PHYSICAL REVIEW B VOLUME 41, NUMBER 3 15 JANUARY 1990-II

Pressure dependence of the electronic properties of cubic III-V In compounds

P. E. Van Camp, V. E. Van Doren, and J. T. Devreese*

Rijksuniversitair Centrum Antwerpen, Universiteit Antwerpen (RUCA), Groenenborgerlaan 171, B-2020 Antwerpen, Belgium

(Received 18 May 1989)

Electronic and ground-state properties of the binary In compounds in the zinc-blende structure are reported. They are evaluated in the local-density approximation using norm-conserving nonlocal pseudopotentials. Besides the lattice constant, the bulk modulus, and its first and second pressure derivative, the first- and second-order pressure coefficients of the main band gaps (at Γ, X, and L) are given. The hydrostatic deformation potentials and the crossover pressure from direct to indirect band gap are presented and compared with recent experimental values.

The effects of pressure on the electronic properties of the III-V In compounds have been investigated experimentally by optical absorption,[1] photoluminescence,[2] reflectance,[3] Hall measurements,[4-6] and x-ray diffraction.[7] In the present paper, *ab initio* calculations of the pressure coefficients are performed and the results are compared with the experimental data. All four binary In compounds (InN, InP, InAs, and InSb) are treated in the zinc-blende (T_d^2) structure, although under normal conditions InN crystallizes in the wurtzite (C_{4v}^6) structure. InP transforms to the rocksalt (O_h^5) structure at 100–115 kbar.[8] InAs first transforms at 70 kbar to the rocksalt structure and later at 170 kbar to the β tin (D_{4h}^{19}) structure.[7] InSb has a transformation at 25 kbar to an orthorhombic structure (C_{2v}^1), at 90 kbar to a hexagonal-type structure, and at 280 kbar to a bcc structure.[9] It should be noted that previous calculations of the pressure coefficients [e.g., using the orthogonalized-plane-wave (OPW) method[10,11] or the empirical pseudopotential method[12]] were all empirical in essence, while a more recent *ab initio* pseudopotential calculation[13] used the experimental value of the lattice constant, bulk modulus, and its pressure derivative as input. The present calculation is solely based on *ab initio* pseudopotentials without any further input of experimental values.

TABLE I. Calculated and experimental values of the lattice constant a (in Å), the bulk modulus B_0 (in Mbar), and the first (B_0') and second (B_0'' in Mbar^{-1}) pressure derivatives of the bulk modulus.

		Calculation	Experiment
InN	a	4.7885	
	B_0	1.5545	
	B_0'	4.0224	
	B_0''	−2.5	
InP	a	5.7021	5.8687[a]
	B_0	0.7614	0.71;[b]0.725[c]
	B_0'	4.2019	4.59;[b]4.67[c]
	B_0''	−5.4	
InAs	a	5.9019	6.0583[d]
	B_0	0.6190	0.579[e]
	B_0'	4.4877	4.79[f]
	B_0''	−7.5	
InSb	a	6.3406	6.473[g]
	B_0	0.4774	0.4563[h]
	B_0'	4.6084	4.58;[i]4.90[h]
	B_0''	−10.2	−2.0±0.9[h]

[a] Reference 17.
[b] Reference 18.
[c] Reference 19.
[d] Reference 20.
[e] Reference 21.
[f] Reference 22.
[g] Reference 23.
[h] Reference 24.
[i] Reference 25.

The theoretical framework has been given before.[14] The exchange-correlation contribution to the electronic energy is expressed by the Kohn-Sham and Wigner formulas. The ionic pseudopotentials, tabulated by Bachelet, Hamann, and Schlüter,[15] are used with kinetic-energy cutoffs of 16 hartrees for InN, 11 hartrees for InP, 10.5

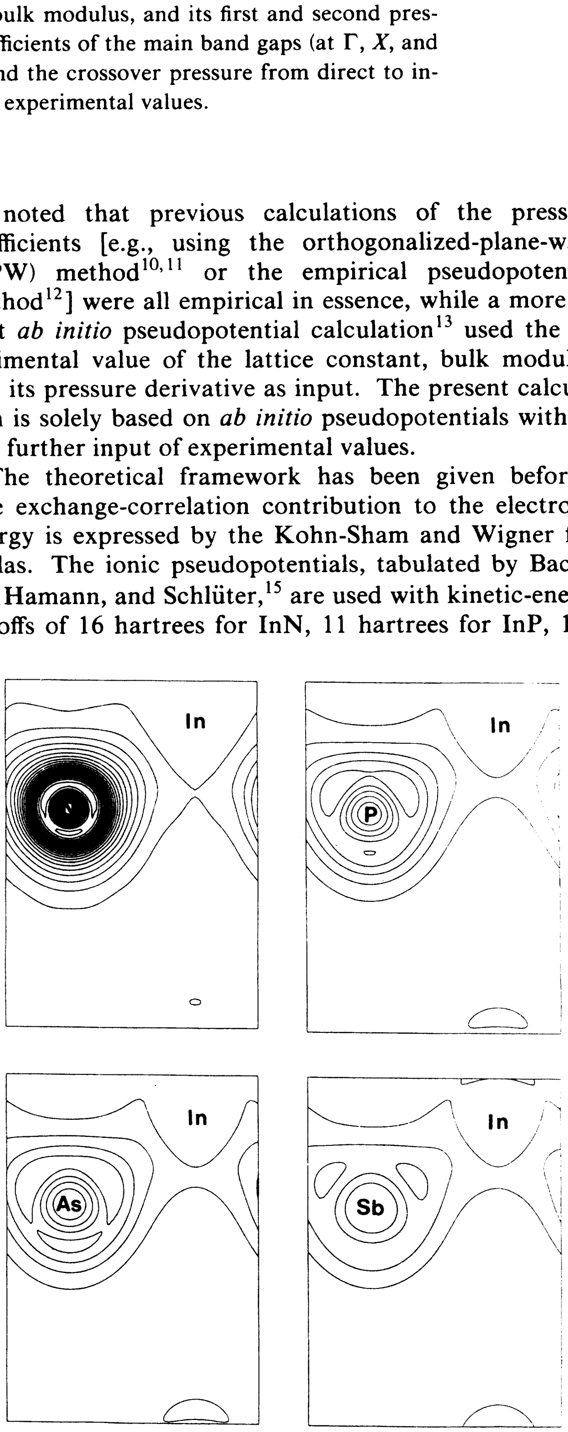

FIG. 1. Valence charge density of In compounds in the (110) plane. Units are $e/\text{a.u.}^3$ and the contour step is $0.02e/\text{a.u.}^3$

TABLE II. Calculated and experimental direct and indirect band gaps (in eV) at zero pressure.

	Calculation			Experiment
	direct	indirect		direct
	$E_{0\Gamma}$	E_{0X}	E_{0L}	direct
InP	1.42	1.51	1.82	1.393[a]
InAs	0.36	1.35	1.21	0.4105[b]
InSb	0.39	1.18	0.75	0.2352[c]

[a] Reference 2.
[b] Reference 26.
[c] Reference 27.

hartrees for InAs, and 9 hartrees for InSb. This corresponds to 609 plane waves in the Γ point at the equilibrium lattice constant. The calculated total energies for eight values of the lattice constant are then fitted to the Birch equation of state[16] yielding the zero-pressure lattice constant a, the bulk modulus B_0, and its pressure derivative B'_0. The theoretical and experimental values are given in Table I. The calculations agree with experiment to within 2% for a, 6% for B_0, and 8% for B'_0.

Figure 1 shows the contour maps of the valence charge density in the (110) plane. It can clearly be seen that InN is much more polar than InSb, i.e., the lighter the anion, the more polar the crystal.

The pressure dependence of the direct (Γ_{15} to Γ_1) and two indirect (Γ_{15} to X_1 and Γ_{15} to L_1) band gaps have been calculated up to second order in the pressure. The direct and indirect band gap at zero pressure are given in Table II and compared with the existing experimental results. Only these direct band gaps have been measured for the three compounds which exist in the zinc-blende structure under normal conditions (InP, InAs, InSb). Although usually the band gaps are underestimated seriously in the local-density approximation (LDA), here it turns out that the agreement with experiment is quite good for InP (1.42 versus 1.393 eV), only 12% too low for InAs (0.36 versus 0.4105 eV), and even too high for InSb (0.39 versus 0.2352 eV). However, spin-orbit interactions have been neglected in the present calculations, while it has been shown by Cardona, Christensen, and Fasol[28] that the shift of the Γ_{15} valence band amounts to 0.040 eV for InP and to 0.266 eV for InSb. Since the lowest Γ_1 conduction band is not affected by the spin orbit interaction, the direct band gaps of InP and InSb given in Table II should be reduced to 1.38 and 0.12 eV, respectively. The smallest indirect band gap is from Γ_{15} to X_1 for InP, while for InAs and InSb it is from Γ_{15} to L_1. Although these values have not been measured, the experimental indirect Γ_{15} to X_1 band gap of InP can be determined

TABLE III. Calculated and experimental pressure coefficients (b in eV/Mbar; c in eV/Mbar^2) of the direct and indirect band gaps.

			Calculation	Experiment
InN	Γ gap	b	2.54	
		c	−1.51	
	X gap	b	0.59	
		c	−0.53	
	L gap	b	3.35	
		c	−1.94	
InP	Γ gap	b	7.81	7.5±0.2;[a] 8;[b] 8.4±0.2;[c] 8.5;[f] 9.25[j]
		c	−10.53	−12±5;[a] −18±3;[c] −26[j]
	X gap	b	−2.09	−3±1;[c] −1[d]
		c	1.65	
	L gap	b	3.79	4[d]
		c	−5.59	
InAs	Γ gap	b	9.56	9.8;[e] 9.6−10.8;[f] 11.4[g]
		c	−18.69	
	X gap	b	−2.50	
		c	3.44	
	L gap	b	4.45	
		c	−7.79	
InSb	Γ gap	b	13.67	12.8−15.5;[h] 14.0±0.4;[i] 15.5−17.6[f]
		c	−36.35	
	X gap	b	−3.49	
		c	6.38	
	L gap	b	4.71	
		c	−11.19	

[a] Reference 2.
[b] Reference 29.
[c] Reference 1.
[d] Reference 4.
[e] Reference 3.
[f] Reference 30.
[g] Reference 5.
[h] Reference 6.
[i] Reference 31.
[j] Reference 33.

from the crossover pressure as will be explained later. This yields an experimental value of 2.41 eV to be compared with the theoretical value of 1.51 eV, or of 1.47 eV if the spin-orbit shift is subtracted.

Table III gives the first- and second-order coefficients of the pressure, b and c, of the three band gaps from Γ_{15} to Γ_1, X_1 and L_1. Theoretically, the Γ gap as well as the L gap increase sublinearly with pressure (b is positive but c negative) for all four materials, while the X gap decreases superlinearly (b is negative but c positive). Compared with the most recent experiment[2] the theoretical values of b and c are in agreement to within 4% (7.81 versus 7.5±0.2 eV/Mbar) and 12% (-10.53 versus -12 ± 5 eV/Mbar). Also for InP the calculated values agree better with the room-temperature measurements of Ref. 1 than with the 20 K measurements of Ref. 2. In general, as was also found in the Ga compounds, the first- and second-order coefficients agree much better with the experimental values than the zero-pressure band gap.[32]

Figure 2 shows the pressure variation of the band gaps Γ_{15} to Γ_1, X_1, and L_1 together with the measurements of Ref. 1 (●) and of Ref. 2 (■), all plotted with respect to the calculated direct band gap Γ_{15} to Γ_1, denoted by $E_{0\Gamma}(0)$, i.e.,

$$E_0(p)-E_{0\Gamma}(0)=bp+cp^2\ , \tag{1}$$

where $E_0(p)$ is the calculated band gap (Γ_{15} to Γ_1, X_1, or L_1) at pressure p. The experiments in Refs. 1 and 2 were performed, respectively, up to 100 and 120 kbar, whereas it should be noted that in the present work the pressure coefficients are determined by calculating the gaps from Eq. (1) up to 250 kbar. As could be expected from the values of the direct gap and the first- and second-order coefficients (Tables II and III), the agreement of the theoretical curve and the data points is quite good. The Γ gap increases with pressure, while the X gap starts decreasing from zero pressure since b is negative. The crossing point of the X curve with the Γ curve gives the transition pressure at which InP goes over from a direct-band-gap to an indirect-band-gap semiconductor (see Table VI). The value of this crossover pressure is 9.9 kbar, while experimentally 104±1 kbar (see Ref. 1) is found. From this experimental value, and with the experimental first- and second-order pressure coefficients from Ref. 1, the indirect band gap Γ_{15} to X_1 can be determined to be 2.41 eV, which has to be compared with the theoretical value of 1.51 eV. The much smaller difference between $E_{0\Gamma}$ and E_{0X} theoretically (1.42 eV versus 1.51 eV) than experimentally (1.39 eV versus 2.41 eV) implies that the theoretical crossover pressure differs considerably from the experimental value. If in Eq. (1) the theoretical values of $E_{0\Gamma}$, b, and c together with the experimental value of 2.41 eV for E_{0X} are used, a transition pressure of 101 kbar is found.

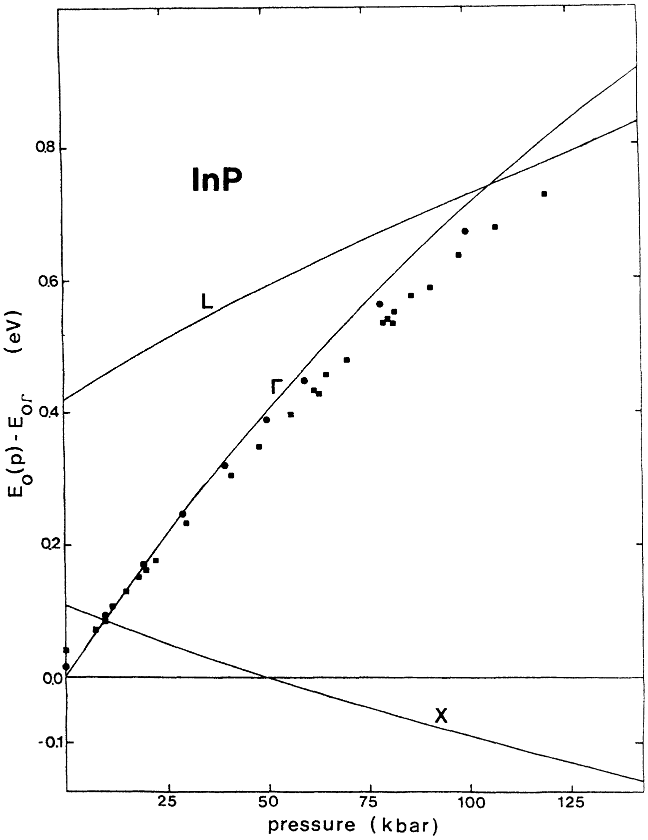

FIG. 2. Indirect and direct band gaps of InP (curves labeled Γ, X, and L), compared with the experimental results of Ref. 1 (●) and Ref. 2 (■). The origin refers to the calculated direct band E_0 at zero pressure.

Furthermore, based on the difference between the theoretical and experimental crossover pressures an esti-

TABLE IV. Calculated and experimental pressure coefficients (b^* in eV/Mbar; c^* in eV/Mbar^2) of the direct and indirect band gaps.

			Calculation	Experiment
InN	Γ gap	b^*	-15.27	
		c^*	-30.71	
	X gap	b^*	-5.19	
		c^*	-39.05	
	L gap	b^*	-20.07	
		c^*	-37.39	
InP	Γ gap	b^*	-19.13	-19.05 ± 0.15[a]
		c^*	5.17	0[a]
	X gap	b^*	4.87	6.6[a]
		c^*	-19.83	
	L gap	b^*	-9.30	
		c^*	4.11	
InAs	Γ gap	b^*	-18.01	
		c^*	15.30	
	X gap	b^*	4.70	
		c^*	-15.05	
	L gap	b^*	-8.35	
		c^*	14.61	
InSb	Γ gap	b^*	-19.64	
		c^*	23.97	
	X gap	b^*	5.02	
		c^*	-18.41	
	L gap	b^*	-6.76	
		c^*	14.44	

[a] Reference 1.

TABLE V. Calculated and experimental values of the hydrostatic deformation potential a_D (in eV).

	Calculation	Experiment
InP	5.949	6.35±0.05[a]
InAs	5.921	6.60[b]
InSb	6.526	6.39±0.18[c]

[a] Reference 1.

[b] References 5 and 21.

[c] References 24 and 31.

TABLE VI. Crossover pressures from direct to indirect band gap at X and L (in kbar).

	To X point	To L point
InP	9.9	116.2
InAs	100.4	83.2
InSb	52.8	45.5

mate can be made of the difference between the X_1 and Γ_1 level due to the self-energy corrections with respect to the LDA calculation. Since the correct band gap is equal to the LDA gap plus corrections due to relativistic and self-energy effects,

$$E_0(0)=E_0^{\mathrm{LDA}}(0)+E_0^{\mathrm{cor}}(0) \tag{2}$$

with

$$E_0^{\mathrm{cor}}(0)=E_0^{\mathrm{rel}}(0)+E_0^{\mathrm{SEC}}(0)\ , \tag{3}$$

one obtains from Eq. (1) at the transition pressure p_t

$$E_{0X}^{\mathrm{cor}}(0)-E_{0\Gamma}^{\mathrm{cor}}(0)=E_{0\Gamma}^{\mathrm{LDA}}(0)-E_{0X}^{\mathrm{LDA}}(0)+(b_\Gamma-b_X)p_t+(c_\Gamma-c_X)p_t^2\ , \tag{4}$$

where b_Γ, c_Γ and b_X, c_X are the experimental pressure coefficients for, respectively, the Γ_{15} to Γ_1 and Γ_{15} to X_1 gaps. On the other hand, one can also write

$$E_{0X}^{\mathrm{cor}}(0)-E_{0\Gamma}^{\mathrm{cor}}(0)=(E_{0X}^{\mathrm{expt}}-E_{0\Gamma}^{\mathrm{expt}})-(E_{0X}^{\mathrm{LDA}}-E_{0\Gamma}^{\mathrm{LDA}}) \tag{5}$$

if one identifies the correct band gap with the experimental one. Since both gaps refer to the top of the valence band one has that

$$E_{0X}^{\mathrm{cor}}(0)-E_{0\Gamma}^{\mathrm{cor}}(0)=E_{X1}^{\mathrm{cor}}(0)-E_{\Gamma1}^{\mathrm{cor}}(0)\ . \tag{6}$$

If one assumes that the relativistic corrections for the lowest conduction band are negligible, the right-hand-side difference of Eq. (6) is solely due to the self-energy corrections (SEC) with respect to the LDA calculation. For the experimental transition pressure of 104 kbar the right-hand side of Eq. (4) yields

$$E_{X1}^{\mathrm{SEC}}(0)-E_{\Gamma1}^{\mathrm{SEC}}(0)=0.93\ \mathrm{eV} \tag{7}$$

while from the right-hand side of Eq. (5) one obtains

$$E_{X1}^{\mathrm{SEC}}(0)-E_{\Gamma1}^{\mathrm{SEC}}(0)=0.93\ \mathrm{eV}. \tag{8}$$

This means that in the case of InP the self-energy corrections to the lowest LDA conduction band are more k dependent than in the case of GaAs where a similar analysis yields the values of 0.24 eV [from Eq. (4)] and 0.17 eV [from Eq. (5)]. One must keep in mind, however, that the pseudopotential for In (and in general for atoms with d cores) is not completly accurate due to the fact that all core states (including the d states) were frozen. All electron calculations show that this introduces errors in the band energies as large as 0.2 eV. Whether these errors are strongly k and/or pressure dependent is not clear at the moment. For InP no calculations of self-energy corrections have as yet been made.

Another way of representing the pressure variation is through the equation

$$E_0(p)-E_{0\Gamma}(0)=b^*\left[\frac{\Delta a}{a}\right]+c^*\left[\frac{\Delta a}{a}\right]^2\ , \tag{9}$$

where $\Delta a=a_p-a$ and a_p and a are the lattice constants at pressure p and at zero pressure. The coefficients b^* and c^* are given in Table IV. In the case of InP a superlinear behavior of the direct band gap is found in contrast to the linear behavior reported in Ref. 1.

The hydrostatic deformation potentials defined as

$$a_D=B_0\frac{dE_0}{dp} \tag{10}$$

are given in Table V. The agreement with the experimental values is better than 10%.

In summary, *ab initio* calculations are presented of the electronic properties of the In compounds in the zinc-blende structure. The lattice constant, bulk modulus, and its first and second pressure derivatives are determined from the total energy of the system. The first- and second-order pressure derivatives of the main band gaps are calculated as well as the hydrostatic deformation potentials and the crossover pressures from direct- to indirect-band-gap material.

ACKNOWLEDGMENTS

This work was performed in the framework of the Institute for Materials Science (IMS) of the University of Antwerp (RUCA and UIA) funded by the IUAP 11 (Interuniversitaire Attractiepool 11 Materials Science) of the Belgian Ministry of Scientific Affairs. CYBER-205 supercomputer time was provided by the NFWO Supercomputer Project of the Belgian National Science Foundation (Nationaal Fonds voor Wetenschappelijk Onderzoek).

---

*Also at Departement Natuurkunde, Universitaire Instelling Antwerpen (UIA), Universiteitsplein 1, B-2610 Wilrijk, Belgium, and Eindhoven University of Technology, NL-5600MB Eindhoven, The Netherlands.

[1] H. Müller, R. Trommer, M. Cardona, and P. Vogl, Phys. Rev. B **21**, 4879 (1980).

[2] C. Menoni, H. Hochheimer, and I. Spain, Phys. Rev. B **33**, 5896 (1986).

[3] R. Zallen and W. Paul, Phys. Rev. **155**, 703 (1967).

[4] G. Pitt, J. Phys. C **6**, 1586 (1973).

[5] Y. Jung, B. Kim, H. Lee, and J. Wolley, Phys. Rev. B **26**, 3151 (1982).

[6] I. Booth, M. Hawton, and W. Keller, Phys. Rev. B **25**, 7713 (1982).

[7] Y. Vohra, S. T. Weir, and A. L. Ruoff, Phys. Rev. B **31**, 7344 (1985).

[8] H. Drickamer, Rev. Sci. Instrum. **41**, 1667 (1970).

[9] C. A. Vanderborgh, Y. K. Vohra, and A. L. Ruoff, Bull. Am. Phys. Soc. **34**, 768 (1989).

[10] F. Herman, R. Kortum, C. Kuglin, and R. Short, in *Quantum Theory of Atoms, Molecules and Solids,* edited by P. O. Löwdin (Academic, New York, 1966).

[11] T. C. Collins, D. J. Stukel, and R. N. Euwema, Phys. Rev. B **1**, 724 (1970).

[12] M. L. Cohen and V. Heine, Solid State Phys. **24**, 37 (1970).

[13] K. J. Chang, S. Froyen, and M. L. Cohen, Solid State Commun. **50**, 105 (1984).

[14] M. T. Yin and M. L. Cohen, Phys. Rev. B **24**, 6121 (1981); P. E. Van Camp, V. E. Van Doren, and J. T. Devreese, *ibid.* **34**, 1314 (1986); Phys. Scr. **35**, 706 (1987).

[15] G. Bachelet, D. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[16] F. J. Birch, Geophys. Res. **57**, 227 (1952).

[17] G. Giesecke and H. Pfister, Acta Crystallogr. **11**, 369 (1958).

[18] D. Nichols, D. Rimai, and R. Sladek, Solid State Commun. **36**, 667 (1980).

[19] R. Trommer, H. Müller, M. Cardona, and P. Vogl, Phys. Rev. B **21**, 4869 (1980).

[20] J. Ozolinsk, G. Averkieva, A. Ilvinsk, and N. Goryuna, Sov. Phys.—Cryst. **7**, 691 (1963).

[21] D. Gerlich, J. Appl. Phys. **34**, 2915 (1963).

[22] M. Vukcevich, Phys. Status Solidi B **54**, 219 (1972).

[23] N. Siroto and E. Gololobov, Dokl. Akad. Nauk SSSR **144**, 398 (1962) [Sov. Phys. Dokl. **144**, 405 (1962)].

[24] I. Bashkin and G. Pereseda, Fiz. Tverd. Tela (Leningrad) **16**, 3166 (1974) [Sov. Phys.—Solid State **16**, 2058 (1975)].

[25] G. Pereseda, Fiz. Tverd. Tela (Leningrad) **14**, 1795 (1972) [Sov. Phys.—Solid State **14**, 1546 (1972)].

[26] E. Adachi, J. Phys. Soc. Jpn. **24**, 1178 (1968).

[27] C. Little and D. Seiler, Appl. Phys. Lett. **46**, 986 (1985).

[28] M. Cardona, N. E. Christensen, and G. Fasol, Phys. Rev. B **38**, 1806 (1988).

[29] W. Zurawsky, J. Littman, and H. Drickamer, J. Appl. Phys. **54**, 3216 (1983).

[30] J. Tsay, S. Mita, and B. Bendow, Phys. Rev. B **10**, 1476 (1974).

[31] S. Huant, L. Dmowski, M. Baj, and L. Brunel, Phys. Status Solidi B **125**, 215 (1984).

[32] P. E. Van Camp, V. E. Van Doren, and J. T. Devreese, Phys. Rev. B **38**, 9906 (1988).

[33] T. Kobayashi, K. Aoki, and K. Yamamoto, Physica B+C **139-140B**, 537 (1986).