

B_{1g} mode softening in FeF_2

D. J. Lockwood, R. S. Katiyar,* and V. C. Y. So

Physics Division, National Research Council, Ottawa K1A 0R6, Canada

(Received 2 May 1983)

Experiments are reported for the temperature dependence of phonon Raman scattering in FeF_2 . The B_{1g} phonon exhibits anomalous frequency softening with decreasing temperature for temperatures in the range $T_N=78-340$ K. This softening is less marked for temperatures below T_N because of spin-lattice effects resulting from the antiferromagnetic ordering. In the higher-temperature region the square of the B_{1g} -phonon frequency is proportional to temperature, which is suggestive of a virtual structural phase transition. However, consideration of other work on the pressure dependences of the Raman-active modes in similar compounds leads us to conclude that the mode softening results largely from the lattice thermal contraction. This contraction disproportionately influences the forces between nearest-neighbor fluorine ions in adjacent planes perpendicular to the c axis.

I. INTRODUCTION

The lattice dynamics of crystals with the rutile (TiO_2) structure have long been of interest both theoretically and experimentally.¹ Most of this work concentrates on explaining experimental results obtained at room temperature and at atmospheric pressure. However, there have been several studies of the pressure dependence of the Raman spectrum²⁻⁶ and the static dielectric constants³ of rutile and their temperature dependences.³ The pressure and temperature dependences of the Raman-active phonons in tetragonal SnO_2 have also been reported.⁷ These studies revealed an anomalous behavior for the B_{1g} phonon in both TiO_2 and SnO_2 . The frequency of this mode decreases with decreasing temperature or increasing pressure contrary to the normal behavior observed for the other Raman-active phonons. It was postulated that this B_{1g} mode softening may be the precursor of a structural phase transition.^{3,4} However, the more recent work of Merle *et al.*⁵ has shown that the stress-dependent softening of the B_{1g} phonon does not exhibit a special sensitivity to an orthorhombic distortion and that it arises directly from atomic displacements associated with pure rotations of anions around the central cation. The positive deformation potentials obtained for this mode are primarily due to strain-induced changes in the bond-bending constants.⁶ No such explanation has been offered for the anomalous temperature dependence of the B_{1g} phonon frequency.

Similar although in most cases less detailed experiments have been performed on several of the isostructural metal fluorides, e.g., MgF_2 , ZnF_2 , MnF_2 , FeF_2 , CoF_2 , and NiF_2 . From the uniaxial-stress dependence of the Raman spectrum of MgF_2 Pascual *et al.*^{8,9} find a negative Grüneisen parameter for the B_{1g} phonon and again conclude that the softening comes directly from the angular displacements associated with this rotational mode. Finally, Sauvajol *et al.*¹⁰ report Raman measurements of the temperature dependences of the A_{1g} and E_g phonons in FeF_2 , MnF_2 , and MgF_2 . They find anomalies in the temperature variation of the frequencies of these phonons in FeF_2 that are attributed to antiferromagnetic ordering below $T_N=78$ K. Otherwise, normal if somewhat diverse variations are

found in all three compounds. In this work we report on results obtained from a temperature-dependent study of the phonons in FeF_2 , including the B_{1g} mode.

II. EXPERIMENT

The Raman measurements were made on a single crystal of FeF_2 of dimensions $6 \times 3 \times 4.5$ mm³. The sample faces were aligned close to (210) and (001) crystallographic planes and were highly polished with $0.25\text{-}\mu\text{m}$ diamond powder. The sample was mounted in the helium exchange-gas space of a Thor S500 cryostat, where the temperature could be controlled to within 0.2 K. The temperature at the surface of the crystal was measured with a gold-iron-chromel thermocouple.

Raman spectra were excited with 800 mW of either 514.5- or 647.1-nm laser light filtered by an Anaspec 300S prism monochromator. The 90° scattered light was analyzed with a Spex 14018 double monochromator at a spectral resolution of 2.48 ± 0.02 cm⁻¹ at 514.5 nm (1.6 cm⁻¹ at 647.1 nm), detected by a cooled RCA 31034A photomultiplier, and recorded under computer control. The high laser power used to obtain the magnon and phonon spectra resulted in appreciable laser heating despite the low absorption of FeF_2 at these wavelengths. This heating was determined from measurements of the Stokes-anti-Stokes intensity ratios for the phonons and varied from ~ 7 K at 20 K to ~ 33 K at 300 K. The nominal sample temperatures were corrected for this laser heating.

III. RESULTS

From group-theoretical arguments the first-order Raman spectrum of FeF_2 should comprise four phonon peaks of A_{1g} , B_{1g} , B_{2g} , and E_g symmetry, respectively.¹¹ Our room-temperature Raman spectrum contained four prominent lines having these symmetries at frequencies of 339, 73, 496, and 258 cm⁻¹, respectively, in good agreement with earlier measurements.^{10,11} The temperature dependences of the B_{1g} and E_g phonons were studied in

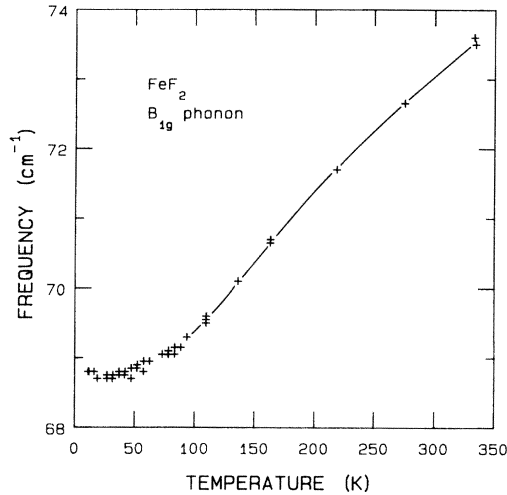


FIG. 1. Temperature dependence of the B_{1g} -phonon peak frequency. The curved line is a guide to the eye.

detail, with the Stokes and anti-Stokes components of the scattering being measured at most temperatures. Features due to one- and two-magnon Raman scattering were also recorded and details of these results are presented elsewhere.¹² At some temperatures the magnetic and B_{1g} -phonon scattering overlap (see Fig. 2 of Ref. 12) but this did not prevent an accurate determination of the phonon line parameters.

Results obtained for the temperature dependences of the B_{1g} - and E_g -phonon frequencies are shown in Figs. 1 and 2, respectively. Since most points are an average of the Stokes and anti-Stokes frequencies the measurement errors are small (ranging from ± 0.05 to ± 0.2 cm^{-1}), as is indicated from the narrow spread in points at similar temperatures. However, the absolute accuracy is limited to ± 0.5 cm^{-1} from the spectrometer specifications. Nevertheless, the relative accuracy is high because the measurements are made over the same small frequency range at each tem-

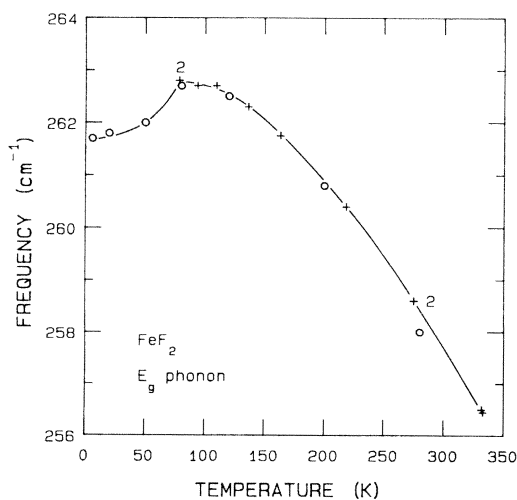


FIG. 2. Temperature dependence of the E_g -phonon peak frequency: this work (+), Ref. 10 (o). The number 2 indicates two identical results and the line is a guide to the eye.

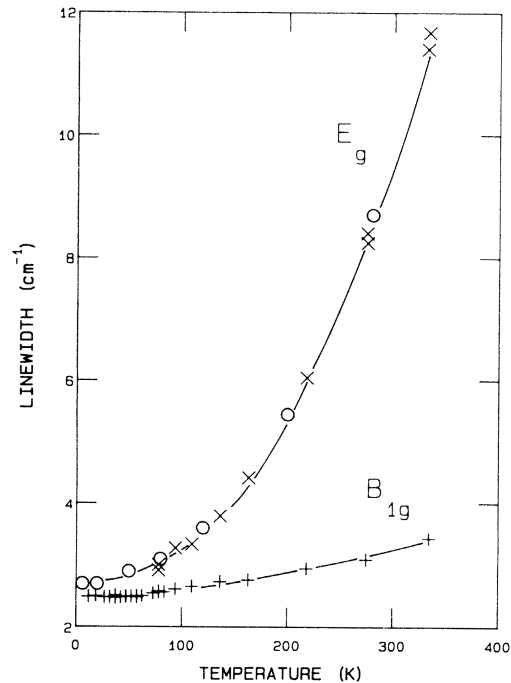


FIG. 3. Temperature dependences of the B_{1g} -phonon (+) and E_g -phonon (x) linewidths (full width at half maximum). The spectrometer resolution was 2.48 cm^{-1} , and the results of Sauvajol *et al.* (Ref. 10) (o) have been corrected to this resolution. The lines are guides for the eye.

perature. Further confidence in a high absolute accuracy comes from the excellent agreement between results obtained using the red and green laser lines, and between this and earlier work¹⁰ (see Fig. 2).

Figure 3 depicts the temperature dependences of the B_{1g} - and E_g -phonon linewidths. The linewidths were measured from data recorded using 514.5 -nm laser light and are not corrected for the spectrometer resolution. Allowing for this, there is excellent agreement between the present and earlier results¹⁰ for the E_{1g} -phonon linewidth (see Fig. 3). The measurement errors increase with increasing temperature from ± 0.03 to ± 0.05 cm^{-1} for the B_{1g} phonon and from ± 0.05 to ± 0.2 cm^{-1} for the E_g phonon.

The integrated intensities for the B_{1g} and E_g phonons were determined in two ways. First, the areas under the Stokes and anti-Stokes lines were evaluated (with due allowance for the background) by integration of the data on a computer. Second, the line intensities were corrected for the Bose population factor and then integrated. The resultant Stokes-anti-Stokes line intensities were then averaged. Correction for the Bose statistics makes a big difference to the integrated intensity at higher temperatures for such a low-frequency phonon. The results are shown in Fig. 4. Our data for the E_g phonon are similar to those obtained by Sauvajol *et al.*¹⁰; the integrated intensity is relatively independent of temperature for $T \gg T_N$, then increases for temperatures near T_N to a maximum at low temperature (see Fig. 6 of Ref. 10).

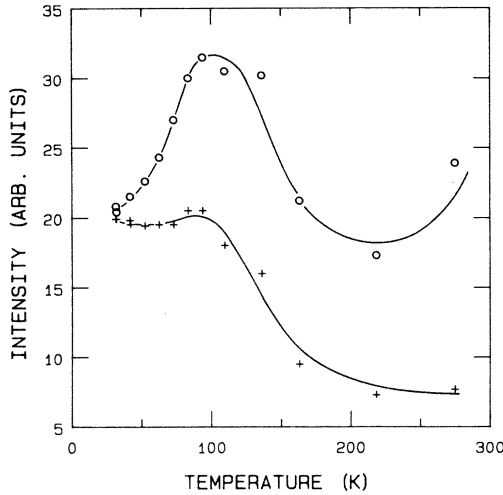


FIG. 4. Temperature dependences of the integrated intensity of the B_{1g} phonon in FeF_2 : Stokes line (\circ) and average of Stokes and anti-Stokes intensity with the Bose population factor removed ($+$). The lines are guides for the eye.

IV. LATTICE DYNAMICS OF FeF_2

A symmetry analysis of the normal vibrations of the rutile structure¹³ shows that the B_{1g} normal mode comprises rotatory motions of the four nearest-neighbor anions around the central cation, which remains stationary. The motions of the anions are perpendicular to the crystal c axis and thus this mode is mainly bond bending in character. Several models have been used to calculate the normal-mode frequencies in rutile compounds. Here we choose the rigid-ion model of Katiyar,¹³ as this model satisfactorily reproduces the observed optic-mode frequencies in MgF_2 . Following Katiyar,¹³ the zero wave-vector Raman frequencies ω may be expressed as

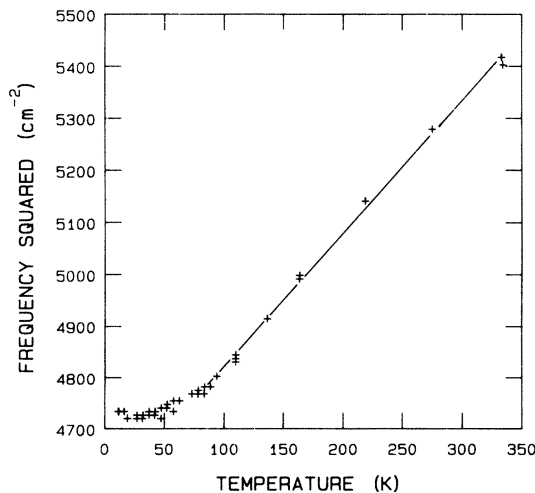


FIG. 5. Temperature dependence of the square of the B_{1g} -phonon frequency. The line represents a straight-line fit to the data for temperatures greater than $T_N=68$ K.

$$K(\omega_{B_{2g}}^2 - \omega_{A_{1g}}^2) = C_1(A_3 - B_3) + C_2Z^2, \quad (1)$$

$$K\omega_{B_{1g}}^2 = C_3(A_3 - B_3) + C_4Z^2, \quad (2)$$

and

$$K\omega_{E_g}^2 = C_5(A_2 - B_2) + C_6(A_3 - B_3) + C_7Z^2, \quad (3)$$

where $K = e^2/2v$. Here e is the electronic charge, v the unit-cell volume, A_i and B_i are dimensionless potential constants as defined in Ref. 13, Z is the effective charge parameter, and C_i 's are structural related constants. In the rigid-ion model with short-range central axially symmetric forces and long-range Coulomb forces the constants C_i are uniquely determined at any given temperature. Using the lattice constants $a_0 = 4.6966$ Å and $c_0 = 3.3091$ Å for FeF_2 at 298 K (Ref. 14), we calculate $C_1 = 7051.1$, $C_2 = 106169.2$, $C_3 = 293.8$, $C_4 = 8099.7$, $C_5 = 1715.4$, $C_6 = 3646.2$, and $C_7 = -105086.0$. By knowing the Raman frequencies, A_i , B_i , and Z may then be calculated from Eqs. (1)–(3).

Using the room-temperature frequencies for FeF_2 quoted earlier, we find from (1)–(3) that $(A_2 - B_2) = -4.10$, $(A_3 - B_3) = 19.14$, and $Z^2 = -0.036$. For MgF_2 Katiyar¹³ obtained $(A_2 - B_2) = 79.712$, $(A_3 - B_3) = 4.142$, and $Z^2 = (0.79)^2 = 0.624$. Even if allowance is made for the fact that the MgF_2 calculation included more experimental information and only reproduced the Raman frequencies to within ± 10 cm^{-1} , we must still conclude that the rigid-ion model fails for FeF_2 . The most disturbing feature is that the effective charge parameter in FeF_2 is approximately zero whereas it should be in the range $0.5 < Z < 1.0$. Secondly, for FeF_2 , $(A_2 - B_2)$ is negative, whereas it should be positive and greater than $A_3 - B_3$. Although a more sophisticated model such as the shell model has successfully been applied to MgF_2 (Ref. 15) there is no reason to suggest it would also work with FeF_2 as, for example, it fails for TiO_2 .¹⁶ An examination of the Raman frequencies of the metal fluorides¹¹ shows that in MgF_2 these frequencies are all considerably higher than those in ZnF_2 , FeF_2 , and MnF_2 , particularly so for the A_{1g} phonon. It is this last fact, when considered in conjunction with (1)–(3), that explains why the rigid-ion model succeeds for the Raman modes in MgF_2 and, conversely, why it fails for ZnF_2 , FeF_2 , and MgF_2 .¹

Despite these shortcomings, the rigid-ion model does indicate the nature of the interionic forces involved in a particular normal model of vibration. For the B_{1g} mode these are force constants A_3 and B_3 , which represent the radial and tangential forces, respectively, between anions that are not in the same plane (perpendicular to the c axis). Equation (2) shows that $\omega_{B_{1g}}^2 \propto (A_3 - B_3)$ and thus the temperature dependence of $(A_3 - B_3)$ can be obtained from our data for $\omega_{B_{1g}}$ provided neither C_3 , C_4 , nor Z^2 vary with temperature. For rutile, Z^2 varies little with temperature³ and the same is probably true for FeF_2 . However, C_3 and C_4 depend on the lattice constants, which will vary with temperature. For example, in rutile a_0 and c_0 increase by approximately 0.15%, although a_0/c_0 varies little when the crystal temperature increases from 4.2 to 298 K.³ Thus the temperature dependence of $\omega_{B_{1g}}^2$ shown in Fig. 5

TABLE I. Comparison of isobaric temperature derivatives at 296 K for the Raman-active phonons in rutile-structure compounds.

Compound	$(\partial \ln \omega / \partial T)_P$ ($10^{-5}/\text{K}$)			
	B_{1g}	E_g	A_{1g}	B_{2g}
FeF ₂	21.5	-13.0	-16.5 ^a	
SnO ₂ ^b	12.5	-1.8	-4.3	-4.4
TiO ₂ ^c	0.6	-6.3	0.6	

^aDeduced from the data of Ref. 10.

^bReference 7.

^cReference 3.

is only an approximate indication of the variation of $A_3 - B_3$ with temperature.

V. DISCUSSION

As noted previously,¹⁰ some line parameters for the Raman-active phonons in FeF₂ show anomalies associated with the magnetic phase transition at 78 K. The A_{1g} - and E_g -phonon frequencies and intensities are considerably influenced by the antiferromagnetic ordering, whereas their linewidths exhibit no anomaly. The same is true for the B_{1g} mode as can be seen in Figs. 1, 3, and 4. There are qualitative differences, however, in that (a) the B_{1g} frequency appears to be raised by the magnetic ordering rather than lowered as for the A_{1g} and E_g modes (see Fig. 2), and (b) the B_{1g} Stokes intensity peaks near T_N rather than near 0 K for the A_{1g} and E_g modes. Sauvajol *et al.*¹⁰ satisfactorily explain these departures from the normal A_{1g} - and E_g -phonon temperature dependences, as seen, for example, in MgF₂, in terms of effects associated with the magnetic-ion spin correlations. Their arguments should also apply to the B_{1g} mode. In the remainder of this discussion we shall consider the temperature-dependent behavior for $T > T_N$ only.

The A_{1g} and E_g phonons in FeF₂ exhibit normal behavior with temperature increasing above T_N : Their frequencies decrease, their linewidths increase, and their intensities are fairly constant (see Table I and Figs. 2 and 3). The frequency of the B_{1g} phonon, however, exhibits the anomalous temperature dependence found earlier for TiO₂ and SnO₂. The mode softening is much stronger in FeF₂ as can be seen from Table I. If this mode softening was a precursor to a structural phase transition then according to soft-mode theory $\omega_{B_{1g}}^2 \propto (T - T_c)$, where T_c is the transition temperature. A least-squares fit of a first-order polynomial to the data for $T > T_N$ gives a very good fit, as can be seen in Fig. 5, with

$$\omega_{B_{1g}}^2 = (2.56 \pm 0.03)T + (4565 \pm 5)$$

in units of cm^{-2} . Use of a second-order polynomial does not significantly improve the fit. Extrapolation of $\omega_{B_{1g}}^2$ to zero results in a virtual transition temperature of -1780 K. Thus it is unlikely that the B_{1g} mode softening in rutile-type compounds would result in a structural phase transition, even if it were extremely first order in nature.

Striefler and Barsch¹ have given explicit expressions for the elastic constants in rutile-structure fluorides, with the internal-strain contributions expressed in terms of the Raman frequencies. Each elastic constant depends only on a

few of the Raman-active modes and different modes contribute to different elastic constants. In particular, the B_{1g} and E_g modes are the sole contributors to the internal strain for the shear elastic constants $C_s = (C_{11} - C_{12})/2$ and C_{44} , respectively. The elastic constants of FeF₂ have been measured for temperatures between 1.5 and 298 K (Ref. 17) and the shear constants do not exhibit anomalies near T_N . However, C_{44} and C_s do show a softening and hardening, respectively, with increasing temperature that closely parallels the frequency behavior of their corresponding Raman modes. From this parallel for the E_g mode Wu *et al.*¹⁷ conclude that the temperature variation of C_{44} depends mainly on the internal strain and that the phonon-frequency contribution dominates for $T \lesssim T_N$. They attribute the softening of C_s in FeF₂ "to a tendency of the lattice to be unstable towards a structural phase transition."¹⁷ However, our results for the B_{1g} mode indicate that the temperature dependence of C_s is also derived from the frequency-dependent term in the internal strain.

The pressure- and temperature-dependent studies of the Raman-active phonons in TiO₂ (Refs. 3 and 4) and SnO₂ (Ref. 7) have shown that the isobaric frequency shifts of the B_{1g} and E_g modes are dependent mainly on the pure volume contribution associated with the thermal expansion of the crystal rather than the pure temperature effect resulting from anharmonicity. Further, the pressure-induced softening of the B_{1g} mode in TiO₂ and MgF₂ (Refs. 5 and 8) is found to be due to strain-induced changes in the bond-bending constants. From these facts we conclude that the temperature-dependent B_{1g} mode softening arises primarily from the thermal contraction of the lattice and is only remotely connected with some possible phase transition, if at all. The lattice contraction produces changes in the anion-anion force constants that could equivalently result from increased pressure. Figure 5 provides a measure of these changes. It would be interesting to compare the temperature dependences of the lattice constants and B_{1g} frequency of FeF₂ but to our knowledge the requisite lattice-constant data are not available at present. However, the lattice constants and B_{1g} frequency of SnO₂ (Ref. 7) do exhibit similar temperature dependences, which would support our conclusion.

VI. CONCLUSION

From a study of the temperature dependences of the Raman-active modes in FeF₂ combined with a knowledge of the pressure dependences of the same modes in other rutile-structure crystals we conclude that the considerable B_{1g} mode softening found by us in FeF₂ is unlikely to be associated with any (virtual) phase transition. We conclude that the softening in frequency with decreasing temperature results from the contraction of the lattice. The force constants between anions in adjacent planes perpendicular to the crystal c axis are thus particularly sensitive to the lattice dimensions. It would be informative to study the B_{1g} mode in other rutile-type compounds.

ACKNOWLEDGMENTS

We wish to thank H. J. Guggenheim (Bell Laboratories) for providing the excellent sample of FeF₂. We also thank H. J. Labbé for technical assistance, and E. J. Gabe and Y.

LePage (Chemistry Division, National Research Council of Canada, Ottawa) for verifying the crystal orientation by x-ray diffraction. R.S.K. is grateful for a Conselho Nacional de Desenvolvimento Científico e Tecnológico do

Brasil—Natural Sciences and Engineering Research Council of Canada exchange fellowship and D.J.L. acknowledges North Atlantic Treaty Organization support through research Grant No. RG-048.80.

*Permanent address: Instituto de Física "Gleb Wataghin," Universidade Estadual de Campinas, 13 100 Campinas, São Paulo, Brasil.

¹See, for example, M. E. Striefler and G. R. Barsch, *Phys. Status Solidi B* **59**, 205 (1973), and references therein.

²M. Nicol and M. Y. Fong, *J. Chem. Phys.* **54**, 3167 (1971).

³G. A. Samara and P. S. Peercy, *Phys. Rev. B* **7**, 1131 (1973).

⁴P. S. Peercy, *Phys. Rev. B* **8**, 6018 (1973).

⁵P. Merle, J. Pascual, J. Camassel, and H. Mathieu, *Phys. Rev. B* **21**, 1617 (1980).

⁶J. Pascual, J. Camassel, P. Merle, and H. Mathieu, *Phys. Rev. B* **21**, 2439 (1980).

⁷P. S. Peercy and B. Morosin, *Phys. Rev. B* **7**, 2779 (1973).

⁸J. Pascual, J. Camassel, P. Merle, B. Gil, and H. Mathieu, *Phys. Rev. B* **24**, 2101 (1981).

⁹J. Pascual, J. Camassel, P. Merle, and H. Mathieu, *J. Phys.*

(Paris) Colloq. **42**, C6-719 (1981).

¹⁰J. L. Sauvajol, R. Almairac, C. Benoit, and A. M. Bon, in *Lattice Dynamics*, edited by M. Balkanski (Flammarion, Paris, 1978), p. 199.

¹¹S. P. S. Porto, P. A. Fleury, and T. C. Damen, *Phys. Rev.* **154**, 522 (1967).

¹²M. G. Cottam, V. So, D. J. Lockwood, R. S. Katiyar, and H. J. Guggenheim, *J. Phys. C* **16**, 1741 (1983).

¹³R. S. Katiyar, *J. Phys. C* **3**, 1087 (1970); **3**, 1693 (1970).

¹⁴R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1963), Vol. 1, p. 251.

¹⁵R. Almairac and C. Benoit, *J. Phys. C* **7**, 2614 (1974).

¹⁶R. S. Katiyar, in *Phonons*, edited by M. A. Nusimovici (Flammarion, Paris, 1971), p. 84.

¹⁷A. Y. Wu, R. J. Sladek, and R. S. Feigelson, *Phys. Rev. B* **26**, 1507 (1982).