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Equation of state of InP to 19 GPa

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X-ray diffraction experiments have been carried out on InP at room temperature to pressures of 19 GPa. The compression curve for the zinc-blende phase (I) was found to fit the Murnaghan equation up to 10.8 GPa where a transformation to the rocksalt structure was observed. Values for the bulk modulus, B_{I0} and its pressure derivative, B'_{I0}, at $P=0$ obtained by a best-fit procedure to the Murnaghan equation were $B_{I0}=76\pm4$ GPa and $B'_{I0}=4\pm0.2$. These values are similar to those obtained from precision elastic constant measurements. Analogous parameters for the rocksalt phase (II) were obtained with reference to the transition pressure $B_{IIt}=130\pm10$ GPa, $B_{IIt}=1.6\pm0.1$. At 19 GPa a further transformation was observed to a phase which was tentatively identified as β-Sn-like. Data for these three phases are given and discussed in terms of models for the transitions.

INTRODUCTION

Group-IV elemental semiconductors and their analogous compounds from groups III—V transform to metallic phases at high pressure. As has been shown recently for Ge and Si there may be several metallic phases. Indeed, a sequence has been found for both elements from cubic (diamond)→tetragonal (β-Sn)→simple hexagonal →intermediate structure→hexagonal close packed.[1-3] Similarly, the III-V compounds exhibit a variety of crystal structures at high pressure. For instance two orthorhombic phases, and a tetragonal (β-Sn analogue) phase have been observed in crystalline InSb.[4]

Metallic phases with relatively high electronic kinetic energy compared to the semiconducting states are favored at high pressure because of the large $P\Delta V$ term in the free energy, as first pointed out by Jamieson.[5] A relatively crude picture then indicates that the transition pressure should be proportional to the semiconducting energy gap,[5] which is roughly obeyed in most of these materials. Van Vechten[6] refined this model using scaling concepts based on Phillips electronegativities. His model did not distinguish between different metallic phases, but was able to predict transition pressures reasonably well for many compounds, and his work stimulated further experimental research into high-pressure phases of these materials.

More recently, *ab initio* calculations have been made for silicon, which have shown startling agreement with experimental data for crystal structures and volumes, as well as transition pressures. (For a review see Ref. 7.) These highly sophisticated calculations have been extended to some III-V compounds, such as AlP, AlAs, GaP, and GaAs,[8] where no relativistic corrections were needed. Earlier, less refined, pseudopotential calculations were carried out for InP by Soma[9,10] who used the experimental observation of Jamieson[5] that the high-pressure phase had the rocksalt structure, and predicted that the transition pressure would be between 11 and 14 GPa, in good agreement with the onset pressure of 10.5—11 GPa observed by Minomura and Drickamer[11] from resistance measurements. Soma also predicted that a further transformation would occur to the tetragonal, β-Sn-like, structure at pressures in excess of 50 GPa. This is similar to the sequence of transitions recently observed in InAs by Vohra *et al.*[12]

In addition to resistivity[11,13,14] and x-ray diffraction measurements,[5] InP has been investigated with Hall measurements[15,16] and optical measurements.[17-21] In the case of luminescence measurements made previously by us,[20] the direct transition Γ_{15V}-Γ_{1C} could be observed to pressures above 10 GPa, but a steep decrease in the luminescence intensity was observed above ~8 GPa, which was irreversible on decrease of pressure. Since the earlier measurements of the transition pressure[5,11] differed from each other and one[11] was made in an apparatus in which the pressure calibration differed from modern pressure scales (see for example Ref. 22) it was felt that a redetermination would be of value. Also, Jamieson's x-ray data[5] were obtained in an apparatus in which a pressure gradient existed in the plane of the x-ray beam. More recent determinations of unit-cell parameters for several semiconductors have differed slightly from his. A final reason for carrying out x-ray diffraction measurements on InP was to obtain the equation of state of the diamond (cubic) and the rocksalt phases, of interest to those carrying out theoretical calculations. Finally, a fourth reason for the measurements became evident as the β-Sn-like phase was discovered at ~19 GPa.

EXPERIMENTAL TECHNIQUES

The InP powdered samples were compressed at room temperature (295±2 K) in a diamond anvil cell, whose design has been previously described by Yu *et al.*[23] The precompressed sample and a ruby chip were loaded in a heat-treated Inconel 718 gasket. The gasket was preindented to a thickness of 100 μm and a hole of diameter 150 μm was then drilled in it. The sample filled about 70% of the volume of the gasket hole. The 4:1 methanol:ethanol mixture was used as the pressure-transmitting medium.[24] The pressure was measured using the ruby fluorescence scale, with a precision of ±0.05 GPa.[25]

TABLE I. Comparison of the calculated and observed interplanar spacing and relative intensities for the different diffraction lines of InP I. At atmospheric pressure, $a = 5.847$ Å. Intensity calculations were done for a sample thickness of 0.1 mm. Temperature factors were also computed. The space group considered is $F\bar{4}3m$.

hkl	d_{obs} (Å)	d_{calc} (Å)	$I/I_{111}\,\vert_{\text{calc}}$	$I/I_{111}\,\vert_{\text{obs}}$
111	3.374	3.376	100	100
200	2.920	2.923	26	18
220	2.068	2.067	60	47
311	1.766	1.763	50	22
222	1.698	1.690	8	3
400	1.458	1.462	10	3
331	1.348	1.341	20	6
420	1.302	1.307	9	6
422	1.189	1.194	18	18

The diffraction information was obtained with angle dispersive techniques using a position-sensitive detector (PSD). A collimator allowed incident radiation from the fixed-anode source to be diffracted from the sample and not the gasket. The geometry used in these measurements was similar to that described by Fujii *et al.*[26] The PSD was placed 130 mm from the scattering center and 23° from the direction of the main beam. The output of the PSD was connected to a multichannel analyzer (MCA) and data storage and analysis were carried out by a microcomputer connected to the MCA. The interplanar spacings d_{hkl} were determined with a relative precision $\Delta d/d$ of 10^{-3}. This precision decreased to 4×10^{-3} in the high-pressure phase, since the diffraction peaks broadened, possibly due to the presence of shear stresses.

EXPERIMENTAL RESULTS

At atmospheric pressure, InP crystallizes in the zinc-blende structure, $F\bar{4}3m$. In a typical spectrum, the (111), (200), (220), (311), (420), and (422) reflections from this crystal structure were observed. Table I compares the observed and calculated interplanar spacings and relative intensities for InP I. The calculated integrated intensities were obtained for angle dispersive techniques following the treatment of Kalman.[27] The volume at each pressure was calculated from the averaged value of the lattice constant obtained from the observed reflections. Experimental data were fitted to the Murnaghan equation.[28] The values of the bulk modulus B_{I0} and its pressure derivative B'_{I0} at $P = 1$ atmosphere obtained from the best fit to the data, with a confidence interval of 5×10^{-4}, were $B_{I0} = 76\pm4$ GPa and $B'_{I0} = 4\pm0.2$. These values are in good agreement with the values $B_{I0} = 71.1$ GPa and $B'_{I0} = 4.59$ obtained from precision elastic constant measurements.[29] The difference between the two curves is not significant when the uncertainties in the unit-cell parameters are taken into account. The standard deviation of the data with respect to the Murnaghan equation calculated with the values of B_{I0} and B'_{I0} from precision elastic constant measurements was found to be 0.075.

At 10.8 ± 0.05 GPa, extra lines appeared in the diffraction pattern, an indication of the presence of a new phase. This phase, InP II, was identified as having the rocksalt structure, $Fm3m$, previously reported by Jamieson.[5] In Table II, the calculated and observed interplanar spacing and integrated intensities for InP II are shown.

The transition occurs when InP I has been compressed to 89% of its initial volume. The volume change associated with this transition is 16.6% (Fig. 1). Data for phase II and for the I→II transition are summarized and compared with previous work in Table III.

Jamieson[5] reported this transition to occur at 13.3 GPa, with a compression of the low-pressure phase of 92%. This value of V/V_0 corresponds to 7.2 GPa when the $V(P)$ relationship obtained in this work is used. This result is consistent with the way in which Jamieson's experiment was performed. In Jamieson's apparatus[31] the diffraction information was obtained from crystallographic planes that were subjected to a large pressure gradient, so that the new phase could be observed at a lower pressure. It is also possible that, as in the case of Ge the transition

TABLE II. Comparison of the calculated and observed interplanar spacings and relative intensities for InP II at $P = 10.8$ GPa, $a = 5.243$ Å. The intensity calculations were done for a sample thickness of 100 μm. The space group considered is $Fm3m$.

hkl	d_{obs} (Å)	d_{calc} (Å)	$I/I_{200}\,\vert_{\text{calc}}$	$I/I_{200}\,\vert_{\text{obs}}$
111	3.025	3.027	63	45
200	2.648	2.651	100	100
220	1.854	1.854	73	56
311	1.581	1.581	30	7
222	1.529	1.514	26	6
400	1.316	1.311	11	4
420	1.172	1.172	26	5

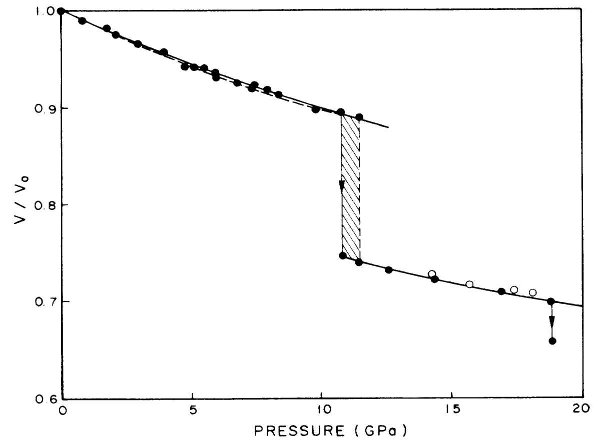

FIG. 1. Equation of state of InP for the different phases. The solid circles correspond to loading data, the open ones to unloading data. The solid curve corresponds to the Murnaghan equation calculated with the values of $B_{I0}=76\pm4$ GPa and $B'_{I0}=4\pm0.2$ obtained from the best fit of the data while the dashed line corresponds to the Murnaghan equation with values of $B_{I0}=71.1$ GPa and $B'_{I0}=4.59$ obtained from precision elastic constant measurements of Ref. 29. The solid line on phase II corresponds to the best fit of the data with a modified Murnaghan equation with values of $B_{IIt}=130\pm10$ GPa and $B'_{IIt}=4\pm0.2$.

pressure would have been lowered, due to the presence of shear stress.[32] The relative volume change

$$\frac{V_I(P_t)-V_{II}(P_t)}{V_I(P_t)}=\frac{\Delta V}{V}$$

obtained by Jamieson differs by 3% from the value obtained in this work.

Resistance measurements[11] on InP, have shown that the high-pressure phase InP II is metallic. Data for InP II were fitted with a modified Murnaghan equation of the form,

$$P=P_t+\frac{B_{IIt}}{B'_{IIt}}\left[\left(\frac{a_t}{a_{II}}\right)^{3B'_{IIt}}-1\right], \tag{1}$$

where P_t is the transition pressure, B_{IIt} and B'_{IIt} the bulk modulus and its pressure derivative at P_t, and a_t and a_{II} are the cubic unit-cell parameters at P_t and P, respectively. The best fit gave $B_{IIt}=130\pm10$ GPa and $B'_{IIt}=1.6\pm0.1$ (confidence interval 5×10^{-4}).

The two phases, I and II, coexisted up to ~(12±0.05) GPa. Above this pressure only phase II (rocksalt) was observed until at 18.9±0.05 GPa a new phase appeared. This phase was tentatively indexed as tetragonal, β-Sn-like. As discussed by Yu *et al.*[4] such a β-Sn-like phase has space-group $I4_1/amd$ if the In and P atoms are positioned at random on the atomic sites, or $I\bar{4}m2$ if they are

TABLE III. Comparison of experimental and theoretical data for phases InP I and II and the I→II transition.

Parameter	Present experiment	Other experiments	Theory
P_T (GPa)	10.8±0.05	13.3[b], 11[a]	11–14[c]
$V(P_T)/V_0$ Phase I	0.893±0.005	0.920[b]	0.891[d]
$V(P_T)/V_0$ Phase II	0.744±0.005		
$\frac{V_I-V_{II}}{V_I}(P_T)$	0.166±0.007	0.196[b]	0.213[d] 0.185[e]
Bulk modulus (GPa) Phase I	76±4	71.1[g]	58.7–71.3[f]
Pressure derivative of bulk modulus—phase I	4±0.2	4.59[g]	
Bulk modulus (GPa) Phase II at P_t	130±10		
Pressure derivative of bulk modulus—phase II at P_t	1.6±0.1		

[a] Reference 11.
[b] Reference 5.
[c] Reference 10.
[d] Reference 9.
[e] Reference 6.
[f] Reference 30.
[g] Reference 29.

TABLE IV. Data for phase III and the II→III transition in InP.

Lattice parameters (Å)	$a=4.98\pm0.02$, $c=2.58\pm0.01$
c/a ratio	0.52 ± 0.005
P_T (GPa)	$18.9\ \pm0.05$
$\frac{V_{\mathrm{II}}}{V_0}(P_T)$	0.70 ± 0.007
$\frac{V_{\mathrm{III}}}{V_0}(P_T)$	0.64 ± 0.03
$\frac{\Delta V_{\mathrm{II\text{-}III}}}{V_{\mathrm{II}}}(P_T)$	0.09 ± 0.02

ordered. Contrary to the case of InSb, where the scattering factors of the two constituents were too similar, for the x-ray diffraction results to distinguish between the two space groups, InP would be an ideal case for the identification of any of these two space groups. In this work no definite assignment can be made with the existing x-ray data, since the intensity of the lines was very weak.

The II-III transition was accompanied by a 9% change in volume. Data for InP III are summarized in Table IV. Unfortunately, gasket failure prevented further measurements beyond 19 GPa, which are needed to fully characterize the compressibility of this high-pressure phase.

When the pressure was completely released from the regime where InP II was stable, a crystal structure, different from zinc blende, was observed. The results on the characterization of this new phase will be published elsewhere.

DISCUSSION OF RESULTS

The sequence of transitions observed for InP is similar to other III-V and II-VI compounds. For instance the zinc-blende to rocksalt transition has been observed in other III-V compounds such as InAs (Refs. 12, 23, and 33) and AlSb (Ref. 34) and in II-VI compounds such as ZnS and ZnO.[34] The sequence zinc-blende→rocksalt →β-Sn-like has been observed in InAs,[12] CdTe,[35] and ZnTe,[36] and is another example showing that higher atomic coordination is favored at reduced volumes as has been observed in Si and Ge (Refs. 2, 3, and 7) and InAs.[37] In this latter case, the sequence 4→6→14 is observed. In the tetragonal structure, an In atom has six nearest neighbors and eight next-nearest neighbors at only slightly greater distance, so this structure is almost 14-fold coordinated.

Van Vechten[6] obtained a transition pressure of 14.8 GPa for the I-II transition, and Soma[10] 11–14 GPa. Normally, the experimental value is somewhat higher than thermodynamic equilibrium, as a result of kinetic factors, so the theoretical values overestimate P_t. Van Vechten used a simple scaling law for the volume change at the transition

$$\frac{\Delta V}{V}=\frac{V^{\mathrm{I}}(P_t)-V^{\mathrm{II}}(P_t)}{V^{\mathrm{I}}(P_t)}=0.209-0.056 f_i\ , \qquad (2)$$

where $f_i=0.421$,[38] then the relative volume change given by (2) is equal to 0.185, compared to the present experimental value of 0.166. Since the calculated transition pressure is proportional to ΔV^{-1}, P_t would be increased to 16.5 GPa in Van Vechten's model, indicating that the enthalpy difference between the two phases was overestimated by his model.

Van Vechten's scaling formula for ΔV was based on limited experimental data. In particular, the values of $\Delta V/V$ for Sn, Ge, Si were all thought to be 0.209 at that time. However, recent values for Ge (Ref. 32) and Si (Ref. 7) are 0.192 ± 0.007 and 0.204 ± 0.004, respectively. Table V recomputes transition pressures for Si, Ge, InAs, and InP and compares with experiment.

The stability of the different crystal structures of InP, has been discussed by Soma, using a pseudopotential approach.[9,10,30] In this approach the rocksalt structure was thought to be obtained by compressing the zinc-blende structure and allowing the anion to move from its tetrahedral position to the octahedral position at the cube center. The transition pressure was calculated to be 11–14 GPa at 0 K. Comparison of the energy curves for the rocksalt and β-Sn structure suggested the possibility of a phase transition at pressures in excess of 50 GPa. It is emphasized that computed values for the transition pressure are very sensitive to small changes in the total energy curves, so that the disagreement is not significant when the approximations in this calculation are considered.

The equation of state for phase I can be used to convert photoluminescence data[20] of $E_{\Gamma\text{-}\Gamma}(P)$ to $E_{\Gamma\text{-}\Gamma}(V)$. This is done in Fig. 2, from which it can be seen that a straight-line fit is obtained. This assumes that B_{10} and B'_{10} are independent of temperature, which is a fairly good approxi-

TABLE V. Calculation of the transition pressure of different semiconductors using Van Vechten's model, with values of $\Delta V/V$ obtained from experiment.

	$\Delta V/V$ (model)	$\Delta V/V$ (experiment)	P_T (model) (GPa)	P_T (calc) (GPa)
Ge	0.209	0.192[a]	9.2	10
Si	0.209	0.204[b]	14.8	15.2
InP	0.185	0.166	14.1	16.5
InAs	0.189	0.17[c]	9.2	10.2

[a] Reference 32.
[b] Reference 7.
[c] Reference 12.

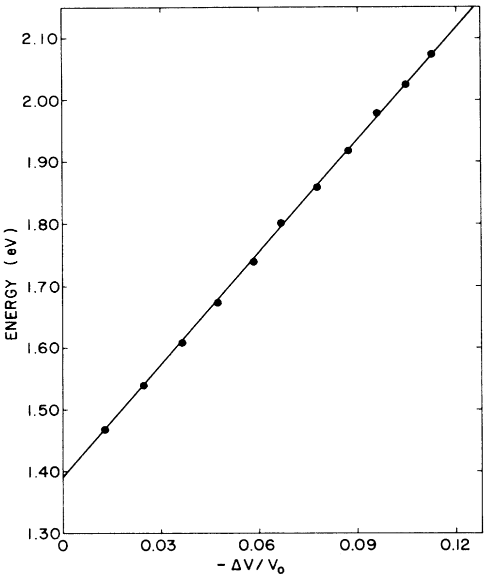

FIG. 2. Volume dependence of the direct gap at 20 K, obtained from photoluminescence measurements of Ref. 20. The solid line represents a least-squares fit to the data.

mation for a relatively incompressible substance such as InP. Analysis of this curve gives the deformation potential constant $\epsilon = dE_{\Gamma\text{-}\Gamma}/d\ln V$. The value obtained is $\epsilon = -6.07 \pm 0.06$ eV. This parameter is important in determining the mobility for electron-acoustic phonon-mode scattering. However, ϵ cannot be deduced from mobility data for InP, since polar optical, and ionized impurity scattering are the dominant scattering mechanisms.

CONCLUSIONS

An x-ray diffraction study of InP has been carried out to 19 GPa at room temperature in a diamond anvil cell. The main conclusions of the work are the following.

(1) The compression curve for the zinc-blende phase could be fitted within experimental error by the Murnaghan equation using values for the bulk modulus, B_{I0}, and its pressure derivative, B'_{I0}, obtained from elastic constant measurements, ($B_{I0} = 71.1$ GPa, $B'_{I0} = 4.59$) although a best-fit curve to the data in which B_{I0} and B'_{I0} were allowed to vary gave slightly different values for these parameters, $B_{I0} = 76 \pm 4$ GPa, $B'_{I0} = 4 \pm 0.2$.

(2) The zinc-blende phase (I) was observed to transform to the cubic, rocksalt structure (II) in agreement with an earlier observation of Jamieson.[5] The onset transition pressure (10.8 ± 0.05 GPa) is somewhat lower than theoretical estimates. Crystal data for phase II have been refined, and differ from Jamieson's earlier values. The relative volume of phase I at the transition was found to be $V/V_0 = 0.893 \pm 0.005$ and the relative volume change at the transition $\Delta V/V = 0.166 \pm 0.007$.

(3) The compression curve for phase II was fitted to a modified Murnaghan equation giving best-fit values for the bulk modulus and its pressure derivative at the transition pressure, $B_{IIt} = (130 \pm 10)$ GPa, $B'_{IIt} = 1.6 \pm 0.1$.

(4) The rocksalt structure was found to transform to another structure (III), at 18.9 ± 0.05 GPa which is tentatively identified as β-Sn-like. Crystal data for this phase at the transition pressure are reported.

(5) Using the equation of state for phase I and published photoluminescence data[20] the deformation potential constant was calculated to be $-(6.07 \pm 0.06)$ eV.

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[1] J. Z. Hu and I. L. Spain, Solid State Commun. **51**, 263 (1984).

[2] H. Olijynk, S. K. Sikka, and W. B. Holzapfel, Phys. Lett. **103A**, 137 (1984).

[3] Y. K. Vohra, K. E. Brister, S. Desgreniers, and A. L. Ruoff, Phys. Rev. Lett. **56**, 1944 (1986).

[4] S. C. Yu, I. L. Spain, and E. F. Skelton, J. Appl. Phys. **49**, 4741 (1978).

[5] J. C. Jamieson, Science **139**, 845 (1963).

[6] J. A. Van Vechten, Phys. Rev. B **7**, 1479 (1973).

[7] J. Z. Hu, L. Merkle, C. S. Menoni, and I. L. Spain, Phys. Rev. B **34**, 4679 (1986).

[8] S. Froyen and M. L. Cohen, Phys. Rev. B **28**, 3258 (1983).

[9] T. Soma, J. Phys. C **11**, 2681 (1978).

[10] T. Soma and H. Matsuo Kasaya, Solid State Commun. **50**, 261 (1984).

[11] S. Minomura and H. G. Drickamer, J. Phys. Chem. Solids **23**, 451 (1962).

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

[13] D. Lancefield, A. R. Adams, and B. J. Gunney, Appl. Phys. Lett. **45**, 1121 (1984).

[14] D. Lancefield, A. R. Adams, B. J. Gunney, and C. N. Ahmad, in *Materials Research Society Symposia Proceedings on High Pressure in Science and Technology*, edited by C. Homan, R. K. MacCrone, and E. Whalley, (North-Holland, Amsterdam, 1984), Vol. 22, p. 269.

[15] G. D. Pitt, Solid State Commun. **8**, 1119 (1970).

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

[17] H. Müeller, R. Trommer, and M. Cardona, Phys. Rev. B **21**, 4879 (1980).

[18] T. Kobayashi, T. Tei, K. Aoki, K. Yamamoto, and K. Abe, in *Physics of Solids Under Pressure*, edited by J. S. Schilling and R. N. Shelton (North-Holland, Amsterdam, 1981), p. 141.

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

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

[21] T. Kobayashi, K. Aoki, and K. Yamamoto, in *Proceedings of the Xth International High Pressure Conference on Research in High Pressure Science and Technology*, edited by N. J.

Trappeniers, S. N. Biswas, H. R. Van der Berg, C. Prins, K. O. Prins, and J. A. Schouten (North-Holland, Amsterdam, 1986), p. 537.

[22] D. L. Decker, W. A. Bassett, H. T. Merrill, H. T. Hall, and J. D. Barnett, J. Phys. Chem. Ref. Data **1**, 773 (1973).

[23] S. C. Yu, C. Y. Liu, I. L. Spain, and E. F. Skelton, in *High Pressure Science and Technology*, edited by K. D. Timmerhaus and M. S. Barber (Plenum, New York, 1979), Vol. 7, p. 274.

[24] G. Piermarini, S. Bloch, and J. Barnett, J. Appl. Phys. **44**, 5377 (1973).

[25] J. Barnett, S. Block, and G. Piermarini, Rev. Sci. Instrum. **44**, 1 (1973).

[26] Y. Fujii, O. Shimomura, K. Takemura, S. Hoshino, and S. Minomura, J. Appl. Crystallogr. **13**, 284 (1980).

[27] Z. H. Kalman, Acta Crystallogr. A **35**, 634 (1979).

[28] F. D. Murnaghan, Am. J. Math **59**, 235 (1937).

[29] D. N. Nichols, D. S. Rimai, and R. J. Sladek, Solid State Commun. **36**, 667 (1980).

[30] T. Soma, J. Phys. C **11**, 2669 (1978).

[31] J. C. Jamieson and A. W. Lawson, J. Appl. Phys. **33**, 776 (1962).

[32] C. S. Menoni, J. Z. Hu, and I. L. Spain, Phys. Rev. B **34**, 362 (1986).

[33] I. L. Spain, J. Z. Hu, C. S. Menoni, and D. Black, J. Phys. (Paris), Colloq. **C8**, 407 (1984).

[34] S. C. Yu, I. L. Spain, and E. F. Skelton, Solid State Commun. **25**, 49 (1972).

[35] I. Y. Borg and D. K. Smith, Jr., J. Phys. Chem. Solids **28**, 49 (1967).

[36] A. Ohtani, M. Motobayashi, and A. Onodera, Phys. Lett. **75 A**, 435 (1980).

[37] A. L. Ruoff, V. K. Vohra, K. E. Brister, and S. Weir, *Proceedings of the Xth International High Pressure Conference on Research in High Pressure Science and Technology*, Ref. 21, p. 209.

[38] J. C. Phillips, Phys. Rev. Lett. **20**, 550 (1968).