PHYSICAL REVIEW B **84**, 115204 (2011)

# Optical properties of triplet states of excitons bound to interstitial-carbon interstitial-oxygen defects in silicon

T. Ishikawa,[1] K. Koga,[1] T. Itahashi,[1] K. M. Itoh,[1,*] and L. S. Vlasenko[2]

[1]*Graduate School of Fundamental Science and Technology, Keio University, Yokohama 223-8522, Japan*

[2]*A. F. Ioffe Physico-Technical Institute of Russian Academy of Sciences, 194021 St. Petersburg, Russia*

(Received 16 May 2011; published 15 September 2011)

Observation of photoluminescence from spin triplet states of excitons bound to interstitial carbon-oxygen complexes ($C_i$-$O_i$) in silicon is reported. New luminescence peak labeled as $C_T$ line emerges at the energy 2.64 meV below the well-known luminescence from the no-phonon transition of a $C_i$-$O_i$ singlet state situating at 790 meV (C line). Observations of local vibrational modes associated with $C_T$ line and the temperature dependence of the relative intensity between $C_T$ and C lines lead to unambiguous identification of $C_T$ line as the no-phonon line from $C_i$-$O_i$ defects. In addition, the host silicon isotope shift of $C_T$ line is equal to that of C line, indicating that $C_T$ line is no-phonon luminescence as well. Furthermore, our photoluminescence measurements carried out in magnetic field show that $C_T$ line is associated with an isotropic spin triplet state due to quenching of orbital angular momentum of the hole composing the bound exciton.

DOI: 10.1103/PhysRevB.84.115204 PACS number(s): 78.55.−m, 71.35.−y, 71.55.Cn

## I. INTRODUCTION

Irradiation of Czochralski-grown silicon (Cz-Si) crystals with $\gamma$-rays, electrons, or neutrons creates interstitial carbon-oxygen complexes ($C_i$-$O_i$) in Si emitting no-phonon (NP) luminescence at 790 meV (C-line) accompanied by phonon replicas at lower energies.[1–3] Optical and electronic properties of the $C_i$-$O_i$ centers have been revealed by infrared absorption spectroscopy,[4–6] photoluminescence (PL),[5,7–11] electron paramagnetic resonance,[12] Hall effect and deep-level transient spectroscopy (DLTS),[13] and local-vibrational mode (LVM) spectroscopy,[15,17] whose results are strongly supported by density functional calculation.[14–17] A $C_i$-$O_i$ center with a bound exction can be regarded as an isoelectronic donor,[10,20] since the hole is trapped by the short-range defect potential while the electron is bound by the long-range Coulombic potential of the hole.[19,20] It is known that an isoelectronic donor can possess spin singlet and triplet states when the short-range potential of the defect is much stronger than the spin-orbit interaction and/or when the defect has low symmetry.[18] Indeed, $C_i$-$O_i$ has both the strong short-range potential (hole binding energy $E_h = 341$ meV)[10] and low symmetry ($C_{1h}$ symmetry).[21] A previous exciton decay study has implied the existence of the spin triplet state at 3.2 meV below the singlet state corresponding to C line.[22] However, experimental observation of the triplet state of $C_i$-$O_i$ has never been reported before. The present paper reports photoluminescence observation of the triplet states ($C_T$ line), whose peak position is 2.64 meV below the spin-singlet C line.

We establish that $C_T$ line is a NP line of $C_i$-$O_i$ by observations of the local vibration modes associated with $C_T$ line, the temperature dependence of the relative intensity between $C_T$ and C lines, and host Si isotope effects on these lines. Based on PL measurements under magnetic fields, we identify $C_T$ line as luminescence from isotropic spin triplet states of the excitons bound to $C_i$-$O_i$.

## II. EXPERIMENTAL PROCEDURES

A commercially available Cz-Si ($^{nat}$Si) and home-made isotopically enriched $^{29}$Si and $^{30}$Si single crystals[23,24] were employed. The samples were irradiated at room temperature by 1 meV electron beam or $\gamma$-ray from $^{60}$Co to form $C_i$-$O_i$ complexes. Table I shows the type of irradiation, host silicon isotopic composition, and neutral $C_i$-$O_i$ concentration estimated by absorption coefficient of the 790 meV NP peak[25] for each sample. During photoluminescence measurements, the samples were immersed in a liquid helium of $T = 1.6 - 4.2$K or placed in a continuous He flow cryostat for higher temperatures in strain-free manners. PL spectra were collected with the BOMEM DA8 Fourier transform interferometer equipped with a liquid nitrogen-cooled germanium detector for the spectral range 750–800 meV and with InSb detector for the lower range down to 550 meV. The excitation was provided by the 1047-nm line of a Nd:YLF laser. A superconducting magnet was used to apply a magnetic field parallel to the optical axis.

## III. RESULTS

### A. Photoluminescence from excitons bound to $C_i$-$O_i$ in $^{nat}$Si

Figure 1 shows a series of PL peaks arising from $C_i$-$O_i$ in $^{nat}$Si without magnetic field at the sample temperature $T \sim 2$ K. The sharp 789.67 meV line corresponds to the NP luminescence from the singlet $C_i$-$O_i$ state and is referred to as C line or $C_0$ line.[7] The phonon replica and LVM shifts of $C_0$ lines are also shown in Fig. 1 and labeled in the manner introduced in Ref. 8. In addition, previously unidentified PL peaks at 787.03 meV labeled $C_T$ line and at 714.26 meV labeled $C_T^{L2}$ emerge. The position of $C_T$ line is 2.64 meV below that of $C_0$ line and that of $C_T^{L2}$ line is 2.63 meV below that of $C_0^{L2}$ peak corresponding to $C_0$ line shifted by L2 vibrational mode. This observation of the same energy separations between $C_0$-$C_T$ and $C_0^{L2}$-$C_T^{L2}$ suggests strongly that the luminescence of the $C_T$ and $C_0$ families arise from the same defect, i.e., $C_i$-$O_i$. Further evidence for $C_T$ and $C_0$ having the same origin is shown in Fig. 2. Here, both $C_T$ and $C_T^{L2}$ are observed at $T \sim 2$ K but not at $T \sim 20$ K. Thus, $C_T^{L2}$ must correspond to $C_T$ line shifted by the L2 vibrational mode. Since L2 is attributed unambiguously to the LVM shift of the $C_i$-$O_i$ luminescence, the identification of $C_T^{L2}$ mode establishes that $C_T$ lines originate from the $C_i$-$O_i$

TABLE I. Type of irradiation, host silicon isotopic composition, and neutral C$_i$-O$_i$ concentration of the three samples investigated in this study.

| Sample | Irradiation | [$^{28}$Si] (%) | [$^{29}$Si] (%) | [$^{30}$Si] (%) | [C$_i$ − O$_i^0$] (cm$^{-3}$) |
|---|---|---|---|---|---|
| $^{nat}$Si | Electron | 92.2 | 4.7 | 3.1 | $2.9 \times 10^{16}$ |
| $^{29}$Si | $\gamma$-ray ($^{60}$Co) | 0.56 | 99.23 | 0.21 | $5.5 \times 10^{15}$ |
| $^{30}$Si | $\gamma$-ray ($^{60}$Co) | 0.67 | 0.59 | 98.74 | $2.1 \times 10^{16}$ |

defects. Note that L1 vibrational mode associated with C$_T$ line couldn't be observed because its position is expected to overlap with the position of $C_0^{L2'}$ in $^{nat}$Si.

Figure 3 shows the logarithm variation of the intensity ratio $I_{C_T}/I_{C_0}$ as a function of $kT$, where $k$ is the Boltzman constant. $I_{C_T}$ and $I_{C_0}$ are the intensities of C$_T$ and C$_0$ lines, respectively. The temperature of the sample in this measurement was determined precisely from the linewidth of free excitons of a commercial float-zone $n$-type silicon sample that was placed right next to those three samples in the cryostat.[3,26] We obtain a solid line in Fig. 3 by fitting of logarithm of the following equation[27]:

$$\frac{I_{C_T}}{I_{C_0}} = \frac{g_{C_T} f_{C_T}}{g_{C_0} f_{C_0}} \exp\left(\frac{\Delta E}{kT}\right), \tag{1}$$

where $g_{C_0,C_T}$ and $f_{C_0,C_T}$ are the degeneracy factors and the transition probabilities, respectively. $\Delta E \sim 1.7 \pm 0.2$ meV obtained by fitting is in reasonable agreement with the experimentally observed line separation of 2.64 meV. Since the relative intensity follows the Boltzmann distribution [Eq. (1)], this temperature dependence also supports our conclusion of C$_T$ lines originating from C$_i$-O$_i$.

Figure 4 shows the photoluminescence of C$_i$-O$_i$ in $^{nat}$Si, $^{29}$Si, and $^{30}$Si. The energy shifts of C$_T$ and C$_0$ lines due to the change in the host Si isotopic compositions are clearly seen. The host Si isotope shift of C$_0$ line agrees very well with the one reported before.[9] The isotope shifts as a function of the average mass of the Si atoms, $M$, is shown in Fig. 5. Both the C$_0$- and C$_T$-line positions change linearly with $M^{-1/2}$. The isotope shift of the NP line arises from thermal expansion, electron-phonon interaction, and zero-point motions of the local vibrational modes. Among them, electron-phonon interaction and thermal expansion are proportional to $M^{-1/2}$. The authors of Ref. 9 concluded that the dominant contribution to the isotope shift of C$_0$ line was the electron-phonon interaction.[9] The same dependence of the shifts by $M$ for C$_T$ and C$_0$ lines suggest that the electron-phonon interaction is also responsible for the

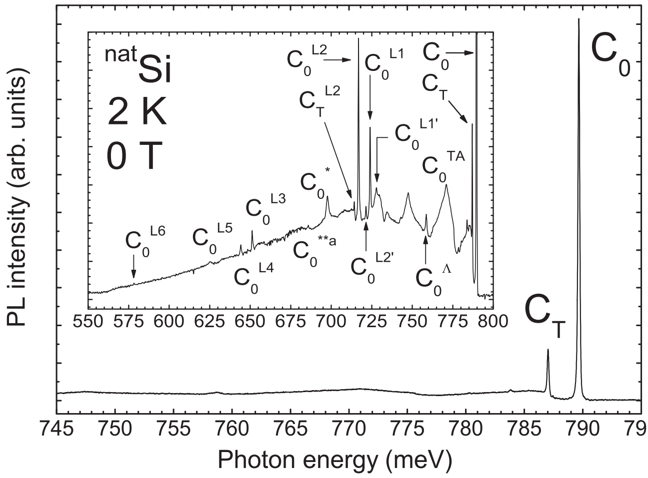

FIG. 1. A series of PL peaks arising from C$_i$-O$_i$ in $^{nat}$Si without magnetic field at the sample temperature $T \sim 2$ K. A sharp 789.67 meV line corresponds to the NP luminescence from the singlet C$_i$-O$_i$ state and is referred to as C line or C$_0$ line.[7] The phonon replica and LVM shifts of C$_0$ lines are seen clearly in the magnified view given in the inset. Those peaks are labeled in the manner introduced in Ref. 8. In addition, previously unidentified PL peaks labeled C$_T$ and $C_T^{L2}$ lines emerge.

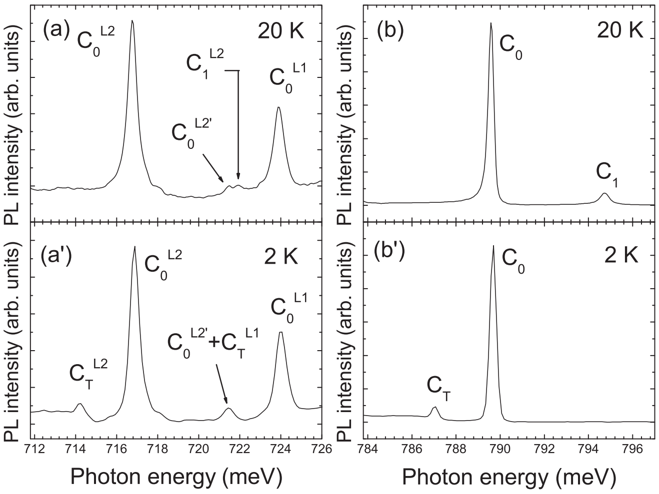

FIG. 2. (a) and (a′) show the phonon replica and LVM shifted PL lines of C$_i$-O$_i$ obtained at $T \sim 20$ K and $\sim 2$ K, respectively. (b) and (b′) show the NP lines of C$_i$-O$_i$ obtained at $T \sim 20$ K and $\sim 2$ K. A NP line of the excited state C$_1$[7,8] is observed clearly in (b).

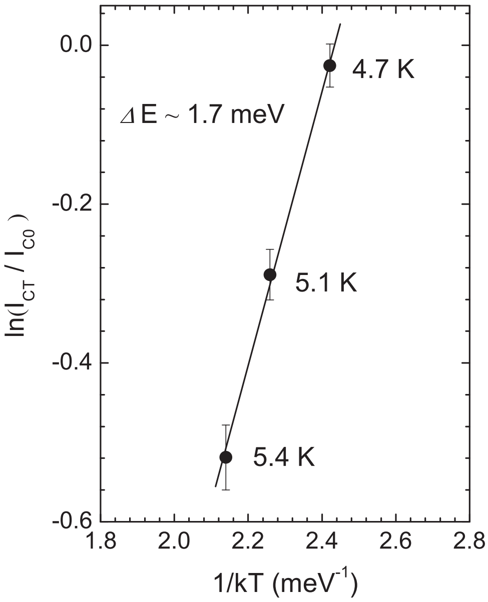

FIG. 3. The natural logarithm variation of the intensity ratio $I_{C_T}/I_{C_0}$ as a function of $kT$, where $k$ is the Boltzman constant. $I_{C_T}$ and $I_{C_0}$ are the intensities of C$_T$ and C$_0$ lines, respectively.

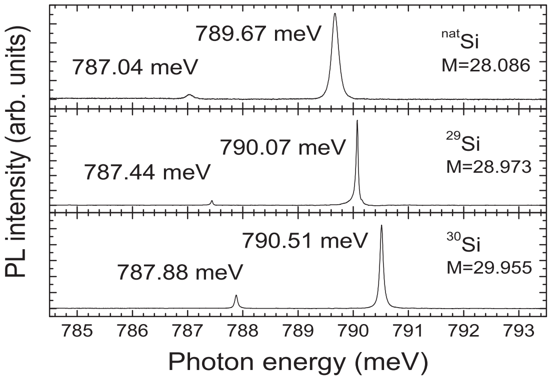

FIG. 4. The top, middle, and bottom panels show the PL spectra of $C_0$ and $C_T$ lines recorded at $T = 2$ K in $^{\mathrm{nat}}$Si, $^{29}$Si, and $^{30}$Si, respectively. $M$ is the average mass of the host Si atoms.

shift of $C_T$ line. Thus, the $C_T$ line can be identified as a NP line from $C_i$-$O_i$.

The fact that the $C_T$-line series originates from triplet states is established by the following Zeeman study of the excitons bound to $C_i$-$O_i$. Figure 6 shows that $C_0$ line has no splitting under the magnetic field because $C_0$ line arises from the singlet state.[10] On the other hand, as shown in Figs. 6 and 7, $C_T$ line is separated into three peaks under the magnetic field. Moreover, the Zeeman peak positions of both $C_0$ and $C_T$ line are found to be independent of the magnetic field direction when the sample is rotated around $[1\bar{1}0]$ axis ($\theta = 0^\circ$ for [001] and $\theta = 90^\circ$ for [110]) as shown in Fig. 7. Therefore, we reach at the conclusion that $C_T$ line is the photoluminescence from a triply degenerate state of the excitons bound to $C_i$-$O_i$. The resulting angular independent spin singlet and triplet states with an isotropic $g$-value $\simeq 2$ are indicative of quenching of the hole angular momentum as the consequence of the low symmetry and/or strong-axial strain field around $C_i$-$O_i$.[18,29]

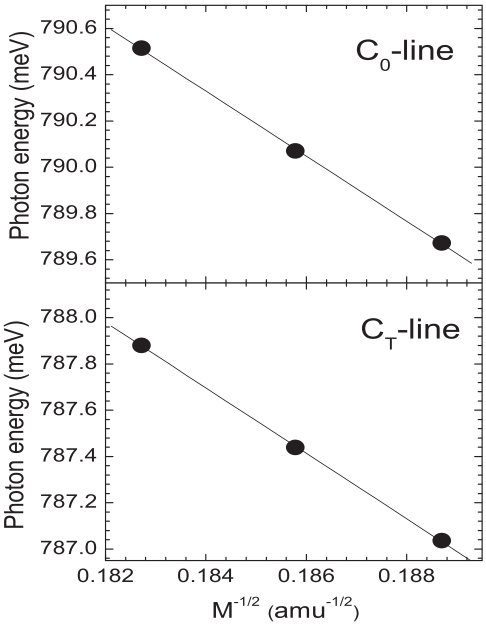

FIG. 5. The isotope shifts of $C_0$- and $C_T$-line positions as a function of $M^{-1/2}$.

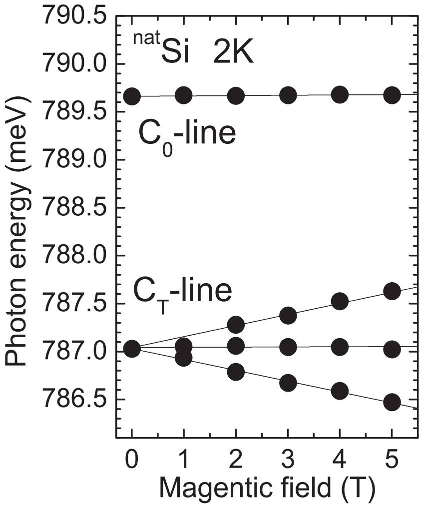

FIG. 6. PL peak positions of $C_0$ and $C_T$ lines as a function of the the externally applied magnetic field along the [001] crystal axis.

## IV. DISCUSSIONS

It has been suggested that the energy difference between the spin singlet state and the triplet state is around 3.2 meV.[22] This value is in good agreement with our 2.64 meV obtained from the difference between $C_T$ and $C_0$ lines. Furthermore, the intercept at $T \to \infty$ in Fig. 3 is $-4.2 \pm 0.4$, which corresponds to the prefactor $g_{C_T} f_{C_T} / g_{C_0} f_{C_0}$ in Eq. (1). Thus, $\log_{10}(f_{C_T}/f_{C_0}) \approx -2.3 \pm 0.2$ is estimated using $g_{C_T} = 3$ and $g_{C_0} = 1$. This value is in good agreement with the previously calculated value $\log_{10}(f_{C_T}/f_{C_0}) \approx -2.8$ for C line,[28] and our estimation also supports our conclusion that the $C_T$ line is luminescence from spin triplet states of the bound excitons. In addition, our study also allows for the estimation of the relative transition probabilities of spin singlet and spin triplet states in $^{29}$Si, i.e., $\log_{10}(f_{C_T}/f_{C_0}) \approx -1.9 \pm 0.2$. Regarding $^{30}$Si, the ratio of single and triplet transition probabilities is $-1.5 \pm 0.1$. The shift of NP luminescence from $^{\mathrm{nat}}$Si due to Si isotopic composition is 0.4 and 0.8 meV for $^{29}$Si and $^{30}$Si, respectively. However, Fig. 3 in Ref. 28 shows that changes

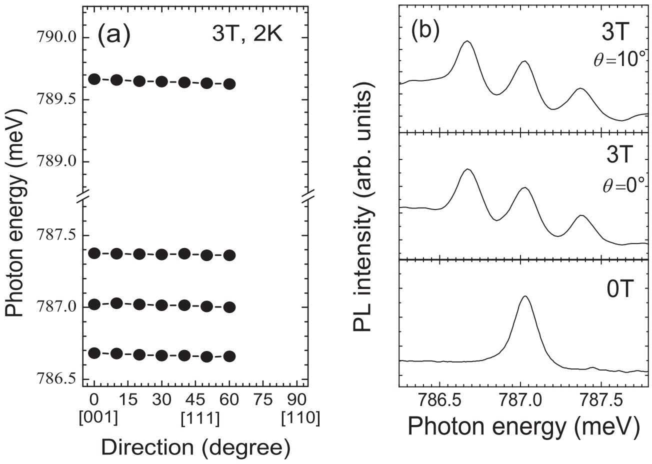

FIG. 7. PL peak positions of $C_0$ and $C_T$ lines when the sample is rotated around $[1\bar{1}0]$ axis where $\theta = 0^\circ$ for $\mathbf{B} \parallel [001]$ and $\theta = 90^\circ$ for $\mathbf{B} \parallel [110]$.

in the binding energy of $^{29}$Si and $^{30}$Si are much more than the peak shifts we observed. Here, the changes in the binding energy were deduced assuming that the local axial field on a hole is the only contribution. Our results imply that the change in the binding energies is caused not only by the change in the local axial field but also by other contributions. Further studies are needed to understand such detail.

One may wonder why the slopes of the photon energy vs. $M^{-1/2}$ are the same for $C_0$ and $C_T$ lines (Fig. 5), since they can be different if the host silicon isotope effect on electron-hole exchange interaction causes the spin singlet-triplet splitting of the bound exciton.[18,29] To estimate this effect, it is useful to compare with the isotope shift of the exciton binding energy of shallow phosphorus donors with ionization energy of 45 meV in silicon since $C_i$-$O_i$ is an isoelectronic donor with ionization energy of 35 meV.[10,20] The isotope shift of the exciton binding energy for phosphorus has been reported as $\Delta E(^{31}\mathrm{P}) = E(^{30}\mathrm{Si}) - E(^{28}\mathrm{Si}) \sim 0.02$ meV.[30] This implies that the isotope shift of the binding energy of $C_i$-$O_i$ is of the order of 0.01 meV and, therefore, the isotope shift of the electron-hole exchange interaction is much smaller than 0.01 meV, since the contribution of the exchange interaction to the Coulombic potential is rather limited.[31,32] Such a small shift of less than 0.01 meV cannot be detected in the our PL system having the resolution of 0.01 meV. Therefore, the isotope shift of the $C_0$ and $C_T$ lines appeared to be the same in our measurements.

## V. SUMMARY

Triplet states of excitons bound to $C_i$-$O_i$ complexes have been observed clearly by photoluminescence measurements. The identification of the peak labeled $C_T$ line as the photoluminescence from the triplet states of $C_i$-$O_i$ has been made by observation of LVMs associated with $C_T$ line, relative intensity between singlet ($C_0$) and triplet($C_T$) emissions, effect of host silicon isotopic composition to $C_0$ and $C_T$ lines, and behavior of photoluminescence with externally applied magnetic fields.

## ACKNOWLEDGMENTS

This work was supported in part by Grant-in-Aid for Scientific Research, in part by Special Coordination Funds for Promoting Science and Technology, in part by FIRST, in part by Global COE Program "High-Level Global Cooperation for Leading-Edge Platform on Access Spaces (C12)," and in part by a Grant-in-Aid for the Global Center of Excellence at Keio University.

---

[*] kitoh@appi.keio.ac.jp

[1] A. V. Yukhnevich, Fiz. Tverd. Tela (Leningrad) **7**, 322 (1965) [Sov. Phys.-Solid State **7**, 259 (1965)].

[2] A. V. Yukhnevich and V. D. Tkachev, Fiz. Tverd. Tela (Leningrad) **8**, 1264 (1966) [Sov. Phys.-Solid State **8**, 1004 (1966)].

[3] G. Davies, Phys. Rep. **176**, 83 (1989).

[4] R. C. Newman and A. R. Bean, Radiat. Eff. **8**, 189 (1971).

[5] G. Davies, A. S. Oates, R. C. Newman, R. Woolley, E. C. Lightowlers, M. J. Binns, and J. G. Wilkes, J. Phys. C **19**, 841 (1986).

[6] L. I. Murin, V. P. Markevich, J. L. Lindström, M. Kleverman, J. Hermansson, T. Hallberg, and B. G. Svensson, Solid State Phenom. **82–84**, 57 (2002).

[7] J. Wagner, K. Thonke, and R. Sauer, Phys. Rev. B **29**, 7051 (1984).

[8] W. Kürner, R. Sauer, A. Dörnen, and K. Thonke, Phys. Rev. B **39**, 13327 (1989).

[9] S. Hayama, G. Davies, J. Tan, J. Coutinho, R. Jones, and K. M. Itoh, Phys. Rev. B **70**, 035202 (2004).

[10] K. Thonke, A. Hangleiter, J. Wagner, and R. Sauer, J. Phys. C **18**, L795 (1985).

[11] K. Thonke, G. D. Watkins, and R. Sauer, Solid State Commun. **51**, 127 (1984).

[12] J. M. Trombetta and G. D. Watkins, Appl. Phys. Lett. **51**, 1103 (1987).

[13] P. M. Mooney, L. J. Cheng, M. Süli, J. D. Gerson, and J. W. Corbett, Phys. Rev. B **15**, 3836 (1977).

[14] S. Hao, L. Kantorovich, and G. Davies, J. Phys. Condens. Matter **16**, 8545 (2004).

[15] L. I. Khirunenko, M. G. Sosnin, Yu. V. Pomozov, L. I. Murin, V. P. Markevich, A. R. Peaker, L. M. Almeida, J. Coutinho, and V. J. B. Torres, Phys. Rev. B **78**, 155203 (2008).

[16] D. J. Backlund and S. K. Estreicher, Phys. Rev. B **77**, 205205 (2008).

[17] J. Coutinho, R. Jones, P. R. Briddon, S. Öberg, L. I. Murin, V. P. Markevich, and J. L. Lindström, Phys. Rev. B **65**, 014109 (2001).

[18] B. Monemar, U. Lindefelt, and W. M. Chen, Physica B + C **146**, 256 (1987).

[19] J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Lett. **17**, 312 (1966).

[20] J. H. Svensson, B. Monemar, and E. Janzén, Phys. Rev. Lett. **65**, 1796 (1990).

[21] C. P. Foy, J. Phys. C **15**, 2059 (1982).

[22] G. Bohnert, K. Weronek, and A. Hangleiter, Phys. Rev. B **48**, 14973 (1993).

[23] K. M. Itoh *et al.*, Jpn. J. Appl. Phys. **42**, 6248 (2003).

[24] K. Takyu, K. M. Itoh, K. Oka, N. Saito, and V. I. Ozhogin, Jpn. J. Appl. Phys. **38**, L1493 (1999).

[25] G. Davies and R. C. Newman, in *Handbook of Semiconductors*, edited by S. Mahajan, Vol. 3B (North-Holland, Amsterdam, 1994), p. 1557.

[26] G. Davies, J. Phys. Chem. Solids **31**, 883 (1970).

[27] M. Singh, D. C. Lightowlers, G. Davies, C. Jeynes, and K. J. Reeson, Mater. Sci. Eng. B **4**, 303 (1989).

[28] G. Davies, Phys. Rev. B **51**, 13783 (1995).

[29] Q. X. Zhao and T. Westgaard, Phys. Rev. B **44**, 3726 (1991).

[30] M. Steger *et al.*, Phys. Rev. B **79**, 205210 (2009).

[31] G. E. Pikus and G. L. Bir, Zh. Eksp. Teor. Fiz. **60**, 195 (1971) [Sov. Phys.-JETP **33**, 108 (1971)].

[32] G. E. Pikus and G. L. Bir, Zh. Eksp. Teor. Fiz. **62**, 324 (1972) [Sov. Phys.-JETP **35**, 174 (1972)].