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SOFT MODE SYSTEMS: SbSI AND RARE EARTH PENTAPHOSPHATES

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ABSTRACT

The pressure and temperature dependences of inelastic light scattering were investigated in SbSI and $Nd_{0.5}La_{0.5}P_5O_{14}$. SbSI exhibits a tricritical point at $p_t \approx 1.4$ kbar and $T_t \approx 235°K$, and the behavior of the soft mode is discussed in terms of mean-field theory. In $Nd_{0.5}La_{0.5}P_5O_{14}$, the soft mode is Raman-active in both phases and a strong interaction is observed between the soft mode and an acoustic mode.

It is well established that many structural phase transitions in solids are accompanied by a so-called soft phonon mode.[1] The frequency of this mode decreases as the transition temperature is approached and, at a second-order phase transition, the soft-mode frequency vanishes at the transition temperature. The soft mode is a normal mode of lattice vibration of the solid and the symmetry of the new phase is determined by the eigenvector of the soft mode; that is, the structure of the low-symmetry phase is just the structure of the high-symmetry phase with the atomic motion associated with the soft mode superimposed on the high-symmetry structure. Thus, both the dynamic and static properties of the transition can be investigated by measuring soft-mode response using either inelastic light or neutron scattering or other techniques.

The two types of soft-mode transitions to be discussed are the ferroelectric transition in antimony sulphoiodide and the ferroelastic transition in the rare earth pentaphosphates. In

the case of a ferroelectric transition, the order parameter is the spontaneous polarization, whereas the order parameter of a ferroelastic transition is the spontaneous strain.

Antimony sulphoiodide (SbSI) is a semiconductor which undergoes a ferroelectric phase transition at 292°K at atmospheric pressure. The crystal has orthorhombic structure in both phases with point groups D_{2h} in the paraelectric phase and C_{2v} in the ferroelectric phase. Although by symmetry the transition is allowed to be second order and there can be no first order (piezoelectric) coupling between the soft mode and any of the acoustic modes of the crystal in the paraelectric phase, the transition is observed to be strongly first order at atmospheric pressure. The transition in SbSI is of interest because it is the only known displacive ferroelectric which exhibits a tricritical point.[2] The tricritical point corresponds to the point in the temperature-pressure space where the phase transition changes from first to second order.[3]

The soft mode is infrared active in both phases, but it is not Raman active in the paraelectric phase. It is, of course, Raman active in the ferroelectric phase. The temperature dependence of the Raman spectra at atmospheric pressure has been investigated by several groups,[4-6] and Balkanski and coworkers[7] have measured the pressure dependence of the Raman spectra in SbSI at very low pressures for temperatures near the atmospheric pressure transition temperature of 292°K. The pressure dependence of the Raman spectra for the spectral region containing the soft mode is shown in Fig. 1 for pressures near the transition pressure of 4.54 kbar at 119°K. These data were taken with the 6764 Å line of a krypton laser where the sample is transparent, and He gas was used as a pressure medium. As the pressure is decreased below the transition pressure, the soft mode first appears as a shoulder on the laser line. On further decreasing the pressure the soft mode moves smoothly out from zero frequency as a well-defined, underdamped excitation. Note that data are shown for very small pressure intervals. Data were actually taken in smaller intervals than shown, and the transition appears to be continuous at this temperature. As the soft mode moves to higher

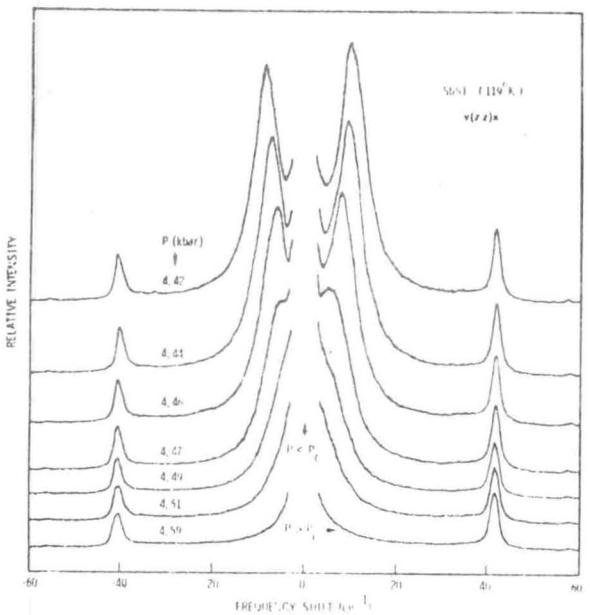


Fig. 1. Raman spectra of SbSI at various pressures near p_c at 119.4°K.

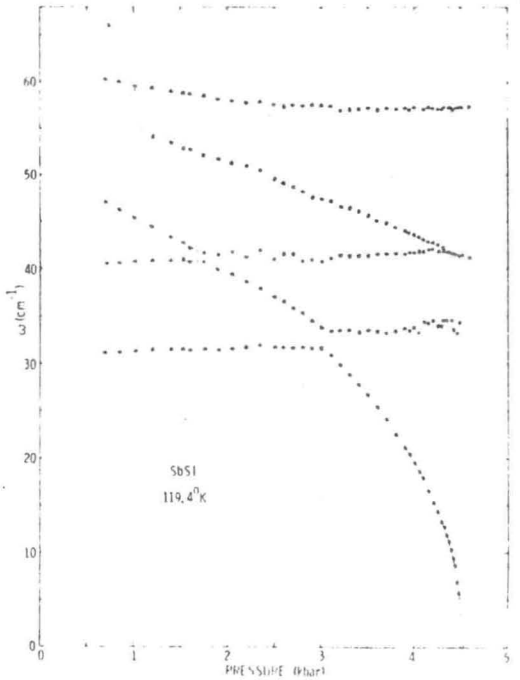


Fig. 2. Pressure dependence of the low-frequency Raman-active phonons in the ferroelectric phase of SbSI.

frequency, it interacts with other optic modes of the lattice.

The pressure dependences of the various mode frequencies in this low frequency region of the spectrum are summarized in Fig. 2. Mode couplings are evident at ∿1.8 and 3 kbar. These couplings are actually quite weak; in fact, computer fits to the spectrum in the region of the interaction with the mode at ∿32 cm^{-1}, assuming damped harmonic oscillator responses for the modes which were coupled through a real interaction, gave couplings of ∿2 cm^{-1} compared with the mode frequencies of ∿30 cm^{-1}. The main point to be made from the data in Fig. 2 is that the transition appears to be continuous at this temperature; the soft-mode frequency goes smoothly to zero, the 40 cm^{-1} mode splits continuously with pressure, and there are no discontinuities in any of the mode frequencies at the transition. I should also emphasize that there is some ambiguity in the soft-mode line shape. The mode is not quite Lorentzian so the soft-mode peak position has been plotted.

Although these data seem to indicate that the transition is second order, it is difficult to determine the order of a phase transition by measuring either the temperature or

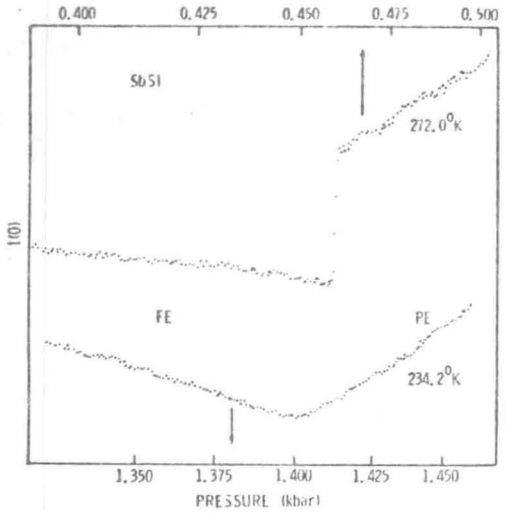


Fig. 3. I(0) versus pressure for temperatures above and below T_t.

pressure dependence of a soft-mode frequency because the frequency can never be followed exactly to zero. We therefore measured the temperature and pressure dependences of the intensity of the elastic, i.e., $\omega = 0$, scattering through the transition. In addition, the intensity of Raman scattering from phonons modes which were active in both phases were monitored through the transition as a function of pressure. Figure 3 shows the pressure dependence of the $\omega = 0$ scattering at two different temperatures. Since the scattering volume is inside the sample, I(0) essentially monitors the intensity of the transmitted laser beam. That is, the dominant contribution to I(0) is observed to be due to changes of the intensity of the laser beam in the scattering volume rather than to changes of the scattering cross section. Quite similar results were obtained by monitoring the intensity of a Raman-active phonon through transition.

Consider first the trace taken at 272°K; as the transition is approached from the paraelectric phase I(0) decreases. At the transition the intensity drops discontinuously as the crystal undergoes a first-order transition and domains are formed which scatter light out of the beam. As the pressure is further decreased the domain size increases and I(0) increases. Completely analogous results are obtained if we make measurements as a function of temperature at constant pressure. In this temperature and pressure range there is also considerable hysteresis in either the transition temperature T_c at constant pressure or the transition pressure p_c at constant temperature. The transition is definitely first order.

As the transition temperature is decreased with pressure the discontinuity in I(0) and the hysteresis in T_c (p_c) decreases until $T_c < 235$°K. I(0) then changes continuously through the transition as illustrated by the data shown for

234°K in Fig. 3. Here I(0) decreases smoothly as T_c is approached, attains a minimum of the transition with no discontinuity, then increases smoothly as the system moves away from the transition. Again, completely analogous results were obtained as a function of temperature at constant pressure, and the behavior is independent of whether the measurements are made with increasing or decreasing pressure or temperature. For $T_c < 235°K$ we observed no hysteresis within experimental uncertainty. The transition thus appears to be second order for pressures above about 1.4 kbar. Since the transition is unambiguously first order for lower pressures, SbSI apparently exhibits a tricritical point at 235°K and 1.4 kbar.

The expected behavior near a tricritical point can be obtained from Landau's theory of continuous phase transitions.[8] The free-energy F can be written as:

$$F = \frac{1}{2}A(T - T_c)P_s^2 + \frac{1}{4}BP_s^4 + \frac{1}{6}CP_s^6 + \ldots \qquad (1)$$

where P_s is the spontaneous polarization, A is a constant and B and C are taken to be slowly varying functions of temperature and pressure. For $C > 0$, Eq. (1) describes a first-order transition if $B < 0$, a second-order transition if $B > 0$, and a tricritical point at $B = 0$. For a second-order transition, the stability conditions yield the inverse susceptibility χ^{-1} as

$$\chi^{-1} = A(T - T_c) \ , \ T > T_c \qquad (2a)$$

$$\chi^{-1} = 2A(T_c - T) \ , \ T < T_c \ , \qquad (2b)$$

and P_s has a temperature dependence of the form

$$P_s \propto (T_c - T)^{\frac{1}{2}} \ . \qquad (3)$$

Near a tricritical point T_t these expressions become

$$\chi^{-1} = A(T - T_t) \ , \ T > T_t \qquad (4a)$$

$$\chi^{-1} = 4A(T_t - T) \ , \ T < T_t \qquad (4b)$$

with

$$P_s \propto (T_t - T)^{\frac{1}{4}} \ . \qquad (5)$$

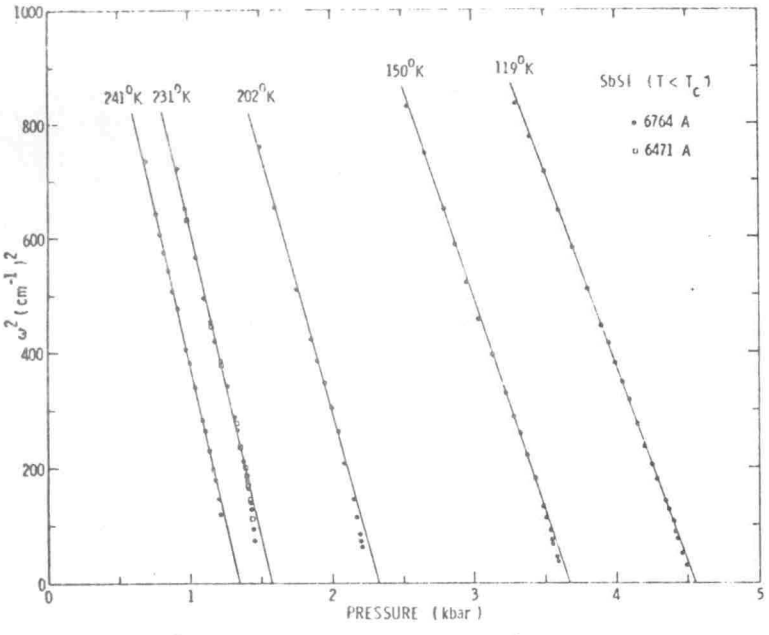


Fig. 4. ω^2 vs p at different temperatures for SbSI.

Since temperature and pressure are equivalent variables, similar results are obtained as a function of p. One therefore expects the exponent of the order parameter to change from ½ to ¼. The exponent for the susceptibility, on the other hand, does not change; rather the slope for χ^{-1} changes from 2 to 4. Since Raman scattering probes $\chi(\omega)$, this treatment predicts that the functional form of ω will not change, but that there will be a change in the slope of ω^2 vs T or p near the tricritical point.

The pressure dependence of the soft mode is illustrated in Fig. 4 for temperatures above and below 235°K. The peak position is again plotted in this figure because of the ambiguity in the line shape. The data follow an $\omega^2 \propto p$ dependence as expected although there is some deviation near p_c; however, this deviation is probably an artifact of the asymmetric line shape and the increase in the ratio of the damping to the frequency as ω decreases. These data illustrate that the slope of ω^2 vs p decreases from $\omega^2 \simeq 218(p_c - p)$ at 231°K to $\omega^2 \simeq 125(p_c - p)$ at 119°K. Unfortunately, the soft mode is not Raman active for $T > T_c$ so that the slope ratio has not been directly measured. However, it is known from dielectric measurements[9] that SbSI obeys a Curie-Weiss law with pressure in the paraelectric phase and that the Curie constant is essentially temperature independent.[9] Combining that observation with the observation that SbSI obeys the Lyddane-Sachs-Teller relation indicates that the change in the slope should be very nearly equal to the change in the slope ratio. In view of the uncertainties in this analysis, the change of 1.75

observed as the temperature is decreased from about 4° below the tricritical point to well below the tricritical point is in reasonable agreement with the mean field value of 2.

Samara[10] has recently measured the pressure dependence of the dielectric constant and directly determined the change in the slope ratio of χ^{-1} near this point. He observed a qualitative change in the dielectric response ε with pressure; the maximum in ε increased with increasing pressure indicating that the transition had become more nearly second order. Although ε did not diverge for $T_c < 235°K$, presumably because of material problems, the slope ratio was observed to change from 2 at low temperatures to 3.4 at 233°K.

Summarizing the results on antimony sulphoiodide, the dielectric measurements seem to corroborate the conclusion drawn from the light-scattering measurements that there is a change in order of the phase transition with pressure. Unfortunately, the dielectric measurements are not as definitive as the light-scattering measurements because of material problems. Light-scattering appears to be a much more reliable technique for investigating tricritical behavior in this material because measurements can be made inside the sample which avoids surface effects.

Another type of soft-mode system is illustrated by the rare earth pentaphosphates. The chemical formula for these materials is REP_5O_{14}, and several crystal structures have been observed for different rare earths depending on the size of the rare earth ion, the temperature, and the pressure of the measurements.[11] We will consider materials which undergo a ferroelastic phase transition from orthorhombic D_{2h} symmetry to monoclinic C_{2h} symmetry on cooling. Examples of crystals with this symmetry change are TbP_5O_{14}, LaP_5O_{14}, NdP_5O_{14} as well as mixed crystals of these constituents.

The phase transition is thought to be a second-order displacive structural transition.[12] It was recently shown by Fox, Scott and Bridenbaugh[13] that this transition is accompanied by a soft zone-center optic mode which is Raman active and underdamped in both phases. Figure 5 shows the Raman spectra as a function of temperature taken at pressure of about 2 kbar for

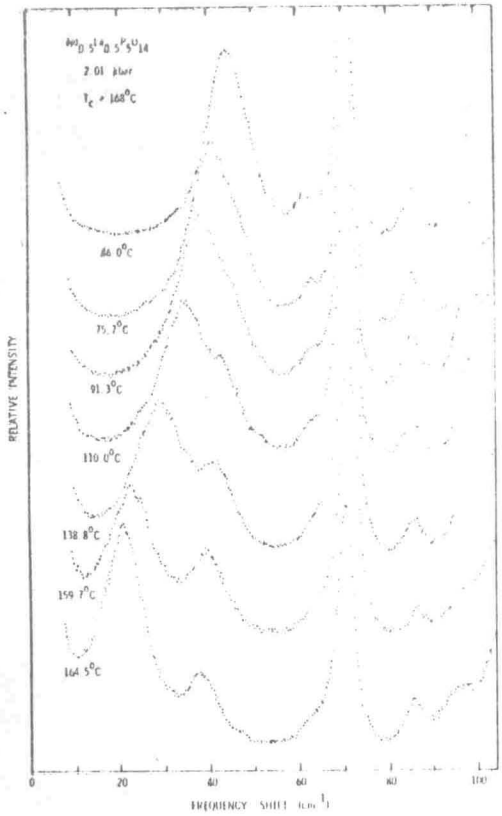


Fig. 5. Raman spectra of $Nd_{0.5}La_{0.5}P_5O_{14}$ at 2 kbar for various temperatures in the ferroelastic phase.

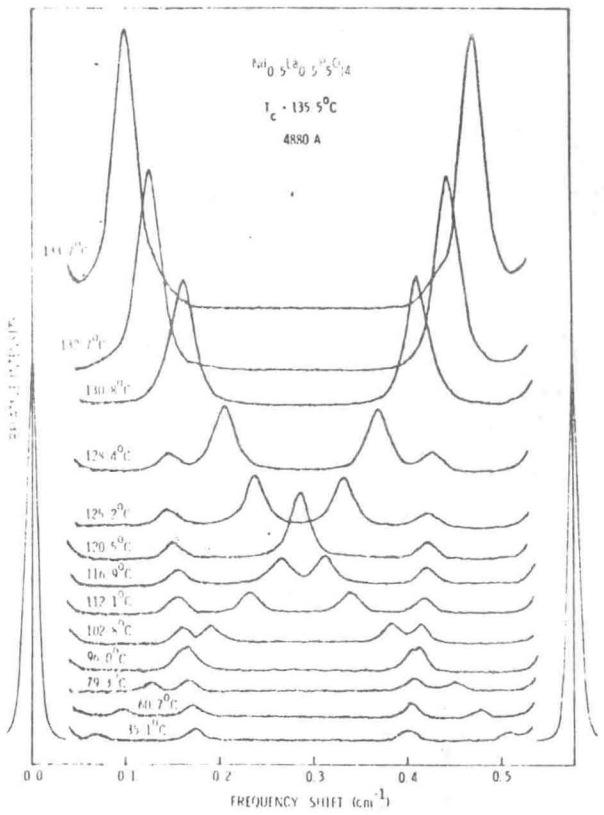


Fig. 6. Brillouin spectra of $Nd_{0.5}La_{0.5}P_5O_{14}$ showing the temperature dependence of the transverse acoustic mode C_{55} and the longitudinal mode (C_{33} in the second order of the Fabry Perot) for temperatures below T_c.

the mixed crystal $Nd_{0.5}La_{0.5}P_5O_{14}$. The frequency of the soft mode decreases as the transition temperature is approached. The mode remains underdamped throughout the region of the transition and interactions of the soft mode with other optic modes of the system can be seen at various temperatures in the ferroelastic phase. Remarkably similar behavior is observed for the isomorphous rare earth pentaphosphates investigated to date. The soft-optic mode does not vanish at the transition. In fact, the lowest frequency observed is 19.5 cm^{-1}.

An interesting question concerning the phase transition between D_{2h} and C_{2h} symmetries accompanied by a soft-optic mode is the possibility of the interaction of the soft mode with an acoustic mode. Although by symmetry there can be no first-order interaction between the optic and acoustic modes for D_{2h} point groups, it was shown by Miller and Axe[14] that

there can be higher order interactions between acoustic modes and Raman-active optic modes which are non-negligible. The effect of this interaction on the acoustic mode is given in Eq. (6),

$$C_{ijkl} = C^{(0)}_{ijkl} - \sum_m \frac{1}{\omega_e^2(m)} F_{ij}(m)\, F_{kl}(m) \ , \qquad (6)$$

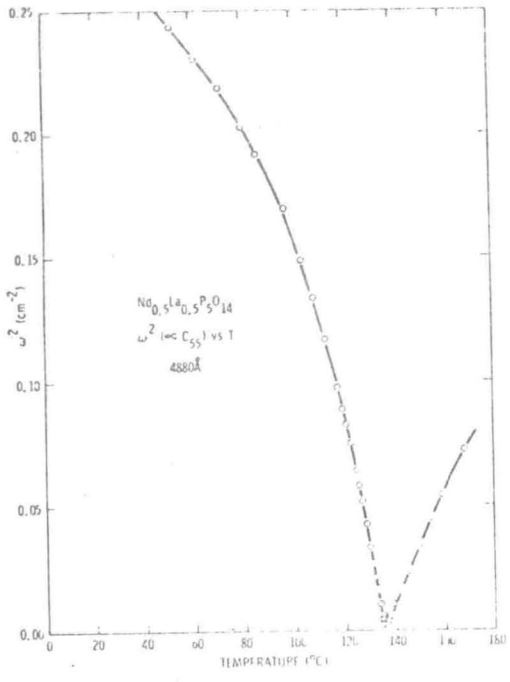
where C_{ijkl} is the renormalized value of the elastic constant $C^{(0)}_{ijkl}$, ω_e is the frequency of the optic mode of branch m with eigenvector e and the $F_{ij}(m)$ are functions of the Raman-scattering cross sections.

Equation (6) indicates that, if a mode of a frequency ω_e softens, as ω_e decreases at some point the elastic constant C_{ijkl} will vanish before $\omega_e = 0$. Thus it is not possible for the frequency of a Raman-active mode to vanish without the crystal first becoming unstable with respect to a homogeneous elastic deformation. For D_{2h} symmetry, this treatment indicates that C_{55} will be renormalized by the soft-optic mode.

To check this prediction, we investigated Brillouin scattering in the rare earth pentaphosphates and Fig. 6 illustrates the Brillouin spectra for various temperatures between room temperature and the transition temperature of 135.5°C. This figure shows one free spectral range of the Fabry-Perot, and the acoustic mode governed by C_{55} as well as the longitudinal mode governed by C_{33} are shown.

The transverse acoustic mode governed by C_{55} softens rapidly and its intensity increases by a factor of ∿300 between room temperature and T_c, reflecting the interaction with the soft-optic mode discussed above. The longitudinal mode, on the other hand, displays only a small frequency increase with increasing temperature with no anomaly at the transition.

The temperature dependence of the acoustic mode frequency, plotted as $\omega^2 (\propto C_{55})$ is shown in Fig. 7. Since the temperature dependences of the density and the refractive index are expected to be small, Fig. 7 is essentially a plot of the temperature dependence of C_{55}. As the temperature is decreased C_{55} decreases, attains a minimum at T_c, then increases as the temperature is further decreased. However C_{55} did not vanish at T_c; the lowest value observed was 0.3% of the room



temperature value. The temperature dependence of C_{55} can be described by Eq. (6) assuming the soft-optic mode has a temperature dependence of the form $\omega_o^2 = A(T - T_o)$. The coupling between the soft mode and C_{55} can thus be understood from a lattice dynamical treatment, and the transition occurs when C_{55} vanishes.

Fig. 7. ω^2 versus temperature.

References:

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1. W. Cochran, Advan. Phys. 9, 387 (1960).
2. P. S. Peercy, Phys. Rev. Lett. 35, 1581 (1975).
3. R. B. Griffiths, Phys. Rev. Lett. 24, 715 (1970).
4. C. H. Perry and D. K. Agrawal, Solid State Commun. 8, 225 (1970).
5. E. F. Steigmeier, G. Harbeke and R. K. Wehner in *Light Scattering in Solids*, ed. by M. Balkanski (Flammarion Sciences, Paris, 1971) p. 396.
6. D. K. Agrawal and C. H. Perry in Ref. 5, p. 401.
7. M. K. Teng, M. Balkanski and M. Massot, Phys. Rev. B5, 1031 (1972).
8. L. D. Landau, Phys. Z. Sowjetunion 8, 113 (1935).
9. G. A. Samara in *Advances in High Pressure Research*, ed.by R. S. Bradley (Academic, New York, 1969), Vol. 3, Chap.3.
10. G. A. Samara, private communication.
11. K. R. Albrand, R. Attig, J. Fenner, J. P. Jeser and D. Mootz, Mat. Res. Bull. 9, 129 (1974).
12. See, e.g., H. P. Weber, B. C. Tofield and P. F. Liao, Phys. Rev. B11, 1152 (1975).
13. D. F. Fox, J. F. Scott and P. M. Bridenbaugh, Solid State Commun. 18, 111 (1976).
14. P. B. Miller and J. D. Axe, Phys. Rev. 163, 924 (1967).