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Compensation and diffusion mechanisms of carbon dopants in GaAs

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We perform first-principles theoretical studies for the doping efficiency and the diffusion mechanism of carbon dopants in GaAs. The C acceptor occupying an As site is found to be the most stable and is responsible for the high doping efficiency; however, the hole concentration is saturated to about 10^{20} cm^{-3} due to the compensation by the donors such as the [100]-split interstitial $(\mathrm{CC})_{[100]}$ complexes. We propose a mechanism for C diffusion accompanied with the formation and dissociation of the $(\mathrm{CC})_{[100]}$ complex, with the activation energy lower than that for atomistic diffusion.

Recently, carbon-doped GaAs has been the subject of growing interest because of its wide applications for high-speed devices such as heterostructure bipolar transistors or optical devices.[1–12] It is known that C acceptors have high doping efficiency[1–9] but lower diffusivity[10,12] than other acceptors such as Zn or Be. Although most C atoms are believed to occupy predominantly the As sublattice as substitutional dopants for C densities up to 10^{19} cm^{-3}, there exists a large discrepancy between the total number of C atoms and the hole concentration above 10^{19} cm^{-3}, which leads to a significant reduction of the doping efficiency.[1–9] The lattice contraction[2,5] and local vibrational mode analysis[1,11] indicated that the C atoms are unlikely to be at the substitutional Ga sites, but may occupy intersitital sites or form some complexes. Annealing studies performed on samples with the C density of 10^{18} cm^{-3} showed no evidence for intersitital C atoms,[10] while for the C concentration exceeding 5×10^{19} cm^{-3} at least 25% of the incorporated C atoms can occupy interstitial sites in diffusion experiments.[4,7] There is an alternative explanation that the reduced electrical activity of C acceptors at high doping level is due to C precipitation.[8] However, the microscopic defect structure, the compensation mechanism of hole carriers in the high doping regime, and the diffusion process of C atoms during thermal annealing are not fully understood.

In this paper we report the results of theoretical investigations on the doping characteristics of C atoms in GaAs. For various defects including C-C complexes, we calculate the formation energies with the use of a first-principles pseudopotential method and determine defect concentrations as a function of C dopants in thermodynamic equilibrium. Our results reveal that the C atom has the minimum energy when located at an As site and becomes the acceptor, while the concentration of the C atom occupying a Ga site is extremely small. Because of the large lattice relaxations, the defect level of the $\mathrm{C_{Ga}}$ donor is found to be deep lying at 0.86 eV below the conduction band minimum. Under high doping conditions, the [100]-split interstitial $(\mathrm{CC})_{[100]}$ complexes are found to compensate for acceptor carriers. Although the $\mathrm{C_{As}}$ acceptor has a high activation energy for C diffusion, the diffusion process via the formation and dissociation of the $(\mathrm{CC})_{[100]}$ complex lowers the energy barrier.

The formation energy (Ω) of a defect or a defect complex is written as a function of the chemical potentials of the constituent elements as follows:[13]

$$\Omega = E_D + Q_D\mu_e - n_{\mathrm{Ga}}\mu_{\mathrm{Ga}} - n_{\mathrm{As}}\mu_{\mathrm{As}} - n_C\mu_C, \qquad (1)$$

where E_D represents the total energy of a supercell with a defect in a charge state Q_D and the n_i's (i= Ga, As, and C) are the number of atoms. The μ_i's represent the chemical potentials for each atomic species under the constraints of $0 \le \mu_e \le E_g$, $\mu_C^{\min} \le \mu_C \le \mu_C^{\max}$, and $-\Delta H \le \Delta\mu \le \Delta H$, where μ_e is the electron chemical potential, E_g is the energy gap, and $\Delta\mu = \mu_{\mathrm{Ga}} - \mu_{\mathrm{As}}$, which controls the degree of stoichiometry of bulk GaAs. ΔH is the heat of formation of bulk GaAs and calculated to be 0.83 eV, in good agreement with the experimental value of 0.73 eV.[14] Then, for a given temperature and $\Delta\mu$, the equilibrium defect concentration[15] and the electron chemical potential are determined with the use of the charge neutrality condition.[13]

Our calculations of defect energies are performed using the first-principles pseudopotential method.[16] The soft pseudopotentials are generated by the scheme of Troullier and Martins;[17] then the Kleinman-Bylander type of fully separable potentials are generated.[18] A plane wave basis set is used with the kinetic energy cutoff of 30 Ry and the energy minimization is achieved by the recently developed modified Jacobi relaxation.[19] Thus the total energy of bulk C is fully converged with the energy difference of 20 meV/atom compared with the converged value. The fully optimized atomic configurations are obtained by calculating the Hellmann-Feynman forces for a supercell geometry containing 32 atoms. For the Brillouin zone summation, we use two special k points, which correspond exactly to ten special k points in the zinc-blende Brillouin zone. Increasing the kinetic energy cutoff, k-point sampling, and supercell size, we estimate the maximum error to be less than 0.1 eV per C atom when comparing relative formation energies.

The formation energies (E_D') (Ref. 20) for C-related defects including native ones in various charge states

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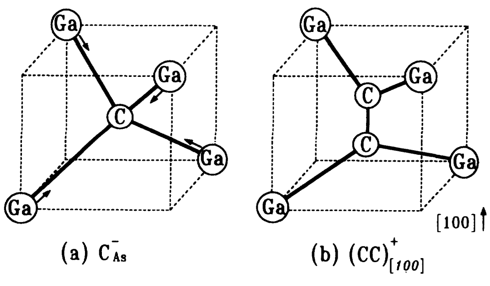
TABLE I. The formation energies (E_D' defined in Ref. 13) are listed for C-related and native defects in GaAs. μ_C is varied in the range of $\mu_C^{\min} \leq \mu_C \leq \mu_C^{\max}$ so that the maximum hole density in Fig. 3 is achieved.

Defect	E_D' (eV)	Defect	E_D' (eV)
Ga_i^{3+}	0.51	$\mathrm{As}_{\mathrm{Ga}}^{2+}$	1.05
Ga_i^{2+}	1.23	$\mathrm{As}_{\mathrm{Ga}}^{+}$	1.83
Ga_i^{+}	2.12	$\mathrm{As}_{\mathrm{Ga}}^{0}$	2.45
$\mathrm{Ga}_{\mathrm{As}}^{0}$	2.32	$\mathrm{C}_{\mathrm{As}}^{-}$	1.04
$\mathrm{Ga}_{\mathrm{As}}^{-}$	3.09	$\mathrm{C}_{\mathrm{Ga}}^{+}$	1.45
$\mathrm{Ga}_{\mathrm{As}}^{2-}$	3.71	C_i^{0}	4.02
As_i^{3+}	3.18	C_i^{+}	2.92
As_i^{2+}	4.20	C_i^{2+}	1.80
As_i^{+}	5.11	$(\mathrm{C}_{\mathrm{As}}\text{-}\mathrm{As}_i)^0$	2.98
As_i^{0}	5.96	$(\mathrm{C}_s\mathrm{C}_i)^+$	1.05
$\mathrm{V}_{\mathrm{As}}^{+}$	2.04	$(\mathrm{C}_{\mathrm{As}}\text{-}\mathrm{C}_i)^0$	2.95
$\mathrm{V}_{\mathrm{As}}^{0}$	2.97	$(\mathrm{C}_{\mathrm{Ga}}\text{-}\mathrm{C}_{\mathrm{As}})^0$	4.74
$\mathrm{V}_{\mathrm{As}}^{-}$	3.61	$(\mathrm{CC})_{[100]}^{0}$	1.34
$\mathrm{V}_{\mathrm{Ga}}^{-}$	3.83	$(\mathrm{CC})_{[100]}^{+}$	0.05
$\mathrm{V}_{\mathrm{Ga}}^{2-}$	4.32	$(\mathrm{CC})_{[110]}^{+}$	1.63
$\mathrm{V}_{\mathrm{Ga}}^{3-}$	5.01		

are listed in Table I. Our calculated formation energies for native point defects agree generally well with other results.[13] For both the substitutional C_{As} and C_{Ga}, the lattice relaxations of the surrounding atoms are significant because of the small ionic radius and strong ionicity of the C atom. In the case of $\mathrm{C}_{\mathrm{As}}^-$, the atomic distortions reducing the C-Ga bond lengths are found to be 0.38 Å for the first nearest Ga atoms (see Fig. 1), as compared to the measured value of 0.44 Å,[21] while the second nearest As atoms exhibit the relaxations of about 0.06 Å towards the acceptor neighboring Ga atoms. Testing a 64-atom supercell, the C-Ga bond length has no change while the second nearest bond lengths are further reduced by 0.02 Å. Despite such large lattice relaxations, the substitutional C_{As} defect induces a shallow acceptor level and has the lowest formation energy. In Fig. 2, the calculated density of the $\mathrm{C}_{\mathrm{As}}^-$ acceptor is plotted as a function of C concentration under As-rich conditions at 850 °C, which is commonly used in annealing experiments.[2,12] Compared with other defects, the substitutional C_{As} acceptor is predominant and its density increases monotonically with the C concentration, while the electron chemical potential decreases slightly because the charge neutrality condition is required. For a substitutional $\mathrm{C}_{\mathrm{Ga}}^+$, similar atomic relaxations are found to be 0.32 Å for the first As neighbors and 0.08 Å for the second nearest atoms. Although the C impurity behaves as a donor at a Ga site, its defect energy level is found to be deep lying at 0.86 eV below the conduction band minimum. Since the formation energy of a $\mathrm{C}_{\mathrm{Ga}}^+$ donor is higher than that for a $\mathrm{C}_{\mathrm{As}}^-$ acceptor by 0.4 eV, its defect density is much smaller by four orders of magnitude for C concentrations around 10^{20} cm^{-3}, compared with the acceptor concentration. As the C incorporation exceeds about 10^{20} cm^{-3}, the strain energies due to lattice relaxations are filled up, increasing the total energy of substitutional defects. Thus the C impurity might be moved out from its substitutional to the neighboring interstitial site. Our calculations show that the interstitial C is most stable at the tetrahedral site of an As atom and acts as a double donor. In previous experiments, the interstitial C atom was considered to be an important species in C diffusion proccess.[2,7,8] However, our calculated concentration of the interstitial C is extremely small well below 10^{15} cm^{-3}, suggesting that the interstitial C is not the stable formation as a sole defect. Instead, the interstitial C is rather captured by a C_{As} acceptor to form a C-C pair, which will be discussed later.



(a) $\mathrm{C}_{\mathrm{As}}^-$ (b) $(\mathrm{CC})_{[100]}^+$

FIG. 1. Atomic structures for (a) the C_{As} acceptor and (b) the split interstitial $(\mathrm{CC})_{[100]}$ complex are drawn.

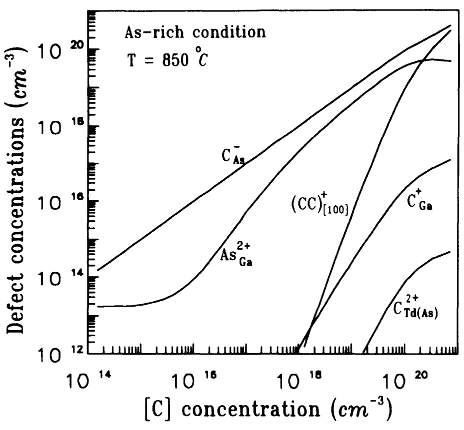


FIG. 2. Concentrations of various C-induced defects are plotted as a function of C density under As-rich conditions at 850 °C.

We find the most stable C-C pair to be the split-interstitial pair at an As site, aligned along the [100] direction. As shown in Fig. 1, the C atoms in the $(\mathrm{CC})_{[100]}$ complex are strongly bonded, with the bond length of 1.33 Å. The C-C double bond resembles that of an ethylene (C_2H_2) molecule, which has the bond distance of 1.34 Å.[14] Since the two C atoms occupy an As site, the atomic relaxations of the neighboring Ga atoms are much smaller, as compared to the substitutional C_{As} atom. The nearest Ga atoms are relaxed by 0.10 Å towards the substitutional site with the bond distance between the C and Ga atoms of 2.04 Å, similar to the bond length of 2.07 Å for the C_{As} acceptor, while the second nearest As atoms are only relaxed by 0.01 Å. The formation energy of the $(\mathrm{CC})_{[100]}$ complex is found to vary sensitively with the C density because two C atoms are involved in Eq. (1). As shown in Fig. 2, the defect density of the $(\mathrm{CC})_{[100]}^+$ pair increases very rapidly from 10^{12} to 10^{20} cm^{-3} as the C concentration increases from 10^{18} to 2 ×

10^{20} cm^{-3}. In the high doping regime, since the $(CC)_{[100]}$ complex becomes donor, the hole carriers provided by the C_{As} acceptors are significantly compensated. The As-antisite defects, which were found to be stable intrinsic defects and more stable than As interstitials under As-rich p-type conditions,[13] also compensate for acceptor carriers. At low C densities below 10^{14} cm^{-3}, the As_{Ga}^{2+} defect is a major donor and its concentration is comparable to that of the C_{As}^{-}. In the C concentration range 10^{18}–10^{20} cm^{-3}, although the concentration of As_{Ga}^{2+} appears very high in Fig. 2, these defects do not compensate significantly the C_{As}^{-} acceptors. In fact, the total hole concentration in Fig. 3 also depends on the effective electron and hole densities which vary with the Fermi level which is determined from the charge neutrality condition.[13] We find the Fermi level to decrease with the increasing of C concentration. Thus the contribution of the effective hole density to the total hole concentration is enhanced as the C concentration increases. As the C concentration goes over 10^{20} cm^{-3}, the As_{Ga}^{2+} density increases rapidly up to about 5×10^{19} cm^{-3}; however, its density becomes smaller than that for the $(CC)_{[100]}$ complex. Thus, in the doping range above 10^{20} cm^{-3}, the major compensating defects are the $(CC)_{[100]}$ pairs. These results provide aspects for understanding the reduced electrical activity of C acceptors at a very high doping level. There is an alternative model that the increased inactivity of C acceptors is due to C precipitation;[8] thus further experimental studies are needed to clarify the compensation mechanism. The compensation of acceptors is well illustrated in Fig. 3, where the hole density begins to deviate from the C concentration above 10^{19} cm^{-3} and is saturated with the maximum hole concentration of about 1.2×10^{20} cm^{-3}. Our calculated value for the maximum hole density in thermal equilibrium is in good agreement with most experiments,[1–8] while to our knowledge there is only one report that the maximum hole concentration is one order of magnitude higher than 10^{20} cm^{-3}.[22] Since this measured hole density was obtained from samples under nonequilibrium condition, we expect that the maximum hole concentration will be lower than 10^{21} cm^{-3} for annealing .

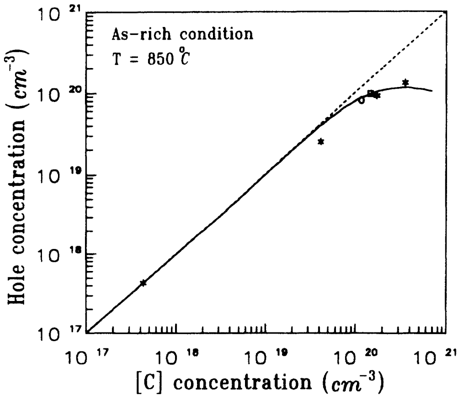


FIG. 3. Hole carrier density vs doped C concentration is plotted under As-rich conditions at 850 °C. Dashed and solid lines represent uncompensated and compensated hole carrier densities, respectively. The square, asterisks, and circle denote experimental data from Refs. 1, 5, and 7, respectively.

We now discuss the diffusion of the C atom in GaAs. Our calculations show that the substitutional C_{As} has a high activation energy, which is estimated to be about 7 eV, for migrating from its substitutional site to the interstitial region, leaving an As vacancy. This activation energy is much higher than for a substitutional Zn acceptor with an activation energy of 4 eV,[23] because the C acceptor is more strongly bonded to its surrounding atoms. However, if we consider a kick-out process, in which the substitutional C atom is kicked out by an interstitial As atom via the reaction of

$$C_{As} + As_i \rightarrow As_{As} + C_i, \qquad (2)$$

the energy barrier can be reduced, as was demonstrated for Zn dopants.[23] In this case, when the interstitial As atom moves towards the substitutional site, the C neighboring Ga atoms are relaxed back to the bulk bonding configuration, thus reducing significantly strain energy. Thus the kick-out process considerably reduces the energy barrier for the C diffusion. For both the As interstitials moving from the [100] and [111] directions, the activation energy is estimated to be 2.5 eV, as compared to the previously calculated value of 1.8 eV for a Zn acceptor in GaAs.[23] This result may explain why the diffusivity of the C atom is much smaller than for other p-type dopants such as Be and Zn.[10,12] Since the interstitial As_i atom in As-rich GaAs acts as a donor,[13] it becomes positively charged, while the C_{As} defect is in a negatively charged state. Because of the attractive interaction between the As_i and C_{As} atoms, the C_{As}-As_i complex is likely to be formed and was in fact considered to exist in irradiated C-doped GaAs.[24] However, since the formation energy of a C_{As}-As_i complex is higher by 3.0 eV than for the split-interstitial $(CC)_{[100]}$ complex, the defect density of the C_{As}-As_i complex is extremely small in thermodynamic equilibrium. Thus the atomistic diffusion of the C atom is expected to be less probable. However, some experiments indicated that the C diffusion is enhanced in highly doped GaAs above 10^{19} cm^{-3}.[4,7,8] We suggest that such an increase of the C diffusivity results from the formation and dissociation of C-C complexes.

Since the carbon atoms in the $(CC)_{[100]}$ complex are double bonded, the direct dissociation of the complex needs a large energy, which is estimated to be 4 eV as shown in Fig. 4. However, if we consider two steps in the dissociation process—in step 1, the $(CC)_{[100]}$ complex is changed to the substitutional-interstitial pair (C_s-C_i) by orienting and displacing the complex along the [111] direction, while in step 2, the interstitial C_i atom is released from the remaining substitutional C_s atom—the energy barrier for the dissociation of a C-C complex is significantly reduced. In the C_s-C_i complex, although the interstitial C atom is mainly bonded to the substitutional C, the C-C bond is slightly weakened with the bond length of 1.34 Å, because the C_i atom also interacts with its three neighboring Ga atoms. Thus the formation energy of the C_s-C_i complex is found to be 1.0 eV higher than that for the $(CC)_{[100]}$ complex. In this case, the energy barrier for changing the $(CC)_{[100]}$ complex into the C_s-C_i complex is estimated to be about 1.5 eV (see

Fig. 4). In step 2, we find the energy required to separate the interstitial C atom from the C_s-C_i complex to the neighboring tetrahedral site to be about 1.3 eV. Although we find a small migration energy of 0.5 eV for the C atom diffusion through the interstitial region of bulk GaAs, we do not expect such an atomistic diffusion because the defect density of interstitial C is extremely small. Since the formation energy of the $(CC)_{[100]}$ complex is comparable to that of the C_{As} acceptor for extremely high C concentrations, the dissociated C atom from the C_s-C_i complex might be recaptured by a C_{As} acceptor to form a $(CC)_{[100]}$ complex. Repeating the two-step process involving the formation and dissociation of C-C complexes, the C atom can diffuse with much reduced activation energies, compared with the direct dissociation of the $(CC)_{[100]}$ complex. These results successfully explain the experimental observation that the diffusion of C atoms is enhanced in highly C-doped GaAs.[4,7,8]

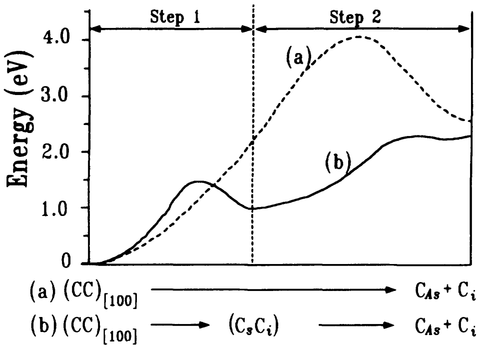


FIG. 4. Energy barriers for the (a) direct and (b) two-step dissociation processes of a $(CC)_{[100]}$ complex are drawn. See the text for more details of steps 1 and 2.

In conclusion we have found that the C_{As} acceptor is a predominant defect in GaAs and its hole carriers are compensated by the split-interstitial $(CC)_{[100]}$ complexes for extremely high C concentrations. The substitutional C_{As} atom is found to be quite stable with a high activation energy for diffusion, causing low diffusivity, because of the large strain energy. However, the split-interstitial $(CC)_{[100]}$ complex which is the stable pair formation in the limit of high doping can dissociate into substitutional and interstitial C atoms with low activation energies; thus the increasing diffusivity of the C atom is in good agreement with experiments.

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[1] C. R. Abernathy, S. J. Pearton, M. O. Manasreh, D. W. Fischer, and D. N. Talwar, Appl. Phys. Lett. **57**, 294 (1990).

[2] M. C. Hanna, A. Majerfeld, and D. M. Szmyd, Appl. Phys. Lett. **59**, 2001 (1991).

[3] M. M. G. de Carvalho, C. L. Barreto, M. A. Cotta, and K. M. Ito, Appl. Phys. Lett. **57**, 680 (1990).

[4] G. E. Höfler, J. N. Baillargeon, K. C. Hsieh, and K. Y. Cheng, Appl. Phys. Lett. **60**, 1990 (1992).

[5] T. J. de Lyon, J. M. Woodall, M. S. Goorsky, and P. D. Kirchner, Appl. Phys. Lett. **56**, 1040 (1990).

[6] S.-I. Kim, K. S. Eom, Y. Kim, M.-S. Kim, S.-K. Min, C. Lee, M. H. Kwak, and D. S. Ma, J. Cryst. Growth **126**, 441 (1993).

[7] G. E. Höfler and K. C. Hsieh, Appl. Phys. Lett. **61**, 327 (1992).

[8] H. M. You, T. Y. Tan, U. M. Gösele, S.-T. Lee, G. E. Höfler, K. C. Hsieh, and N. Holonyak, Jr., J. Appl. Phys. **74**, 2450 (1993).

[9] M. C. Hanna, Z. H. Lu, and A. Majerfeld, Appl. Phys. Lett. **58**, 164 (1991).

[10] B. T. Cunningham, L. J. Guido, J. E. Baker, J. S. Major, Jr., N. Holonyak, Jr., and G. E. Stillman, Appl. Phys. Lett. **55**, 687 (1989).

[11] M. J. Ashwin, B. R. Davidson, K. Woodhouse, R. C. Newman, T. J. Bullough, T. B. Joyce, R. Nicklin, and R. R. Bradley, Semicond. Sci. Technol. **8**, 625 (1993).

[12] T. F. Kuech, M. A. Tischler, P.-J. Wang, G. Scilla, R. Potemski, and F. Cardone, Appl. Phys. Lett. **53**, 1317 (1988).

[13] J. E. Northrup and S. B. Zhang, Phys. Rev. B **47**, 6791 (1993); S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991).

[14] *Handbook of Chemistry and Physics*, 73rd ed., edited by R. C. Weast (CRC, Boca Raton, FL, 1992).

[15] The contributions from the formation entropy are neglected because they tend to cancel when comparing relative free energies, while they may affect defect concentrations at very high temperatures.

[16] M. L. Cohen, Phys. Scr. **T1**, 5 (1982).

[17] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[18] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[19] C. H. Park, I.-H. Lee, and K. J. Chang, Phys. Rev. B **47**, 15 996 (1993).

[20] Under equilibrium conditions, Eq. (1) can be rewritten as in Ref. 13; $\Omega = E_D' + Q_D\mu_e - \frac{1}{2}(n_{\mathrm{Ga}} - n_{\mathrm{As}})\Delta\mu - n_C(\mu_C - \mu_{C(\mathrm{bulk})})$.

[21] I. Fujimoto, S. Nishine, T. Yamada, M. Konagai, and K. Takahashi, Jpn. J. Appl. Phys. **31**, L296 (1992).

[22] M. Konagai, T. Yamada, T. Akatsuka, K. Saito, and E. Tokumitsu, J. Cryst. Growth **98**, 167 (1989).

[23] C. Wang, Q. M. Zhang, and J. Bernholc, Phys. Rev. Lett. **69**, 3789 (1992).

[24] J. D. Collins, G. A. Gledhill, R. Murray, P. S. Nandhra, and R. C. Newman, Phys. Status. Solidi. B **151**, 469 (1989).