Evidence of a sulfur-boron-hydrogen complex in GaAs grown by the liquid encapsulation Czochralski technique

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In LEC-grown GaAs:S, two vibrational absorption lines are measured at 2382.2 and 2392.8 cm^{-1} ($T=7$ K) and assigned to ^{11}B-H and ^{10}B-H stretching modes. Uniaxial stress experiments reveal that the symmetry of the responsible complex is C_s. Bond strength considerations suggest that this complex is a S_{As}-B_{Ga} pair passivated by hydrogen bonded to boron. The constituents of this S-B-H complex are located within a {110} plane.

I. INTRODUCTION

GaAs single crystals for substrates up to diameters of 6 inches are grown by the liquid encapsulation Czochralski (LEC) technique. This growth technique implies the unavoidable presence of the light-element impurities carbon, nitrogen, boron, oxygen, and hydrogen in the grown GaAs. The water-containing boric oxide (B_2O_3) encapsulant is at the origin of boron, oxygen, and hydrogen contamination; moreover the use of pyrolitic boron nitride crucibles can also be at the origin of boron contamination. Hydrogen can be bonded to these light impurities giving rise to local vibrational modes with frequencies far above the intrinsic lattice absorption. These vibrational modes can be measured by Fourier transform infrared (FTIR) absorption spectroscopy and their analyses give information about the hydrogen-impurity complexes. Several complexes of hydrogen with oxygen, carbon, and nitrogen have already been investigated and some knowledge about their structure is available.[1–6] However, up to now there is no evidence for a boron-hydrogen complex neither in GaAs nor in other III-V compounds. It has to be noted that substitutional boron (B_{Ga}) is an isoelectronic impurity, i.e., it is neutral in the GaAs lattice and should not attract charged hydrogen. On the other hand, the complex of hydrogen with the isoelectronic substitutional nitrogen (N_{As}) exists and is well investigated;[3] this is due to the large nitrogen electronegativity. In n-type GaAs doped with group-VI donors, it has been shown that hydrogen makes complexes with the donors in which it is located in an antibonding position close to one of the gallium atoms nearest neighbors to the chalcogen.[7–9] In this paper, it is shown that in LEC-grown GaAs doped with sulfur, the sulfur atom tends to sit close to a boron atom and hydrogen binds boron.

II. EXPERIMENTAL DETAILS

The GaAs samples investigated are taken from different parts of two boules grown by the liquid encapsulation Czochralski (LEC) technique and doped with sulfur. They are slightly n conducting ($n \approx 0.5$ to 2×10^{17} cm^{-3}) because of sulfur doping. The boron content in the samples is about 2×10^{17} cm^{-3} derived from the intensity of the ^{11}B$_{Ga}$ local vibrational mode absorption at 517.3 cm^{-1}. The infrared absorption experiments have been performed with either a Bruker IFS 120 HR or a Bomem DA3+ Fourier transform spectrometer using spectral resolutions from 0.05 to 0.2 cm^{-1}. The samples were investigated in the temperature range from 7 to 300 K mounted in Oxford Instruments optical cryostats. Experiments with applied uniaxial stress were carried out using a home made push rod apparatus inserted inside one of the cryostats. The oriented samples for the stress experiments have the dimensions $10 \times 4 \times 2.5$ mm^3 with the long edges along to the three main crystallographic directions.

III. LOCAL VIBRATIONAL MODES

In the LEC-grown GaAs:S samples two sharp absorption lines are measured superimposed on the broad free carrier absorption (see Fig. 1). These two lines measured at T
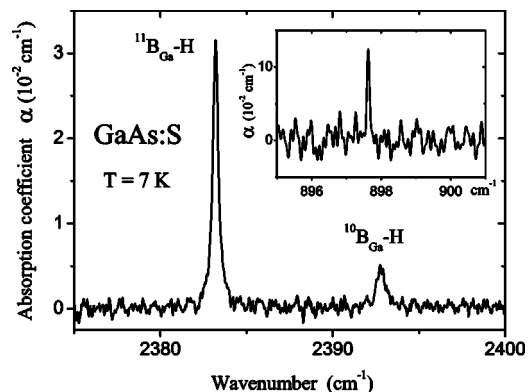

FIG. 1. Absorption spectrum of a GaAs:S sample measured at $T=7$ K with a resolution of 0.08 cm^{-1} showing the B$_{Ga}$-H stretching modes. The inset shows the absorption line assigned to the ^{11}B$_{Ga}$-H wagging mode. The background due to the absorption of the conduction electrons has been subtracted in both spectra.
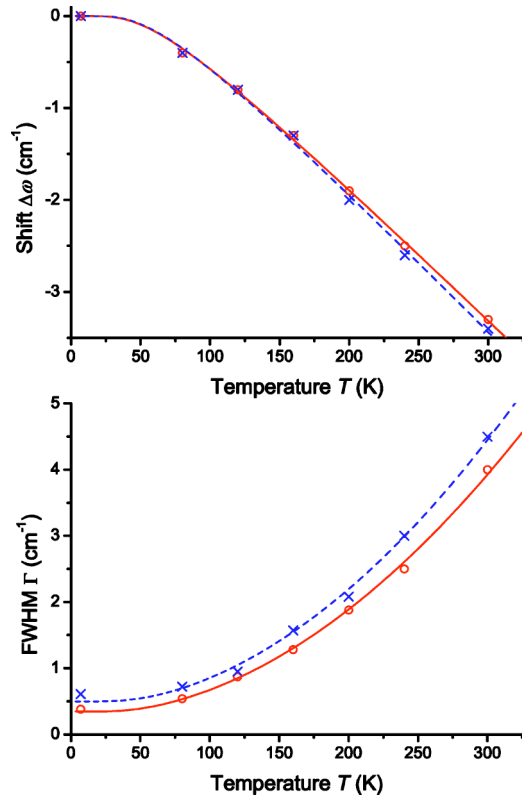
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FIG. 2. (Color online) Temperature dependences of the shifts of the line positions $\Delta\omega$ and full widths at half maximum (FWHM) Γ of the $^{11}B_{Ga}$-H bond vibrational mode at 2383.2 cm^{-1} (open circles) and of the $^{10}B_{Ga}$-H bond mode at 2392.8 cm^{-1} (crosses). The full and dotted lines are the fits with Eqs. (1) and (2) and the parameters given in the text for the $^{11}B_{Ga}$-H and $^{10}B_{Ga}$-H data, respectively.

=7 K are located at 2383.2 cm^{-1} (full width at half maximum $\Gamma=0.4$ cm^{-1}) and 2392.8 cm^{-1} ($\Gamma=0.6$ cm^{-1}). The integrated intensities ratio $I_{2383}/I_{2393}=4\pm0.4$ is sample independent; this shows that there exists a correlation between the centers responsible of these two absorption lines. The lines are still measurable at $T=300$ K and Fig. 2 shows the temperature dependence of the shift and the broadening of both lines confirming their vibrational nature.

The two vibrational lines can be assigned to the stretching modes of hydrogen directly bonded to the isotopes $^{11}B_{Ga}$ and $^{10}B_{Ga}$ of substitutional boron in GaAs. The main arguments in favor of this interpretation are the following.

(i) The ratio of their integrated intensities of about 4 fits very well that of the natural abundances of $^{11}B/^{10}B=4$.

(ii) The difference $\Delta\omega=9.6$ cm^{-1} of the vibrational frequencies for the two isotopes is very close to that calculated for a "free" diatomic B-H molecule having a frequency of 2392.8 cm^{-1} for the ^{10}B-H bond ($\Delta\omega_{calc}=9.9$ cm^{-1}).

(iii) The frequencies of the C_{As}-H, N_{As}-H, and Si_{Ga}-H bonds in GaAs are about 10 to 20 % smaller than in corresponding molecules. The frequencies of the B-H bonds in molecules are around 2600 cm^{-1}. Therefore, the downshift of about 200 cm^{-1} found for B_{Ga}-H in GaAs is consistent with this rule.[10]

In the spectral region where a wagging mode connected with the B-H stretching modes can be expected, indeed a vibrational line at 897.6 cm^{-1} ($\Gamma=0.09$ cm^{-1}) is observed (see inset of Fig. 1). Its integrated intensity I^w is correlated to that of the $^{11}B_{Ga}$-H stretching mode I^s with $I^w/I^s\approx1$. A corresponding wagging mode of $^{10}B_{Ga}$-H could not be detected. The main reason for this is the considerably decreased signal to noise ratio in this spectral region compared with the frequency region of the stretching modes due to the higher background absorption coefficient α_{FC} of the free carriers ($\alpha_{FC}\propto\lambda^p, p\approx2$).

An estimation of the concentration of the detected B-H center gives $[B\text{-}H]\approx2\times10^{14}$ cm^{-3}, using the calibration factor of the C-H stretching mode.[11] This means that about 0.1% of the B_{Ga} present in the samples is complexed with hydrogen.

IV. EXPERIMENTS WITH UNIAXIAL STRESS

To get more information about the structure of the B-H complex, experiments under uniaxial stress have been performed on the ^{11}B-H line at 2383.2 cm^{-1} with stresses $\boldsymbol{\sigma}$ up to 240 MPa applied along the $\langle001\rangle$, $\langle111\rangle$, and $\langle110\rangle$ crystallographic directions and polarized light with its electric vector E parallel or perpendicular to the stress directions; for $\sigma\|\langle110\rangle$, the perpendicular polarization corresponds to $E\|[1\bar{1}\bar{1}]$. This line splits into two components for stress $\sigma\|\langle001\rangle$, with the relative intensities of both components depending on the polarization of the light. This splitting clearly indicates that the B-H complex does not have trigonal symmetry. For stress $\sigma\|\langle111\rangle$ a splitting into three components is observed with strongly differing intensity ratios for the two polarization directions. The splitting behaviors for $\sigma\|\langle001\rangle$ and $\sigma\|\langle111\rangle$ correspond to those given in Table I and show that the symmetry type of the B-H complex is monoclinic I.[12] For centers of this symmetry, as shown in Table I, a splitting into four components should occur for $\sigma\|\langle110\rangle$; only three components were observed as shown in Fig. 3. From the shifts and splittings for $\sigma\|\langle001\rangle$ and $\sigma\|\langle111\rangle$ the fitting parameters defined in Table I for a monoclinic I type center (symmetry C_s) in a cubic crystal can be derived: $A_1=+5.3$ cm^{-1}/GPa, $A_2=-1.1$ cm^{-1}/GPa, $A_3=+2.2$ cm^{-1}/GPa, and $A_4=+1.1$ cm^{-1}/GPa, a compressive stress being considered as positive. As can be seen in Fig. 3, this set of parameters describes well also the splitting pattern for stress $\sigma\|\langle110\rangle$; in particular, the frequency difference of two of the four components is very small up to the highest stress values used, so that only three components are measurable.

V. DISCUSSION

Two most important points have to be noted. (i) Even though sulfur and hydrogen are present in the LEC-grown samples used in this study, no "traditional" trigonal sulfur-hydrogen complexes[7-9] are observed in the material. (ii) A large variety of semi-insulating GaAs samples was investigated with boron contents 2×10^{16} cm$^{-3}<[B_{Ga}]<2\times10^{18}$ cm^{-3} and resistivities in the range 10^2-10^8 Ω cm, in which no trace of the B-H lines could be detected, even

TABLE I. Stress-induced splittings for a nondegenerate vibrational mode at a monoclinic I center in a cubic crystal. ω is the frequency at zero stress, σ is the magnitude of the stress; A_1, A_2, A_3, and A_4 are fitting parameters. $I_\parallel$ and $I_\perp$ are the relative intensities of the lines with polarizations, respectively, parallel and perpendicular to the stress direction; for $\sigma\|\langle 110\rangle$ the perpendicular polarization is parallel to the $[1\bar{1}\bar{1}]$ axis. Θ is the angle between the $\langle 001\rangle$ axis and the electric dipole moment of the mode as shown in Fig. 4.

Direction of stress	Frequency	$I_\parallel$	$I_\perp$
$\langle 001\rangle$	$\omega+A_1\sigma$	$4\cos^2\Theta$	$2\sin^2\Theta$
	$\omega+A_2\sigma$	$4\sin^2\Theta$	$2(2\cos^2\Theta+\sin^2\Theta)$
$\langle 111\rangle$	$\omega+1/3(A_1+2A_2+2A_3)\sigma$	$2\cos^2\Theta$	$2\cos^2\Theta+3\sin^2\Theta$
	$\omega+1/3(A_1+2A_2-2A_3+4A_4)\sigma$	$(\cos\Theta-\sqrt{2}\sin\Theta)^2$	$(\cos\Theta-1/\sqrt{2}\sin\Theta)^2$
	$\omega+1/3(A_1+2A_2-2A_3-4A_4)\sigma$	$(\cos\Theta+\sqrt{2}\sin\Theta)^2$	$(\cos\Theta+1/\sqrt{2}\sin\Theta)^2$
$\langle 110\rangle$	$\omega+(A_2+A_3)\sigma$	0	$2/3(\cos^2\Theta+2\sin^2\Theta)$
	$\omega+(A_2-A_3)\sigma$	$2\sin^2\Theta$	$2/3\cos^2\Theta$
	$\omega+1/2(A_1+A_2+2A_4)\sigma$	$(\sin\Theta+\sqrt{2}\cos\Theta)^2$	$2/3[\cos^2\Theta+(\cos\Theta-\sqrt{2}\sin\Theta)^2]$
	$\omega+1/2(A_1+A_2-2A_4)\sigma$	$(\sin\Theta-\sqrt{2}\cos\Theta)^2$	$2/3[\cos^2\Theta+(\cos\Theta+\sqrt{2}\sin\Theta)^2]$

though the presence of hydrogen was evidenced by the detection of As-H, N-H, or O-H centers. The same holds for p-type GaAs.

In the investigated n-conducting GaAs:S samples the free electron concentration is about 10^{17} cm^{-3}. It is known that hydrogen migrates in GaAs as H$^+$ when the Fermi level is located at or below $E_v+0.5$ eV (Ref. 1) and as H$^-$ when the Fermi level is within the conduction band at or above E_c
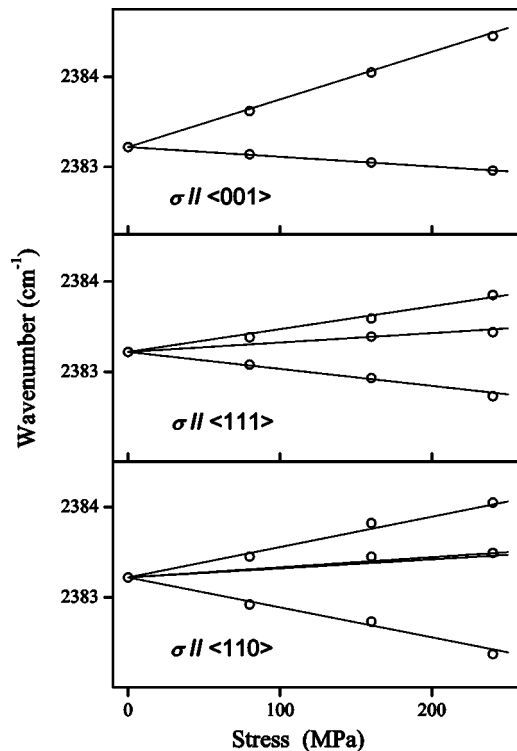

FIG. 3. Effects of uniaxial stress applied along the $\langle 001\rangle$, $\langle 111\rangle$, and $\langle 110\rangle$ directions of GaAs:S on the vibrational line at 2383.2 cm^{-1}. The open circles are the measured positions of the split components, the solid lines are the fit with the parameters A_1 to A_4 for a monoclinic I center given in the text.

+0.08 eV.[13] Therefore, in the samples in which the complexes are observed, hydrogen migrated in the negative charge state; therefore H$^-$ is responsible for the formation of the detected B-H complexes.

Isolated substitutional boron on Ga site is an isoelectronic impurity, i.e., B_{Ga} is neutral in the GaAs lattice. Therefore, a complexing of H$^-$ with this impurity is hardly understandable. This suggests that a positively charged complex consisting of B_{Ga} and an additional defect must attract H$^-$. The favorite for this defect is the sulfur donor, present in the samples as dopant with a concentration about 10^{17} cm^{-3}. As a matter of fact, boron sulfur bonds are very strong (581 kJ mol^{-1} in gaseous phase) and are therefore favored in order to minimize the total energy of the crystal; this is why the number of pairs formed is clearly larger than the one expected from a purely statistic distribution of sulfur and boron atoms. In n-GaAs the S donor is positively charged, therefore the S_{As}-B_{Ga} pairs are positively charged. Thus H$^-$ can be attracted by S_{As}-B_{Ga} and passivate the sulfur donor by forming a bond with the neighboring B_{Ga}. This is, basically, the same process as verified for the passivation of the group-VI donors S, Se, and Te in GaAs, where the passivating H is bonded to one of the four Ga nearest neighbors to the chalcogen donor in an antibonding position.[7–9] One can explain that the H passivating the S_{As}-B_{Ga} pair is bonded to boron and not to one of the three surrounding Ga as follows. To minimize the total energy of a hydrogen related complex in a solid, hydrogen tends to bind to that atom, with which it has the strongest bond. The bond strength (in gaseous molecules) of B-H is 340 kJ mol^{-1}, i.e., considerably larger than for Ga-H (274 kJ mol^{-1}). It must also be noted that in LEC-grown materials, only hydrogen complexes that are stable up to rather high temperatures are present, this is not the case for complexes involving Ga-H bonds.

As proposed theoretically[14] and confirmed by uniaxial stress experiments on the vibrational lines of "traditional" passivated chalcogen donors (D_{As}),[9] hydrogen is bonded to a Ga nearest neighbor in an antibonding position and directed along $\langle 111\rangle$, i.e., the D_{As}-Ga-H complex in GaAs has trigo-
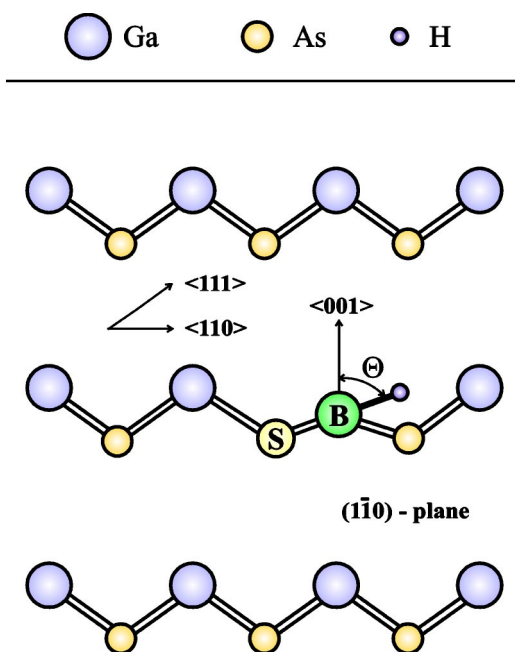
FIG. 4. (Color online) Schematic representation of the microscopic structure of the S_{As}-B_{Ga}-H complex in a {110} plane. The complex has the symmetry C_s, $\Theta \approx 70°$ is derived from the intensity ratios of the polarized split components under uniaxial stress.

nal symmetry (C_{3v}). In contrast, uniaxial stress measurements show that the S_{As}-B_{Ga}-H complex has a lower (C_s) symmetry; the symmetry elements are the {110} mirror planes. For such a center, it has been shown[15,16] that the intensities of the split components for the two polarizations depend upon the angle Θ in the {110} plane between the dipole moment of the vibrational mode and the $\langle 001 \rangle$ axis (see Fig. 4); these dependencies are given in Table I. The intensity ratios of the split components for $\sigma \| \langle 001 \rangle$ and $\sigma \| \langle 111 \rangle$ measured with parallel and perpendicular polarization could be fairly well fitted with an angle $\Theta = 70° \pm 5°$. Because of the low signal to noise ratio for the split components, the estimated angle Θ is not very accurate, compared with the Θ values derived for the passivated S, Se, and Te donors in GaP, where the D_P-P-H complexes have also the symmetry C_s.[17] Therefore, the experimental results allow to propose the microscopic model for the S_{As}-B_{Ga}-H complex schematized in Fig. 4. The three constituents are located within a {110} plane and there are twelve equivalent configurations of the complex. The antibondinglike position of the hydrogen also explains the occurrence of a wagging mode at frequencies as high as about 900 cm^{-1}.

In the "traditional" hydrogen sulfur complexes, the bond between sulfur and the nearest gallium atom to which hydrogen is bonded is broken.[7] The extrapolation of this situation to the sulfur-boron-hydrogen complex discussed in this paper would imply a breaking of the S-B bond. As this bond is very strong, the breaking of the S-B bond would not be energetically favorable. Energetically more favorable is the breaking of two B-As bonds together with the bonding of the two corresponding arsenic atoms. This leaves the boron atom threefold coordinated in a kind of off-center location;

as a matter of fact, boron is threefold coordinated in lot of molecules. Such a structure has the C_s symmetry as observed experimentally and explains the fact that the Θ angle measured is larger than 54.7°.

The shifts of the vibrational transitions and the line widths as a function of temperature can be explained by an anharmonic coupling to a low-frequency mode of energy $\hbar \omega_0$. Including the zero-point contribution in the calculations of Persson and Ryberg,[18] one obtains the shift $\Delta \omega$ of the line at temperature T taking the $T=0$ position as reference:

$$\Delta \omega = \frac{\delta \omega}{e^{\hbar \omega_0/kT} - 1} \tag{1}$$

and the full width at half maximum Γ

$$\Gamma = \frac{2(\delta \omega)^2}{\eta} \left(\frac{1}{2} + \frac{1}{e^{\hbar \omega_0/kT} - 1} \right)^2, \tag{2}$$

where $\delta \omega$ and η are the parameters defined by Persson and Ryberg.[18] The temperature dependences of the complex involving ^{11}B can be fitted with $\omega_0 = 115$ cm^{-1}, $\delta \omega = -2.44$ cm^{-1}, $\eta = 10.6$ cm^{-1} and the one involving ^{10}B with $\omega_0 = 120$ cm^{-1}, $\delta \omega = -2.67$ cm^{-1}, $\eta = 10.6$ cm^{-1}. The lines in Fig. 2 represent the fit of the experimental data with these parameters. ω_0 is about 4% larger for the ^{10}B mode than for the ^{11}B mode. This isotopic effect indicates that the low-frequency mode, to which the high-frequency B-H stretching mode is coupled, is not a lattice phonon mode, but a low-frequency mode of the S-B-H complex in resonance with the lattice modes. It has to be noted that the ω_0 values found above are very close to the frequency of the boron related resonant mode observed in LEC-grown GaAs.[19]

VI. CONCLUSION

In this paper, it has been shown that in sulfur doped LEC-grown GaAs, the complexes resulting from the neutralization of the sulfur donors by hydrogen involve boron atoms unintentionally present in the material. In these complexes, boron is a nearest neighbor of sulfur and hydrogen is bonded to boron. The reason for the occurrence of this complex only is that the total energy of the crystal with it is lower than with the "traditional" trigonal complex and is, therefore, stable to higher temperatures.

[1] B. Clerjaud, F. Gendron, M. Krause, and W. Ulrici, Phys. Rev. Lett. **65**, 1800 (1990).

[2] B. Pajot and C.Y. Song, Phys. Rev. B **45**, 6484 (1992).

[3] B. Clerjaud, D. Côte, W.S. Hahn, A. Lebkiri, W. Ulrici, and D. Wasik, Phys. Status Solidi A **159**, 121 (1997).

[4] W. Ulrici and M. Jurisch, Physica B **308–310**, 835 (2001).

[5] W. Ulrici and M. Jurisch, Phys. Status Solidi B **233**, 263 (2002).

[6] C.Y. Song, B. Pajot, W.K. Ge, and D.S. Jiang, Phys. Rev. B **52**, 4864 (1995).

[7] R. Rahbi, B. Theys, R. Jones, B. Pajot, S. Öberg, K. Somogyi, M.L. Fille, and J. Chevallier, Solid State Commun. **91**, 187 (1994).

[8] J. Vetterhöffer, J.H. Svensson, J. Weber, A.W.R. Leitch, and J.R. Botha, Phys. Rev. B **50**, 2708 (1994).

[9] J. Vetterhöffer and J. Weber, Phys. Rev. B **53**, 12 835 (1996).

[10] J. Chevallier, B. Clerjaud, and B. Pajot, Semicond. Semimetals **34**, 447 (1991).

[11] B.R. Davidson, R.C. Newman, T.B. Joyce, and T.J. Bullogh, Semicond. Sci. Technol. **11**, 455 (1996).

[12] A.A. Kaplyanskii, Opt. Spektrosk. **16**, 602 (1964); Opt. Spectrosc. **16**, 329 (1964).

[13] B. Machayekhi, C.M. Grattepain, R. Rahbi, B. Theys, M. Miloche, and J. Chevallier, Mater. Sci. Forum **143–147**, 951 (1994).

[14] K.J. Chang, Solid State Commun. **78**, 273 (1991).

[15] G. Davies, E.C. Lightowlers, M. Stavola, K. Bergman, and B. Svensson, Phys. Rev. B **35**, 2755 (1987).

[16] B. Bech Nielsen and H.G. Grimmeis, Phys. Rev. B **40**, 12 403 (1989).

[17] B. Clerjaud, D. Côte, and W. Ulrici, Physica B **273–274**, 803 (1999).

[18] B.N.J. Persson and R. Ryberg, Phys. Rev. B **32**, 3586 (1985).

[19] J.F. Angress, G.A. Gledhill, and R.C. Newman, J. Phys. Chem. Solids **41**, 341 (1980).