $V$ -type centers mostly at the expense of  $Fe^{3+}$  ions. It was also shown that concurrently there was a component which distributed holes directly from  $Fe^{3+}$  to the  $V$ -type centers.

[S0163-1829(99)07829-7]

### I. INTRODUCTION

Magnesium oxide is a simple oxide with fcc structure and a melting temperature of  $\sim 3000$  K. The band gap is 7.8 eV. Defects produced in this material can be characterized by their optical properties.<sup>1</sup> Defects in the form of vacancies can be produced principally by two methods. The first is by irradiation with energetic particles, such as neutrons, electrons, and ions.<sup>2-9</sup> The second is by thermochemical reduction performed under very stringent environmental conditions resulting in stoichiometric deficiency of the oxygen sublattice.<sup>8,10-12</sup>

The present communication addresses photoconversion of the two charge states of the anion vacancies in neutron-irradiated MgO:  $F^+$  and  $F$  centers, which are oxygen vacancies with one and two electrons, respectively. The superscript refers to the net charge on the defect.

Elastic collisions with energetic particles do not produce cation vacancies, because the cation interstitials are unstable and quickly recombine with the vacancies.<sup>13</sup> However, cation vacancies can be produced by the displacement of protons substituting for magnesium ions via an ionization mechanism.<sup>14,15</sup> This latter mechanism is not reflected in the present study.

In MgO both the  $F^+$  and the  $F$  centers absorb essentially at the same energy, 4.92 and 5.01 eV, respectively.<sup>6</sup> In neutron-irradiated MgO, the equilibrium charge state of the anion vacancy is the  $F^+$  center; that is, at equilibrium anion vacancies are primarily in the one-electron state.<sup>16</sup> Therefore the present study will address the mechanism of the  $F^+$

$\rightarrow F$  photoconversion when excitation of the  $F^+$  absorption band results in  $F$  center formation. The simplest explanation is that an electron of the excited  $F^+$  center is ionized into the conduction band and then trapped by another  $F^+$  center thus giving rise to the two-electron  $F$  center. If this were true, no new defects are expected to arise except bare O vacancies. However, as we demonstrate in this paper both theoretically and experimentally, trapped-hole centers are produced and thus the photoconversion probably occurs through another mechanism.

The plan of the paper is as follows: in Sec. II we present results on theoretical simulations of the  $F^+$ ,  $F$  centers and their photoconversion. In Sec. III experiments are presented which complement the theory, in particular, hole release as a product of this process. A dynamic charge recycling process is described to account for the disproportionately larger hole release than there are  $F^+$  sites. In Sec. IV the main results are summarized.

### II. THEORY

In this study we used the semiempirical method of the intermediate neglect of the differential overlap (INDO) which is a simplified version of the Hartree-Fock formalism.<sup>17</sup> Its modification for ionic solids and oxides is described in Ref. 18. INDO allows simulations of quantum clusters containing hundreds of atoms with optimization of lattice geometry around defects. Recently, this method has been successfully applied to numerous pure and defective oxide crystals, including  $SiO_2$ ,  $Al_2O_3$ ,  $Li_2O$ ,  $ZrO_2$ .<sup>19</sup> More

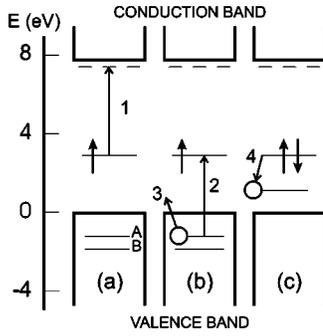


FIG. 1. Schematic model of the photoconversion mechanism. (a) Traditional model via  $F^+$  center electronic excitation (1) and electron release to the conduction band. (b) A mechanism based on the electron transition to the ground state of the  $F^+$  center (2) from the quasilocal states induced by the  $F^+$  center which leads to the hole formation in the VB (3). (c) Tunneling recombination is possible between a closely spaced  $F$  center and a hole center (4).

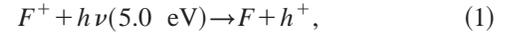
details for its application to MgO crystals can be found in Ref. 20. In recent studies of the  $F^+$  and  $F$  centers in MgO their optical and ESR properties<sup>21</sup> as well as activation energy for their diffusion<sup>22</sup> were discussed. Good agreement with a number of experimental data was achieved and several experiments on the luminescence of the  $F$  centers and their diffusion were interpreted. The important aspect of the present paper is that the positions of the ground state levels for both  $F^+$  and  $F$  centers are 3 eV above the top of the valence band, and their excited states are very close to the conduction band.

In this work, we have used 125-atom clusters of a cubic shape having  $O_h$  symmetry and embedded into the electrostatic field of the rest of the crystal. The calculated optical gap is close to the experimental value of 7.8 eV, with the bottom of the conduction band close to the vacuum level. Analysis of the  $F^+$  results showed the presence of two quasilocal states induced by the charged  $F^+$  center in the valence band (VB) [labeled A and B in Fig. 1(a)]. These levels are located at 1.2 and 2.0 eV below the top of the VB. Their molecular orbitals arise mainly from atomic orbitals of O atoms of the two spheres surrounding the O vacancy at (1,1,0) and (2,0,0) in the Mg-O lattice spacing units (Table I). Other similar quasilocal states are neither observed in calculations, nor expected from symmetry considerations, since the perturbation induced by the  $F^+$  center on the sur-

TABLE I. Atomic orbital coefficients of the molecular orbital in the two quasilocal energy states [A and B in Fig. 1(a)] induced in the valence band by the  $F^+$  center. Coordinates are in units of the Mg-O distance in the perfect lattice.

Atom	Level A	Level B
O (1,1,0)	$p_x = -0.204$	$p_x = -0.041$
	$p_y = 0.204$	$p_y = -0.041$
	$p_z = -0.1374$	$p_z = 0.0$
O (2,0,0)	$p_x = 0.04$	$p_x = 0.307$
	$p_y = -0.035$	$p_y = 0.0$
	$p_z = 0.0$	$p_z = 0.0$

rounding crystal decreases rapidly and is negligible at distances exceeding twice the Mg-O spacing. Since the ground-state energy level of the  $F^+$  center lies 3 eV above the VB, the excitation energy of the electron from the quasilocal state is close to that for the  $F^+$  center intrinsic excitation (5 eV). Based on this observation, we suggest the following interpretation of the  $F$ -type center photoconversion: under excitation, some of the  $F^+$  centers do not become electronically excited into the  $2p$ -type state, rather, electrons are photoexcited from the quasilocal states in the VB [Fig. 1(b)] to the ground state of the  $F^+$  centers; as a result,  $F$  centers in the ground state are produced. Simultaneously, a hole is produced on the quasilocal level. As is well known, in MgO holes are not self-trapped.<sup>23</sup> Since it is degenerate in energy with the VB, a hole is released into the latter and migrates until it is trapped by some impurity or defect. There is evidence<sup>24–29</sup> that this model is quite general in alkali halides and is valid, also, for other oxides, e.g.,  $Al_2O_3$ . In alkali halides, positively charged impurities induce local states in the valence band, and this is why excitation of electrons from quasilocal states leads to the hole center formation.<sup>24–29</sup> Creation of hole centers under photoexcitation is a key feature of our photoconversion model:



where  $h^+$  is a hole which migrates through the crystal and is eventually trapped by a defect. Experimental results complement this finding (see below): after photoexcitation with 5.0 eV light in the  $F^+$  absorption band, trapped-hole centers were observed by optical absorption spectroscopy. Another manifestation of this mechanism could be the prediction of the temperature-independent tunneling recombination of the  $F$  centers with holes trapped by vacancies or nearby impurities, probably accompanied by luminescence [Fig. 1(c)]. Similar processes have long been known in doped alkali halides.

### III. EXPERIMENTS

The MgO crystals used were grown at the Oak Ridge National Laboratory using the arc fusion technique.<sup>30</sup> The starting material was MgO powder from the Kanto Chemical Company, Japan. To a greater or lesser extent all MgO starting powders contain Fe impurities. Typical chemical analysis of the crystals has been reported previously.<sup>13,30,31</sup> In this particular sample, the iron concentration was estimated by optical absorption measurements<sup>32</sup> to be  $\sim 4 \times 10^{17} \text{ cm}^{-3}$ . The neutron irradiation was carried out in the Oak Ridge Bulk Shielding Reactor to a dose of  $5.3 \times 10^{15} \text{ neutrons cm}^{-2}$  ( $E \geq 0.1 \text{ MeV}$ ). The irradiating temperature was estimated to be 320 K. The samples were mechanically polished using a fine emery paper and the damaged regions were removed by chemical polishing in orthophosphoric acid solution at 360 K. No thermal annealing of defects occurs at this temperature.<sup>8</sup>

The spectrophotometer used in the UV-VIS-IR region was a Perkin-Elmer, Lambda 19 spectrophotometer. Far-infrared data were taken with a Perkin-Elmer FT-IR 2000 spectrophotometer. The errors involved in the optically determined results are  $\pm 25\%$ . The samples were excited with a low-intensity 5.0-eV light, the source being a 400-W Xe

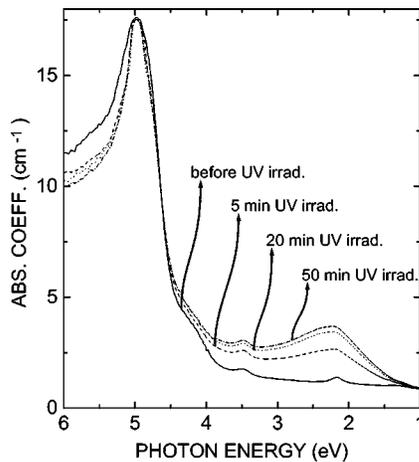


FIG. 2. Optical-absorption spectra of a neutron-irradiated MgO crystal before and after UV irradiations (crystal thickness: 3.1 mm).

lamp in conjunction with a 7200 Oriel monochromator set at 250 nm.

The neutron-irradiated crystal had an anion vacancy concentration of  $\approx 8 \times 10^{16} \text{ cm}^{-3}$  as determined<sup>13</sup> from the absorption coefficient at 5.0 eV. This crystal was excited with 5.0 eV light. These photons in principle will excite both  $F^+$  and  $F$  centers, since their absorption bands peak at 5.0 eV. Given that in neutron-irradiated crystals the anion vacancies at equilibrium are primarily in the paramagnetic  $F^+$  charge state, photoconversion will primarily involve the release of a hole from a  $F^+$  center, according to Eq. (1).

### A. Trapped-hole centers

We shall use optical-absorption measurements to determine where the holes are ultimately trapped. The result of photon excitation with 5.0 eV light is shown in Fig. 2. With continued excitation, an absorption band centered at 2.3 eV increased. Some activity, albeit small, occurred at 5.0 eV. Photoconversion resulting in  $F$  centers would still have absorption at 5.0 eV. The 2.3-eV band is known to be due to holes trapped at centers compensated primarily by  $\text{Al}^{3+}$ ,  $\text{F}^-$ , or  $\text{OH}^-$  ions.<sup>14,33,34</sup> The resulting defects, referred to as  $V_{\text{Al}}$ ,  $V_{\text{F}}$ , or  $V_{\text{OH}}$  centers, are due to:



where the linear configurations are  $\text{Al}^{3+}-\text{O}^{2-}-[\text{Mg vacancy}]-\text{O}^-$ ;  $\text{Mg}^{2+}-\text{F}^- - [\text{Mg vacancy}]-\text{O}^-$ ; and  $\text{Mg}^{2+}-\text{OH}^- - [\text{Mg vacancy}]-\text{O}^-$ , respectively.<sup>34</sup> The  $\text{O}^-$  represents an  $\text{O}^{2-}$  ion with a trapped hole. The trapped holes at these centers are metastable and have a half-life of several hours at room temperature.<sup>34</sup>

Infrared spectroscopy can be used to monitor the trapping of holes by one of the  $V$ -type centers,  $V_{\text{OH}}^-$ , to form  $V_{\text{OH}}$  centers. It is well established<sup>35-37</sup> that the  $\text{OH}^-$  stretching frequency for the  $V_{\text{OH}}^-$  occurs at  $3296 \text{ cm}^{-1}$  and for the  $V_{\text{OH}}$  is at  $3323 \text{ cm}^{-1}$ . The bands at  $3340$  and  $3375 \text{ cm}^{-1}$  have been attributed to  $V_{\text{OH}}^-$  centers perturbed by nearby

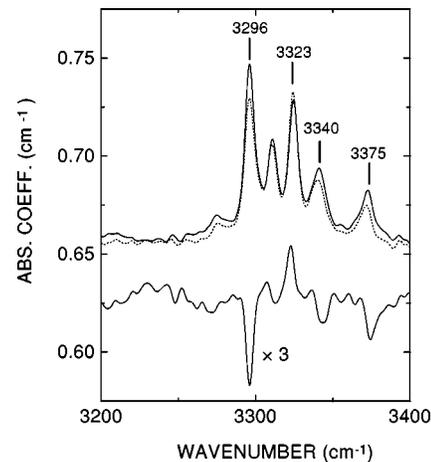


FIG. 3. Top: Infrared optical-absorption spectra of a  $n$ -irradiated MgO crystal before (solid line) and after UV irradiation for 1 h (dotted line). The differential spectrum (bottom) is enlarged by a factor of 3.

impurities.<sup>35,36</sup> The infrared spectra before and after excitation with 5.0 eV light is shown in Fig. 3. The differential spectrum is shown at the bottom. It is clear that during excitation,  $V_{\text{OH}}$  centers are formed at the expense of  $V_{\text{OH}}^-$  centers, indicating that holes had been trapped.

The increase in concentration of trapped-hole centers during irradiation can be estimated<sup>14</sup> from the optical-absorption coefficient using the equation  $\Delta N = 1.4 \times 10^{17} \Delta \alpha_{\text{max}}$ , where  $\Delta \alpha_{\text{max}}$  is the increase in the absorption coefficient at the peak of the 2.3-eV band. The value for  $\Delta \alpha_{\text{max}}$  was obtained after computer deconvolution of the spectrum. The resulting value after 75 min of UV irradiation was  $4 \times 10^{17} \text{ cm}^{-3}$ . This value is five times the total concentration of anion vacancies. Even assuming that all the anion vacancies were in the  $F^+$  state and all the  $F^+$  centers were converted to  $F$  centers, there are still not enough holes to account for all the holes trapped at  $V$ -type centers.

### B. Dynamic hole recycling process

Where did the holes come from? How are the holes processed to form trapped-hole centers? One possibility is that an aliovalent impurity, such as Fe, also absorbing at 5.0 eV, directly transfers holes to the  $V$ -type centers under 5.0 eV excitation. The results we will present later in Figs. 4–6 show that this possibility can occur concurrently with another mechanism, which we shall refer to as a dynamic hole recycling process. In this process we propose that the  $F^+$  centers serve as the main recycling depot to provide holes for distribution and that  $\text{Fe}^{3+}$  ions serve as the main source of holes. Cheng and Kemp<sup>38</sup> have demonstrated conclusively from double resonance studies (electron paramagnetic resonance-Faraday rotation) that the bands at 4.3 and 5.7 eV are due to charge-transfer bands of the  $\text{Fe}^{3+}$  ion.<sup>38</sup> Figure 2 shows that the absorption in the vicinity of 5.7 eV decreases. To obtain better resolution in the UV region, we thinned down a neutron-irradiated crystal to 1.8 mm and excited it with 5.0 eV light. The results are shown in Fig. 4. The differential spectrum is shown at the bottom. The gain at 2.3 eV

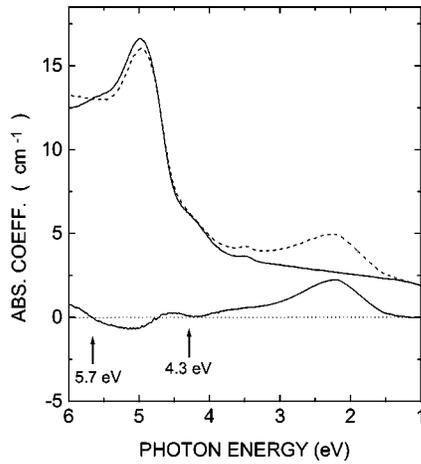


FIG. 4. Optical-absorption spectra of a  $n$ -irradiated MgO crystal before and after UV irradiation. The differential spectrum is shown at the bottom (crystal thickness: 1.8 mm).

was unmistakable and the corresponding  $V$ -type center concentration was again  $4 \times 10^{17} \text{ cm}^{-3}$ . A small decrease at 4.3 eV was observed. Mainly a decrease was noted in the neighborhood of 5.3 eV, which can be attributed to activities of  $F^+ \rightarrow F$ , and  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$  reactions; the latter can be described according to



The recycling process may be described as follows: (a)  $F^+ + h\nu(5.0 \text{ eV}) \rightarrow F + h^+$ , the hole is trapped by a  $V$ -type center and becomes thermally metastable; (b) The  $F$  center left behind traps a hole from somewhere, most likely aliovalent impurities such as Fe, and becomes an  $F^+$  center, according to  $F + h^+ \rightarrow F^+$ . The cycle proceeds again.

The question now arises whether holes from the  $\text{Fe}^{3+}$  can contribute *directly* to the trapped-hole centers (without the presence of anion vacancies).  $F^+$  centers were completely annealed out by heating the same sample at 1273 K for 30

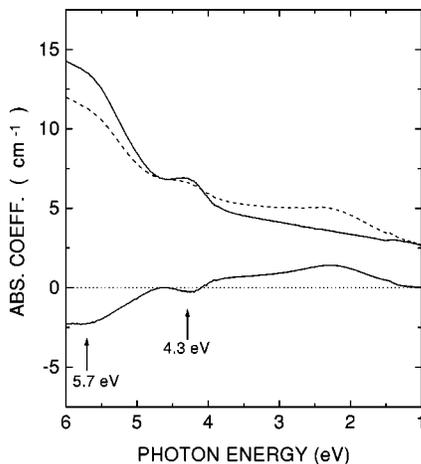


FIG. 5. Optical-absorption spectra of a  $n$ -irradiated MgO crystal, annealed at 1273 K for 30 min in flowing Ar, before (solid line) and after UV irradiation (dotted line). The differential spectrum is shown at the bottom.

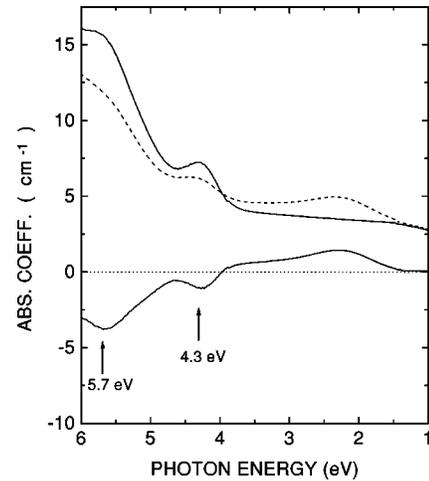


FIG. 6. Optical-absorption spectra before (solid line) and after UV irradiation (dotted line) of a  $n$ -irradiated MgO crystal annealed at 1273 K for 30 min in flowing Ar and at 1473 K in flowing  $\text{O}_2$  for 30 min.

min in flowing argon. The sample was then excited with 5.0 eV light for 75 min. The spectra before and after UV excitation are shown in Fig. 5. It is noted that the  $\text{Fe}^{3+}$  bands at 4.3 and 5.7 eV are sufficiently broad that 5.0 eV light excites both of these bands, albeit weakly. The net hole transfer was nearly half the amount when  $F^+$  centers were present. The concentration of  $V$ -type centers became  $1.7 \times 10^{17} \text{ cm}^{-3}$  instead of  $4 \times 10^{17} \text{ cm}^{-3}$ . Correspondingly the absorption at 4.3 and 5.7 eV decreased.

Finally, we demonstrate that more intense  $\text{Fe}^{3+}$  absorption bands enhance hole transfer to the  $V$ -type centers. We know from past studies<sup>32</sup> that  $\text{Fe}^{3+}$  concentration can be enhanced by oxidation at high temperatures. The same sample was heated in flowing oxygen, instead of argon, at 1273 K. The trapped-hole concentration after 75 min UV photoexcitation increased slightly to  $2.0 \times 10^{17} \text{ cm}^{-3}$ , half of what it was when  $F^+$  centers were present (Fig. 6). The decrease of the 4.3 and 5.7 eV bands was more pronounced (Fig. 6).

The present study indicates that during UV excitation of a neutron-irradiated MgO crystal there are two different channels which provide holes to create  $V$ -type centers. Holes from  $\text{Fe}^{3+}$  ions are transferred *directly* to the  $V$ -type centers, as well as *indirectly* via the  $F^+$  centers.

#### IV. SUMMARY AND CONCLUSIONS

In neutron-irradiated MgO crystals, theory and experiments indicate that the photoconversion mechanism of anion vacancies probably occurs via electron transfer to the  $F^+$  center from the quasilocal states which it induced in the valence band. Thus  $F$  centers and holes are produced.

There are two mechanisms by which holes from an aliovalent impurity can be transferred to the  $V$ -type centers during photoexcitation at 5.0 eV. (In MgO the prevalent aliovalent impurity is Fe.) The first is the direct transfer of holes from  $\text{Fe}^{3+}$  ions, which absorb at 4.3 and 5.7 eV, to the  $V$ -type centers (cation vacancies charge compensated by aliovalent impurities such as  $\text{Al}^{3+}$ ,  $\text{F}^-$ , and  $\text{OH}^-$  ions). The second is an indirect transfer of holes via anion vacancies: The excessively high concentration of trapped-hole centers

observed during the photoexcitation dictates a dynamic recycling process. In this model the  $F^+$  centers serve as a depot to release holes to the  $V$ -type centers and subsequently to trap holes from  $Fe^{3+}$  ions. The conclusion from the present study is that the increase of trapped-hole centers occurs mainly at the expense of  $Fe^{3+}$  ions, both directly or indirectly via a recycling process at the anion-vacancy sites.

In general, the prevalence of charge recycling processes during photoexcitation in any material with a sufficiently wide band gap should not be surprising. After all, electron/hole transfer processes during excitation are dynamic, not static.

## ACKNOWLEDGMENTS

Research at the University Carlos III was supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT) of Spain and the Comunidad Autónoma de Madrid (CAM). The research of Y.C. is an outgrowth of past investigations performed at the Oak Ridge National Laboratory. A.I.P. was supported by the Latvian Research Council (Grant No 96. 0666) and E.A.K. by the Deutsche Forschungsgemeinschaft through the grant to the Osnabrück University. A.I.P. acknowledges the Dirección General de Enseñanza Superior e Investigación Científica of Spain for a sabbatical grant.

- 
- \*Also at: Fachbereich Physik, Universität Osnabrück, D-49069 Osnabrück, Germany.
- <sup>1</sup>J. H. Crawford, Jr., *Adv. Ceram. Mater.* **10**, 793 (1983); *Nucl. Instrum. Methods Phys. Res. B* **1**, 159 (1984).
  - <sup>2</sup>I. K. Ludlow and W. A. Runciman, *Proc. Phys. Soc. London* **86**, 1081 (1965).
  - <sup>3</sup>B. Henderson and R. D. King, *Philos. Mag.* **13**, 1149 (1966).
  - <sup>4</sup>I. K. Ludlow, *Proc. Phys. Soc. London* **88**, 763 (1966).
  - <sup>5</sup>B. Henderson and J. E. Wertz, *Adv. Phys.* **17**, 749 (1968).
  - <sup>6</sup>Y. Chen, J. L. Kolopus, and W. A. Sibley, *Phys. Rev.* **186**, 865 (1969).
  - <sup>7</sup>Y. Chen and X. Sibley, *Philos. Mag.* **20**, 217 (1969).
  - <sup>8</sup>Y. Chen, R. T. Williams, and W. A. Sibley, *Phys. Rev.* **182**, 960 (1969).
  - <sup>9</sup>L. A. Kappers, R. L. Kroes, and E. B. Hensley, *Phys. Rev. B* **1**, 4151 (1970).
  - <sup>10</sup>L. A. Kappers and E. B. Hensley, *Phys. Rev. B* **6**, 2475 (1972).
  - <sup>11</sup>R. González, Y. Chen, and M. Mostoller, *Phys. Rev. B* **24**, 6862 (1981).
  - <sup>12</sup>Y. Chen, R. González, O. E. Schow, and G. P. Summers, *Phys. Rev. B* **27**, 1276 (1983).
  - <sup>13</sup>W. A. Sibley and Y. Chen, *Phys. Rev.* **160**, 712 (1967).
  - <sup>14</sup>Y. Chen, M. M. Abraham, L. C. Templeton, and W. P. Unruh, *Phys. Rev. B* **11**, 881 (1975).
  - <sup>15</sup>Y. Chen, M. M. Abraham, and H. T. Tohver, *Phys. Rev. Lett.* **37**, 1757 (1976).
  - <sup>16</sup>B. Henderson and R. D. King, *Philos. Mag.* **13**, 1149 (1966).
  - <sup>17</sup>J. A. Pople and D. Beveridge, *Approximate Molecular Orbital Theory* (McGraw-Hill, New York, 1980).
  - <sup>18</sup>A. L. Shluger and A. V. Stefanovich, *Phys. Rev. B* **42**, 9664 (1990); E. V. Stefanovich, E. K. Shidlovskaya, A. L. Shluger, and M. A. Zakharov, *Phys. Status Solidi B* **160**, 529 (1990).
  - <sup>19</sup>P. W. M. Jacobs and E. A. Kotomin, *Phys. Rev. Lett.* **69**, 1411 (1992); A. L. Shluger and N. Itoh, *J. Phys.: Condens. Matter* **2**, 4119 (1990); J. L. Gavartin, C. R. A. Catlow, A. L. Shluger, A. N. Varaksin, and Y. N. Kolmogorov, *Modell. Simul. Mater. Sci. Eng.* **1**, 29 (1992); E. V. Stefanovich, A. L. Shluger, and C. R. A. Catlow, *Phys. Rev. B* **49**, 11 560 (1994).
  - <sup>20</sup>A. L. Shluger, E. A. Kotomin, and L. N. Kantorovich, *J. Phys. C* **19**, 4183 (1986); A. L. Shluger, J. D. Gale, and C. R. Catlow, *J. Chem. Phys.* **96**, 10 389 (1992).
  - <sup>21</sup>R. I. Eglitis, M. M. Kuklja, E. A. Kotomin, A. Stashans, and A. I. Popov, *Comput. Mater. Sci.* **5**, 298 (1996); E. A. Kotomin, M. M. Kuklja, R. I. Eglitis, and A. I. Popov, *Mater. Sci. Eng., B* **37**, 212 (1996).
  - <sup>22</sup>A. I. Popov, E. A. Kotomin, and M. M. Kuklja, *Phys. Status Solidi B* **195**, 61 (1996).
  - <sup>23</sup>N. Itoh, *Mater. Sci. Forum* **239-241**, 509 (1997).
  - <sup>24</sup>E. A. Kotomin, A. I. Popov, and A. Stashans, *J. Phys.: Condens. Matter* **6**, L569 (1994).
  - <sup>25</sup>N. N. Kristoffel, *Bull. Acad. Sci. USSR, Phys. Ser.* **30**, 1533 (1966).
  - <sup>26</sup>V. S. Osminin, G. S. Zavt, S. G. Zazubovich, and A. I. Nijlisk, *Bull. Acad. Sci. USSR, Phys. Ser.* **38**, 1235 (1974).
  - <sup>27</sup>E. A. Kotomin, A. L. Shluger, and I. A. Tale, *Solid State Commun.* **46**, 625 (1983).
  - <sup>28</sup>S. N. Mysovskiy, A. I. Nepomnyashchikh, and A. L. Shluger, *Opt. Spektrosk.* **63**, 129 (1987); A. L. Shluger, S. N. Mysovskiy, and A. I. Nepomnyashchikh, *J. Phys. Chem. Solids* **49**, 1043 (1988).
  - <sup>29</sup>A. G. Badalyan, P. G. Baranov, and R. A. Zhitnikov, *Fiz. Tverd. Tela (Leningrad)* **19**, 3575 (1977) [*Sov. Phys. Solid State* **19**, 2089 (1977); **19**, 1847 (1977) [**19**, 1079 (1977)]]].
  - <sup>30</sup>M. M. Abraham, C. T. Butler, and Y. Chen, *J. Chem. Phys.* **55**, 372 (1971).
  - <sup>31</sup>C. Ballesteros, R. González, S. J. Pennycook, and Y. Chen, *Phys. Rev. B* **38**, 4231 (1988).
  - <sup>32</sup>Y. Chen and W. A. Sibley, *Phys. Rev.* **154**, 842 (1967).
  - <sup>33</sup>Y. Chen and R. González, *Opt. Lett.* **10**, 276 (1985).
  - <sup>34</sup>Y. Chen and M. M. Abraham, *J. Phys. Chem. Solids* **51**, 747 (1990).
  - <sup>35</sup>A. M. Glass and T. M. Searle, *J. Chem. Phys.* **46**, 2096 (1967).
  - <sup>36</sup>B. Henderson and W. A. Sibley, *J. Chem. Phys.* **55**, 1276 (1971).
  - <sup>37</sup>B. Henderson, J. L. Kolopus, and W. P. Unruh, *J. Chem. Phys.* **55**, 3518 (1971).
  - <sup>38</sup>J. C. Cheng and J. C. Kemp, *Phys. Rev. B* **4**, 2841 (1971).