

Light scattering studies of rubidium cyanide under hydrostatic pressure

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The Raman and Brillouin spectra of RbCN were measured at pressures up to 0.8 GPa and at temperatures down to 80 K. The phase diagram of RbCN was obtained by using the change of the spectra at a phase transition as indicator for the phase line. The Raman spectra of the different phases of RbCN show a high similarity to the spectra of the high-pressure phases of KCN and the assignment of several Raman bands with the help of inelastic neutron-scattering data supports this expected correspondence. An introduction of pressure into the Landau-type expansion to describe the pressure dependence of the elastic constant C_{44} is discussed.

INTRODUCTION

The close relation of the alkali cyanides and the alkali halides with respect to their physical properties has stimulated general considerations and the use of methods to trace the relatively small perturbations that are introduced by the lower symmetry of the cyanide ion in the cubic ionic lattice back to the well-known basis of the alkali halides. It has long been known¹ that the stability of the crystalline phases of the alkali halides can be characterized by the ratio r_C/r_A of the radii of the cation and the anion. An increase of this parameter leads to the typical phase sequence from fourfold via sixfold to eightfold-coordinated lattices, and since the halide ion is the more compressible component in the lattice, increasing pressure pushes an alkali halide crystal into higher coordinated phases as well. The orientational disordered high-temperature phases of the alkali cyanides also fit into this scheme; only the lattice-filling factor of the higher coordinated phases is distinctly smaller, due to a widening of the lattice by more or less freely rotating CN^- dumbbells.² Even the low-temperature phases of the alkali cyanides in which the

CN^- ions are ordered in various orientational patterns were effectively classified in this way.³ RbCN plays a central part in testing these suggestions: Its phase diagram should exhibit the high-pressure phases of KCN but at lower and easier accessible pressures because of the larger radius of the Rb^+ cation.⁴ One expects the phase diagram of RbCN to look like the phase diagram of KCN (see Fig. 1); only the temperature ordinate would have to be shifted to about 1.5 GPa and scaled. Earlier x-ray structural investigations⁵ supported this idea in so far as the low-temperature phase of RbCN seemed to be highly correlated to the high-pressure phase *Aa* of KCN.⁶ Specific-heat measurements,⁷ on the other hand, did not show a second low-temperature phase transition in RbCN at zero pressure. The Raman spectrum and dielectric investigations of RbCN at zero pressure distinctly show only

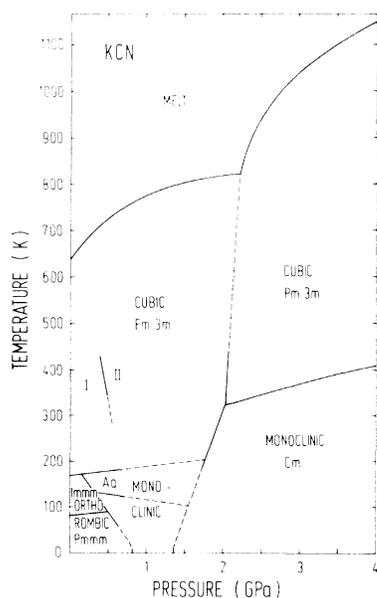


FIG. 1. Phase diagram of KCN.

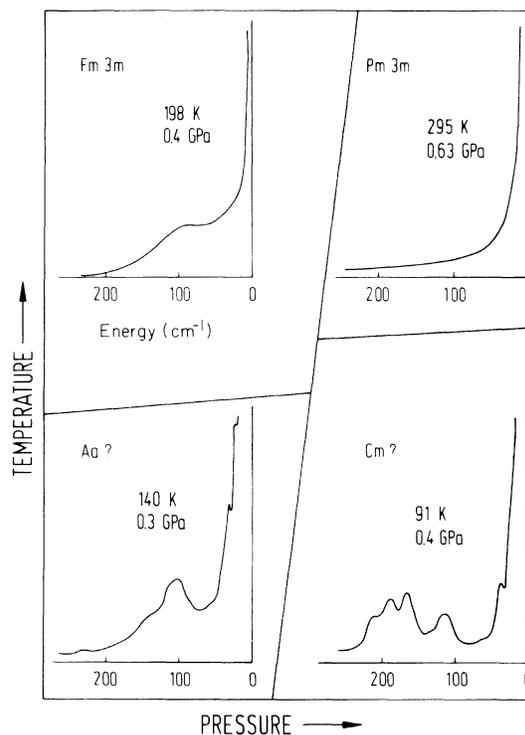


FIG. 2. Raman spectra of RbCN in the different phases of RbCN.

one phase transition at 132 K (Ref. 8) as well. In the higher-pressure region the NaCl→CsCl-type phase transition was found at 0.56 GPa at room temperature⁹ as expected from Fig. 1 and the corresponding transition pressures for the rubidium halides.¹⁰

We determined the phase diagram of RbCN at temperatures down to 90 K and at pressures up to 0.8 GPa, using the change of the Raman spectrum as an indicator for the phase line. We reached the high-pressure phase corresponding to the KCN phase *Cm*, which has a distorted CsCl-type structure, and measured its Raman spectrum.

For KCN the transition line between the cubic NaCl-type phase *Fm 3m* and the ordered low-temperature phases contains a triple point at about 0.1 GPa, where the three phases *Fm 3m*, *Immm*, and *Aa* are in coexistence⁴ (see Fig. 1). A characteristic softening of the elastic constant C_{44} in the cubic phase is connected with this phase line.^{11,12} In RbCN, where this triple point is not expected, the dynamics of the order-disorder transition from the disordered cubic phase *Fm 3m* should be less intricate. Ultrasonic and Brillouin measurements of the elastic constants C_{ij} of RbCN show a softening of C_{44} as found for KCN and little pressure dependence.^{13,14} No dispersion of the $C_{ij}(q)$ was found in the low-wave-number region for NaCN (Ref. 15) and KCN. We measured the Brillouin spectrum of RbCN under pressure in the NaCl-type phase and found the pressure derivatives of the elastic constant in agreement with the results from ultrasonic measurements.

EXPERIMENTS

The Raman spectra of melt-grown RbCN single crystals were measured in a coolable high-pressure He-gas cell¹⁶

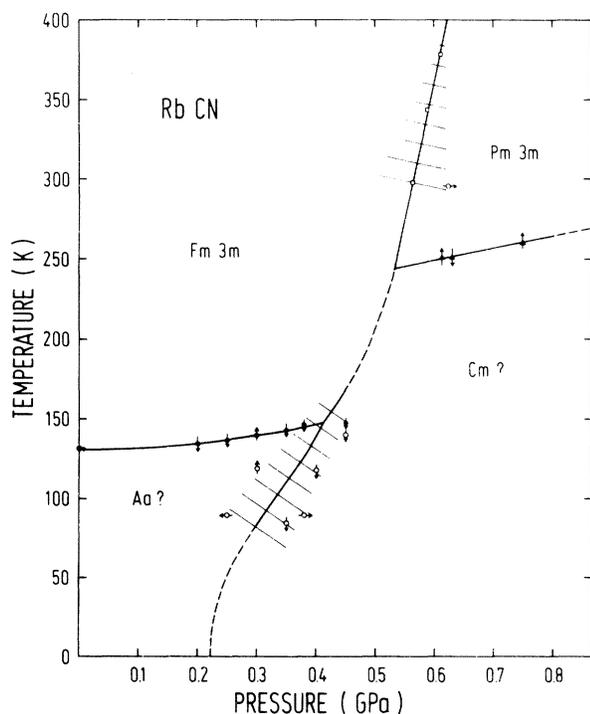


FIG. 3. Phase diagram of RbCN.

using a 4-W Ar laser, a 1-m double monochromator, and photon-counting equipment. We varied the temperature between 300 and 90 K and pressure in the range up to 0.8 GPa with an accuracy of ± 1 K and ± 5 MPa, respectively. No polarized Raman spectra were taken since the phase transitions of RbCN are destructive or lead to multi-domain opaque phases. The Brillouin spectra in the disordered NaCl-type phase *Fm 3m* of RbCN were recorded with an triple-pass Fabry-Perot interferometer.^{17,18} The same high-pressure cell and cryostat were used as for the Raman experiments.

Figure 2 shows the Raman spectrum of the different phases of RbCN in a schematic phase diagram. The typical changes of the spectrum at the phase line—the appearance (transparent or opaque) of the crystal in different phases and the softening of the elastic constant C_{44} at the transition—were used to obtain the actual phase diagram of RbCN (see Fig. 3). Above room temperature, three points of the steep phase line that divides the diagram into a left and a right part were taken from other experiments.¹⁹ This phase line represents the phase change from the NaCl-type structure or a distorted NaCl-type structure on the left to the CsCl-type—or below 250 K—to a distorted CsCl-type structure on the right. In contrast to the more horizontal phase lines, it is connected with a hysteresis of about ± 0.05 GPa when polycrystalline or multi-domain samples are used. A hysteresis of several tenths of a gigapascal was found when virginal single crystals were pressurized to cross this phase line. The structures of the phases on the upper left and upper right of the phase diagram are known. In these cubic phases the CN^- molecules are orientationally disordered; for the structure *Fm 3m* the [111] directions of the octahedral lattice cell are the distinctly preferred orientations of the molecular axes.²⁰ This disorder is probably lifted in the two phases at the lower part of the phase diagram. They are tentatively assigned with respect to corresponding monoclinic phases of KCN (see Fig. 1).

Our low-energy Raman spectra of the NaCl-type phase and the distorted NaCl-type phase under pressure are in agreement with earlier measurements at zero pressure.⁸ Compared to the cubic NaCl-type phase *Fm 3m* the Raman spectrum of the cubic CsCl-type phase *Pm 3m* shows no typical feature in our experiments, but note that the strong Rayleigh scattering of the polycrystalline sample in the high-pressure cell may hide broad structures at low energies. The spectrum of the distorted CsCl-type phase in the lower right-hand corner of the phase diagram shows several bands in the energy region up to 220 cm^{-1} and is much more distinct than the reported Raman spectrum of the corresponding phase *Cm* of KCN.^{21,22}

As in KCN the CN^- -stretching mode of RbCN shows the typical decrease in energy of $4\text{--}5 \text{ cm}^{-1}$ when the NaCl→CsCl-type phase line is crossed (see Fig. 4). The Raman band of this mode shifts with a rate of $8.0 \text{ cm}^{-1} \text{ GPa}^{-1}$ at 295 and 232 K in the disordered NaCl-type phase.

We found good agreement of the elastic constants $C_{ij}(T, P=0)$ with earlier Brillouin¹⁴ and ultrasonic¹³ measurements. The elastic constants C_{44} and $C' = C_{11} + C_{12} + 2C_{44}$ were measured at various temperatures and pressures in the cubic NaCl-type phase of RbCN. Figure 5 shows a plot of C_{44} versus temperature at three different

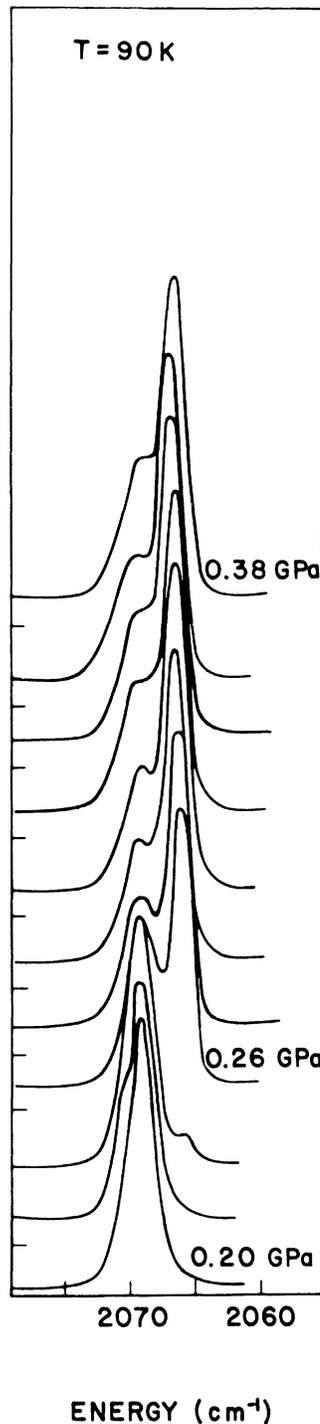


FIG. 4. Raman spectrum of the CN-stretching mode under pressure.

pressures. A small pressure change $dC_{44}/dP = -0.4 \pm 0.2$ at room temperature was found for the elastic constant of the shear mode, which goes soft at the transition line between the cubic phase $Fm\bar{3}m$ and the low-temperature phase with the distorted NaCl-type structure; for $C' = C_{11} + C_{12} + 2C_{44}$ we found $dC'/dP = 12 \pm 1$ at room temperature. Both values are in agreement with the ul-

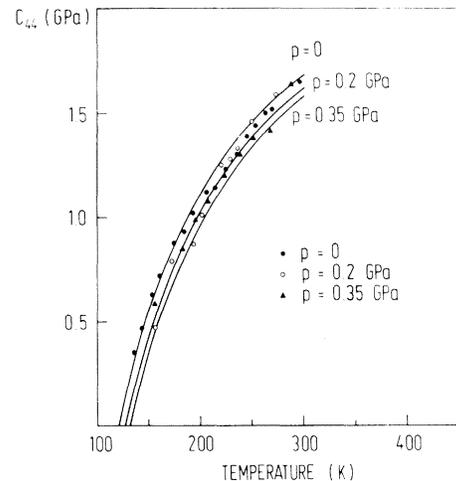


FIG. 5. Pressure and temperature dependence of the elastic constant C_{44} of RbCN.

trasonic measurements. The refraction index and density were taken from Ref. 14 and corrected with respect to their temperature and pressure dependency.

DISCUSSION

Phase diagram

The phase diagram of RbCN (Fig. 3) confirms the structural sequence that is expected for an orientationally disordered sixfold-coordinated ionic crystal: At higher pressures RbCN undergoes a transition to an eightfold-coordinated structure and at lower temperatures the orientational disorder freezes in on both sides of the phase diagram, leading to more ordered structures of respective coordination. The slopes of the coexistence lines between different phases are closely related to the nature of the transition according to the Clausius-Clapeyron equation

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S}, \quad (1)$$

where ΔV and ΔS are the volume change and entropy change at the phase transition. At the order-disorder transitions the structural change is small while the entropy change is large; thus the slope of the phase line is gentle. The change in coordination is connected with relatively large volume changes, and the slope of the corresponding phase line is much steeper. This argument supposes that the phase transition is of first order, which is the case for the transitions connected with the coordination change. The drastic softening of the elastic shear mode (C_{44}) at the order-disorder transition at low pressures would be an indication of a second-order transition, but the discontinuous structural jump that occurs at the phase line permits the application of Eq. (1). Of course, this discordant behavior of the system makes a small volume change ΔV plausible. For the order-disorder transition on the high-pressure side of the phase diagram similar conditions are probable.

The phase diagram includes two triple points at 240 K, 0.53 GPa and at 150 K, 0.41 GPa, where Eq. (1) allows an

interesting quantitative analysis. The slopes of the bifurcating phase-line branches are defined by three equations of type (1). In addition, the volume and entropy changes on a short isothermal and isobaric path that circles around the triple point add up to zero:

$$\sum_{i=1}^3 \Delta V_i = \sum_{i=1}^3 \Delta S_i = 0.$$

It follows, e.g., that an obtuse angle between two adjoining branches is not possible or, in other words, that the three elongations of the branches into the metastable region lie between stable lines, and by circling around the triple point one crosses alternately stable and metastable phase lines.²³ These rules have forced us to bend the phase lines of RbCN (see Fig. 2) especially near the lower triple point where only a slight change in slope is indicated by the experimental points at the order-disorder transition line on the left side. Note that within the coexistence regions the phase lines of Fig. 2 are merely guides to the eye that try to fulfill the physical conditions explained above. The broken phase-line elongation to zero temperature has an infinite slope to meet the requirements of Nernst's theorem $S(T=0)=0$ for phases in thermodynamic equilibrium. In spite of the considerable uncertainty of the slope of the central phase line in RbCN, it can be useful to deduce all the volume and entropy changes near a triple point from the five equations given above and one additional piece of information, e.g., the volume change at one line.¹⁹

The phase-transition temperature T_c from the cubic NaCl-type phase to the ordered low-pressure phase decreases strongly for the alkali cyanides from 288 K for NaCN to 168 K for KCN and 132 K for RbCN. A linear dependency of T_c on the cation radius r_C (Ref. 8) and also a proportionality of T_c to $r_C^{1.9}$ or to $a_0^{-5.6}$ where a_0 is the lattice parameter describe the experiments fairly well. In none of these cases can the slope of the phase line be obtained by merely introducing the compressibility into the derivative of the relation. We think that reorientations of the cyanide ions under pressure and perhaps bonding effects in the tighter crystal lattices must be considered to obtain a more quantitative understanding. An increasing tendency from a preferred [100] orientation of the CN^- molecules near the phase line in NaCN to preferred [111] and [110] orientations in RbCN is established by neutron scattering experiments.^{20,24} Hydrostatic pressure may work in the opposite direction and facilitate the [100] orientation. Since the indirect interaction of the CN^- molecules via small displacements of the cation is responsible for the phase transition,²⁵ this idea is further supported. An interesting feature of KCN is the existence of a metastability in the middle of the NaCl-type phase $Fm\bar{3}m$, which is called the KCN I \rightarrow II transition (see Fig. 1).^{26,27} The partial reorientation of the rotating and librating CN^- molecules in the octahedral lattice cell under

pressure without a change of the overall symmetry may explain this phenomenon. This would be a new type of disorder-disorder phase transition without any change of the space group of the crystal lattice.

In analogy to the phase diagram of KCN (see Fig. 1) the high-pressure low-temperature phase of RbCN should have the eightfold-coordinated structure Cm , which should also be the zero-pressure low-temperature phase of CsCN. X-ray investigations show the structure D_{3d}^5 ($R\bar{3}m$) for CsCN, but since the same structure originally was also found for this phase in KCN and revised by neutron scattering investigations,²⁸ the question whether all three cyanides have the same structure Cm in this phase is not settled.

Raman spectra

The Raman spectra of the different phases of RbCN in combination with the phonon dispersion of the phase²⁰ $Fm\bar{3}m$ give additional information about the space groups. Only the TA phonons from the L point [33 cm^{-1} at 150 K (Ref. 20)] of the NaCl-type phase $Fm\bar{3}m$ of RbCN have an energy sufficiently low to create the Raman band at 34 cm^{-1} below the nearly continuous transition. At the transition $Fm\bar{3}m \rightarrow Aa$ in KCN the cell doubles in a [111] direction of the cubic lattice, and the L point of the Brillouin zone folds into the Γ point⁴; all the L point phonons are Raman-allowed from symmetry considerations in phase Aa . The intensive Raman band at 104 cm^{-1} can hardly be assigned to a phonon originally coming from an X -point phonon of cubic RbCN (Ref. 20); thus the structure Aa is again the favored structure. If the structure is ordered in RbCN as in KCN, the existence of another low-temperature phase is not imperative and only considered because of the similarity of RbCN and KCN.

In addition to the similarity of the phase diagrams, no information about the structure of the high-pressure—low-temperature phase of RbCN is available, and the assignment (Cm) in Fig. 2 should therefore be considered tentatively. The Raman spectrum of RbCN in this phase shows more structure than that in the corresponding phase Cm of KCN (Refs. 21 and 22) (see Fig. 3) but this may partly be due to the much larger sample size we could use in the He-gas cell compared to a diamond squeezer.

Table I shows the energies of the Raman bands in different phases of RbCN together with their assignments in the NaCl-type phase.

Elastic constants

The pressure dependence of the elastic constants of RbCN in the phase $Fm\bar{3}m$ is comparable to KCN and NaCN.¹³ For continuous phase transitions that exhibit a soft mode, a reasonable assumption would be that the lines of constant soft-mode frequency lie parallel to the phase lines. This is, for instance, the case for the mercury (I)

TABLE I. The low-energy Raman bands of RbCN at high pressure.

T (K)	P (GPa)	Energy (cm^{-1})	Phase
140	0.3	34 [TA(L)], 104 [LA(L)], 140	$Aa?$
91	0.4	37, 113, 166, 189, 212	$Cm?$

halides, where a mode from the zone boundary of the prototype phase softens and folds into the center below the transition temperature.²⁹ For an elastic soft mode this would mean that the corresponding elastic constant would depend on pressure only via $T - T_c(P)$.

For the alkali cyanides the order-disorder transition from the cubic NaCl-type phase at lower temperatures is slightly first order, and the actual transition temperature $T_c(P)$ lies several degrees above the temperature T_0 where the elastic constant C_{44} would go to zero. The dependence of C_{44} on temperature

$$C_{44} = C_{44}^0 \left[\frac{T - T_0}{T - T_0'} \right] \quad (2)$$

was derived from a Landau-type expansion of the free energy.^{30,31} The noncubic representations of the orientational distribution of the CN molecules represent the order parameters that were linearly coupled to the strain. Without coupling, an ordering would take place at the temperature T_0' . Equation (2) can only be written in the form $C_{44} = C_{44}(T - T_c(P))$ if complicated pressure and temperature dependencies are assumed for the parameters, which is, of course, not in the spirit of the Landau expansion. In fact, experimentally, it was found for KCN that the temperature T_0 , where C_{44} should go soft, is much less pressure dependent than $T_c(P)$.³² Figure 5 shows the curve that represents the fit of Eq. (2) to the Brillouin data

of C_{44} in RbCN at $P=0$, as taken from Ref. 14 together with our data points. It shows that our zero-pressure data are in excellent agreement with the earlier results. For the other curves pressure was introduced into Eq. (2) just by replacing T_0 by $T_0 + (dT_c/dP)P$. The same parameters $T_0 = 121$ K, $T_0' = 1.5$ K, and $C_{44} = 2.78$ GPa were used; $dT_c/dP = 30$ K/GPa⁻¹ was determined as the average slope of the phase line from Fig. 2. We find that the pressure dependence of C_{44} is somewhat smaller than expected from the phase-line slope, although not as much smaller as was found for KCN. Thus hydrostatic pressure changes the phase-transition temperature T_c not only considerably more than one would expect from the compression of the lattice parameter, but also more than expected from the pressure dependence of the parameter $T_0(P)$ in the free-energy expansion.

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¹W. Biltz, *Raumchemie der festen Stoffe* (Voss, Leipzig, 1934).

²W. Dultz, Habilitationsschrift, Universität Regensburg, 1977 (unpublished).

³W. Dultz and H. Krause, *Phys. Rev. B* **18**, 394 (1978).

⁴W. Dultz, H. H. Otto, H. Krause, and J. L. Buevoz, *Phys. Rev. B* **24**, 1287 (1981).

⁵Struc. Rep. **2**, 142 (1942-44).

⁶G. S. Parry, *Acta Crystallogr.* **15**, 601 (1962).

⁷M. Sugisaki, T. Matsuo, H. Suga, and S. Seki, *Bull. Chem. Soc. Jpn.* **41**, 1747 (1968).

⁸Y. Kondo, D. Schoemaker, and F. Lüty, *Phys. Rev. B* **19**, 4210 (1979).

⁹J. B. Clark and C. W. F. T. Pistorius, *Solid State Commun.* **7**, 787 (1969).

¹⁰A. J. Darnell and W. A. McCollum, *J. Phys. Chem. Solids* **31**, 805 (1970).

¹¹S. Haussühl, *Solid State Commun.* **13**, 147 (1973).

¹²S. Haussühl and W. Michaelis, *Acta Crystallogr. Sect. A* **35**, 240 (1979).

¹³S. Haussühl, *Solid State Commun.* **32**, 181 (1979).

¹⁴W. Krasser, B. Janik, K. D. Ehrhardt, and S. Haussühl, *Solid State Commun.* **30**, 33 (1979).

¹⁵W. Rehwald, *Phys. Lett.* **87A**, 245 (1982).

¹⁶W. Dultz, H. Krause, and J. Ploner, in *High Pressure Science and Technology*, edited by K. D. Timmerhaus, and M. S. Barber (Plenum, New York, 1979), Vol. 1, p. 441.

¹⁷W. Rehwald, X. Vonlanthen, E. Rehaber, and W. Prettl, *Z. Phys. B* **39**, 299 (1980).

¹⁸J. R. Sandercock, *J. Phys. E* **2**, 566 (1976).

¹⁹J. B. Clark and C. W. F. T. Pistorius, *Solid State Commun.* **7**, 787 (1969).

²⁰K. D. Ehrhardt, thesis, Kernforschungsanlage Jülich, 1981 (unpublished).

²¹D. M. Adams and S. K. Sharma, *Trans. Faraday Soc. II* **74**, 1355 (1978).

²²M. Stock and W. Dultz, *Phys. Status Solidi A* **53**, 237 (1979).

²³G. Tamann, *Aggregatzustände* (Voss, Leipzig, 1922).

²⁴J. M. Rowe, D. G. Hinks, D. L. Price, S. Susman, and J. J. Rush, *J. Chem. Phys.* **58**, 2039 (1972).

²⁵K. H. Michel and J. Naudts, *Phys. Rev. Lett.* **39**, 212 (1977).

²⁶P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **72**, 79 (1937).

²⁷P. T. T. Wong, *J. Chem. Phys.* **69**, 2096 (1978).

²⁸D. L. Decker, R. A. Beyerlein, G. Roullet, and R. G. Worlton, *Phys. Rev. B* **10**, 3584 (1974).

²⁹E. Rehaber, H. Fischer, and W. Dultz, *Phys. Rev. B* **25**, 5889 (1982).

³⁰W. Rehwald, J. R. Sandercock, and H. Rossinelli; *Phys. Status Solidi A* **42**, 699 (1977).

³¹M. Boissier, R. Vacher, D. Fontaine, and R. M. Pick, *J. Phys. (Paris)* **39**, 205 (1977).

³²H. D. Hochheimer, W. F. Love, and C. T. Walker, *Phys. Rev. Lett.* **38**, 832 (1977).