

Elastic properties of  $(\text{KBr})_{1-x}(\text{KCN})_x$ 

R. Feile, A. Loidl, and K. Knorr

*Institut für Physik, Universität Mainz, Federal Republic of Germany*

(Received 2 August 1982)

The elastic constants  $c_{11}$  and  $c_{44}$  of the mixed crystals  $(\text{KBr})_{x-1}(\text{KCN})_x$  ( $x=0, 0.008, 0.035, 0.16, \text{ and } 0.20$ ) were measured for temperatures from 3 to 300 K at MHz frequencies. The elastic constants soften with decreasing temperature and pass through a minimum at characteristic, concentration-dependent temperatures  $T_F$ , which signal the freezing in of the CN reorientations. The results well above the minima will be analyzed in terms of a coupling of the lattice strains to the electric quadrupolar susceptibilities of the CN system. Significant dispersion effects around  $T_F$  are reported, which support the viewpoint of a dynamic freezing process.

## INTRODUCTION

Hausühl's observation of the anomalous thermoelastic behavior of KCN (Ref. 1) stimulated intensive research on the alkali cyanides. Their structural and dynamic properties, mainly determined from neutron and light scattering experiments,<sup>2,3</sup> are now understood by a coupling of the translational modes (phonons) to the reorientations of the dumbbell-shaped CN molecules, which reside in a hindering Devonshire potential.<sup>4</sup> In the mixed crystals  $(\text{KBr})_{x-1}(\text{KCN})_x$  the coupling leads for  $x > 0.56$  to structural phase transitions from cubic (NaCl) high-temperature phases to orthorhombic low-temperature phases,<sup>5-10</sup> whereas for lower concentrations of  $x$  there is evidence of a low-temperature pseudocubic glass state.<sup>11-15</sup> Here the orientations of the CN molecules are frozen in a random way along the easy directions of the potential.

In the present study we report measurements of the elastic constants  $c_{11}$  and  $c_{44}$  from room temperature down to 3 K for concentrations of  $x$  from 0.008 to 0.20. The results above the freezing temperature will be analyzed quantitatively in terms of the coupling mentioned above. We will also comment on some new details of the freezing process.

## EXPERIMENTS AND RESULTS

In addition to the reference system KBr, single crystals with four different CN concentrations of  $x$  were investigated, which were grown in the crystal-growth laboratory of the University of Utah. The nominal concentrations of the melt were 0.01, 0.05,

0.20, and 0.25. A chemical analysis of the second and third compound yielded concentrations of 0.04 and 0.14.<sup>16</sup> Gravimetric and infrared-absorption determinations of the CN content lead to  $x$  values of 0.008, 0.035, 0.16, and 0.20, where in the gravimetric analysis a linear interpolation between the densities of KBr and KCN was assumed. Since the last set of figures seems to be the most reliable one to us, we refer to these concentrations in the present paper, though one should keep in mind that  $x=0.035$  and 0.16 here, and 0.04 and 0.14 in Refs. 13, 14, 16, and 17, which refer to pieces of the same single crystal.

The temperature of the samples could be set to values between 3 and 300 K with the use of a continuous helium flow cryostat, while being measured with a calibrated silicon diode. The elastic properties of the mixed crystals were investigated by measuring the velocity of sound waves of frequencies ranging from 10 to 70 MHz. Quartz transducers—cross-cut transducers for longitudinal waves and ac-cut transducers for the transverse waves—were bonded to the cleaved (100) faces of the samples. Sometimes when the cleavage was not perfect the faces had to be grounded and polished to optical quality, which was, in particular, necessary for the operation of the 10-MHz transducers in the overtone mode. The pulsed excitation voltage for the transducers was supplied by commercial equipment,<sup>18</sup> which also contained additional electronic features to detect and amplify the ultrasonic echoes from the multiple reflections of the sound wave within the sample. The sound velocity was determined by measuring the transit time of the ultrasonic pulse with the use of the standard pulse-echo overlap method.<sup>19</sup> The coarse determination

of the velocity was achieved by superposing the envelopes of two successive pulses. This gives the absolute value for the sound velocity with an error of about 4%. The finer resolution for the measurements of the temperature dependence was achieved by superposing the single oscillations within the bursts. This gives an accuracy of about  $10^{-4}$ .

The main problem for these experiments was the bonding of the transducers to the samples. The conventionally used bonds—pumping oils and vacuum greases—gave rather good signal from room temperature down to about 40 K below their solidification points. Also the common acrylic glues gave excellent signals for longitudinal as well as for transverse waves. However, the different thermal expansion coefficients of quartz and the samples produced so much stress along the bond on cooling that either the bond or the sample cracked. With these common bonding techniques we were only able to measure down to about 100 K.

The problem of measuring at lower temperatures was solved by using gases with sufficiently low boiling and melting points as bonds (see Table I).<sup>20</sup> The substances were condensed onto the samples, which were held at temperatures below the boiling points of these substances by means of a capillary. On the surface they creep, due to capillary forces, into the narrow gap between transducer and sample. Already in the liquid phase these substances are good bonds for the longitudinal sound waves; transverse echoes appear the moment the liquids solidify on further cooling.

The gases used in our experiment are listed in Table I together with their melting and boiling temperatures. The results of the measurements at 10 MHz are shown in the first two figures. Figure 1 shows the temperature dependence of the elastic constant  $c_{11}$ , which is the squared velocity of longitudinal waves along [100] times the density.  $c_{11}(T)$  of pure KBr decreases monotonically with increas-

TABLE I. Melting (mp) and boiling (bp) points of the substances used for bonding the transducers to the samples.

	mp (K)	bp (K)
N <sub>2</sub>	63	77.4
CH <sub>4</sub>	90	111
C <sub>2</sub> H <sub>6</sub>	90	184
C <sub>2</sub> H <sub>4</sub>	104	169
CCl <sub>2</sub> F <sub>2</sub>	115	243
C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>	179	277
C <sub>5</sub> H <sub>12</sub>	257	283

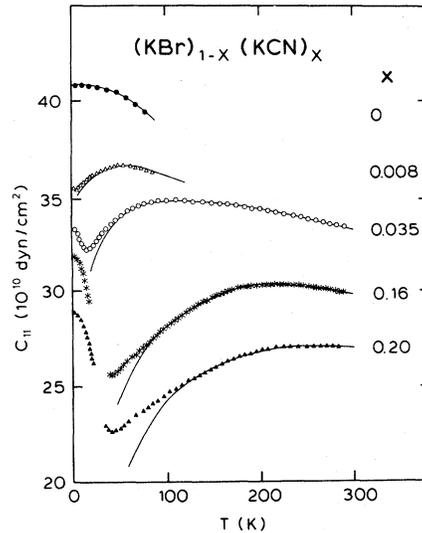


FIG. 1. Elastic constant  $c_{11}$  vs temperature for five concentrations of  $x$ . The solid lines are the results of the mode-mode coupling model.

ing temperature. The data of the mixed crystals exhibit minima at characteristic temperatures  $T_F$ , which are deeper the higher the CN concentration.

The minima shift to higher temperatures with in-

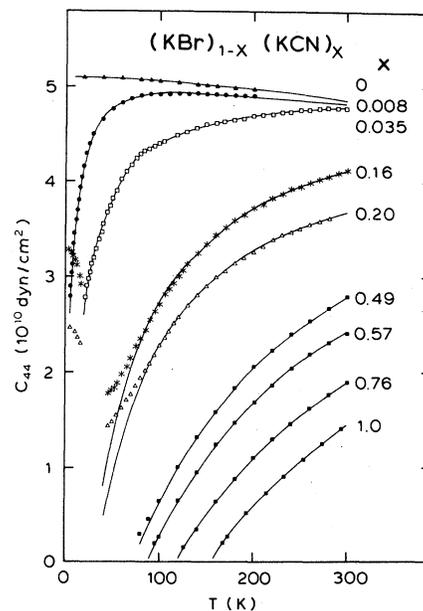


FIG. 2. Elastic constant  $c_{44}$  vs temperature for several concentrations of  $x$ . The results of Haussühl (Ref. 1) ( $x=1$ ) and Garland *et al.* (Ref. 10) ( $x \geq 0.5$ ) are also shown. The solid lines are the results of the mode-mode coupling model. For  $x \geq 0.5$  the theoretical lines are calculated with the use of the parameters determined by Garland *et al.*

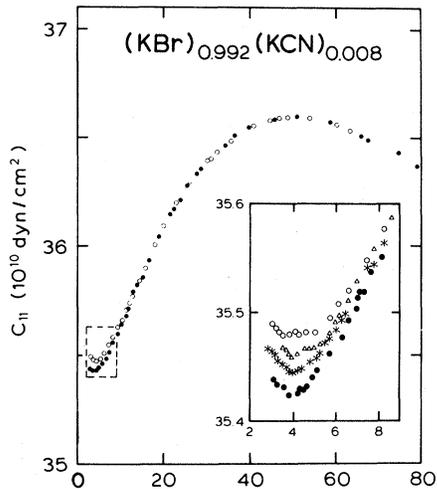


FIG. 3. Frequency dependence of the elastic constant  $c_{11}$  for  $x=0.008$ . The inset shows the different minima for four frequencies: 10 MHz ( $\bullet$ ), 30 MHz ( $*$ ), 50 MHz ( $\Delta$ ), and 70 MHz ( $\circ$ ).

creasing concentration. For the two lower concentrations the echoes could be followed through the minima, whereas for the two higher-doped crystals the echoes were lost near  $T_F$  due to a high attenuation of the sound waves. The absolute values of the elastic constants differ somewhat from those values we had given in a preliminary report.<sup>13,16</sup> They now represent a mean value of different runs that we performed in the course of this experiment.

Figure 2 shows the  $T$  dependence of the elastic constant  $c_{44}$ , which was determined from the velo-

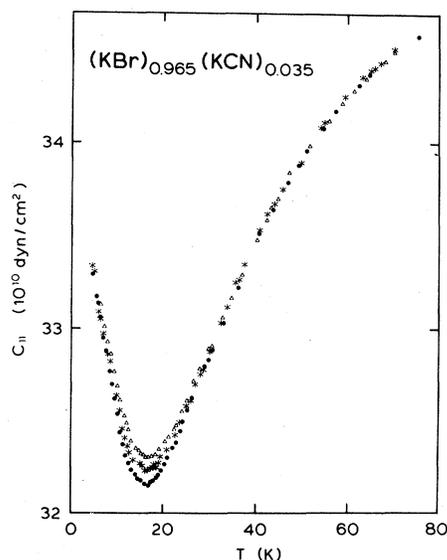


FIG. 4. Elastic constant  $c_{11}$  for three measuring frequencies: 10 MHz ( $\bullet$ ), 30 MHz ( $*$ ), and 50 MHz ( $\Delta$ ).

city of the transverse wave along [100]. We also included the data obtained by Garland *et al.*<sup>10</sup> for  $x=0.49, 0.57,$  and  $0.76,$  and those of Haussühl<sup>1</sup> for pure KCN. Whereas the elastic constants almost completely soften for the high concentrations, the low concentrations again show minima, which are more pronounced than those of the  $c_{11}$  data. As the attenuation of the transverse modes is higher, compared to the longitudinal ones, the echoes are lost in a wider range near  $T_F$ , and appear again only for  $x=0.16$  and  $x=0.2$  at the low-temperature side of  $T_F$ . The solid lines in Figs. 1 and 2 show the theoretical results, which will be described later.

The frequency dependence of the elastic constant  $c_{11}$  is demonstrated in Figs. 3 and 4. The data obtained for  $x=0.008$  below 80 K are shown in Fig. 3 for 10 MHz (solid dots) and 70 MHz (open circles). The original data were scaled to one another so that they coincide at high temperatures between 50 and 80 K. The inset gives the detailed temperature dependence around  $T_F=4$  K for low measuring frequencies 10, 30, 50, and 70 MHz, which were obtained as overtones of the transducer. Since switching to the overtones can be performed without mechanical changes, the measurements can be com-

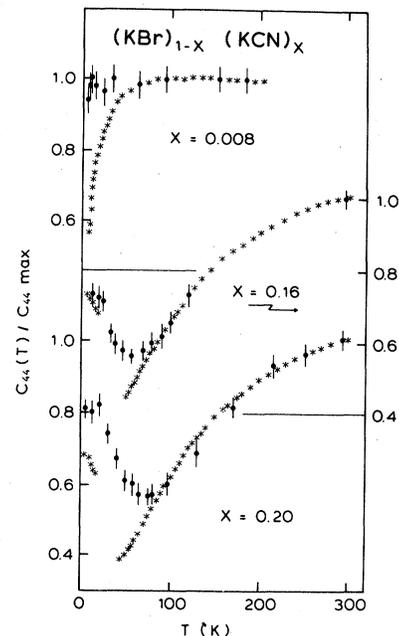


FIG. 5. Elastic constant  $c_{44}$  normalized to a high-temperature value, as measured by ultrasonic experiments ( $*$ ), and by inelastic neutron scattering ( $\bullet$ ) experiments. The mismatch at the lowest temperatures for  $x=0.20$  might be due to an absolute error in the ultrasonic measurements in this region; a unique scaling is impossible due to the loss of the signal around  $T_F$ .

pared directly with one another without any further adjustment. The data obtained for  $x=0.035$  at frequencies 10, 30, and 50 MHz near  $T_F$  are shown in Fig. 4. In Fig. 5 we show a comparison of the elastic constant  $c_{44}$ , once measured by ultrasonic sound propagation, and once by inelastic neutron scattering at a reduced wave vector  $q/q_{\max}=0.1$ . The neutron results were obtained on a triple-axis spectrometer, located at the cold neutron source of the reactor DR3 at Risø, Denmark. One notes that the neutron data agree well with the ultrasonic data at higher temperatures, but that for  $x=0.16$  and 0.20 the minima of the neutron experiment are more shallow and occur at higher temperatures. The largest discrepancy between both methods was observed for the lowest concentration  $x=0.008$ , where the ultrasonic elastic constant shows a temperature variation of 40%, but the neutron data stay practically temperature independent.

#### ANALYSIS OF THE PARAELASTIC REGIME

We address our interest first to the temperature range above the minima. We call this high-temperature range the paraelastic regime since the CN molecules are expected to reorient at high rates in a way very similar to that of spins in the paramagnetic phase. The results on the  $T$ -dependence of the elastic constant,  $c_{11}$  and  $c_{44}$ , respectively, will be analyzed in terms of the following expression:

$$c_i(T) = c_i^0 \left\{ 1 + \alpha_i \Theta / [\exp(\Theta/T) - 1] - g_i^2 / (T - T_{ci}) \right\}, \quad (1)$$

where  $i=11$  and 44, respectively.  $c_i^0$  is the  $T$ -independent background constant. The second term describes approximately the temperature dependence due to anharmonic effects within the phonon system in the absence of the aspherical CN molecules.  $\Theta$  is the Debye temperature. The third term

is due to the interaction between the translational modes and the CN molecules with the coupling coefficient  $g_i^2$ . Here the quadrupolar susceptibility of the decoupled CN system is assumed to obey a Curie-Weiss law.  $T_{ci}$  is a measure of the effective interaction between the CN quadrupoles. (In previous publications we worked with more elaborate expressions for the susceptibility, but for the high temperatures and the low frequencies of the present problem the Curie-Weiss law is a good approximation for the static susceptibility.<sup>13,16</sup>)

In the absence of the anharmonic contribution, i.e.,  $\alpha_i=0$ , Eq. (1) reduces to the well-known form

$$c_i(T) = c_i^0 (T - T_{si}) / (T - T_{ci}) \quad (2)$$

with  $T_{si} = T_{ci} + g_i^2$ .  $T_{si}$  is the temperature at which the elastic constant would go soft, signalling a continuous structural phase transition. The free parameters of Eq. (1),  $c_0$ ,  $\alpha$ ,  $\Theta$ ,  $T_c$ , and  $g^2$ , were determined from fits to the data. The Debye temperature  $\Theta$  was at once adjusted to a value of 125 K from an inspection of the CN-free reference system KBr, and then held constant in the following calculations. The four parameters remaining were obtained from individual experimental curves (given mode and given concentration). The parameters were often highly correlated and we selected parameter sets with a reasonable, i.e., monotonic trend, with the concentration  $x$ . The final values are listed in Table II for the elastic constant  $c_{11}$ , and in Table III for  $c_{44}$ . The theoretical  $T$  dependence obtained with these values is shown as solid lines in Figs. 1 and 2. For  $c_{44}$  the results of the fits of Garland *et al.* on  $x=0.49, 0.57, 0.76$ , and 1.0 are included. These authors used an expression equivalent to Eq. (2). One notes a good agreement between experiment and theory for both modes at all concentrations. The coupling coefficients  $T_c$  and  $g^2 + T_c$  scale approximately linearly with the CN concentration. The background elastic constants vary

TABLE II. Parameters of the coupled-mode model for the elastic constant  $c_{11}(T)$  in the paraelastic regime to produce the theoretical temperature dependence of the elastic constants as in Fig. 1.

$x$ (nom)	$x$ (anal)	$g^2 + T_c$ (K)	$T_c$ (K)	$c_{11}^0$ ( $10^{10}$ dyn cm $^{-2}$ )	$\alpha$ ( $10^{-4}/\text{K}$ )
0				40.9	8.1
0.01	0.008	-0.64	-1.6	37.5	6.0
0.05	0.035	-2.1	-7.0	37.2	3.8
0.20	0.16	-9.6	-44.8	38.6	5.0
0.25	0.20	-10.0	-54.0	35.1	4.5
1		-57.0	-232.0	32.7	3.7

TABLE III. Parameters of the coupled-mode model for the elastic constant  $c_{44}(T)$  in the paraelastic regime to produce the theoretical temperature dependence of this elastic constant as in Fig. 2. The values for  $x \geq 0.5$  were taken from a recent work by Garland *et al.* (Ref. 10) and demonstrate the continuous behavior of  $g^2 + T_c$  and of  $T_c$  over the whole concentration range.

$x$ (nom)	$x$ (anal)	$g^2 + T_c$ (K)	$T_c$ (K)	$c_{44}^0$ ( $10^{10}$ dyn cm $^{-2}$ )	$\alpha$ ( $10^{-4}/\text{K}$ )
0				5.11	1.8
0.01	0.008	1.0	-3.4	5.2	2.5
0.05	0.035	5.5	-8.1	5.05	0.5
0.20	0.16	28.8	-35.2	5.22	1.0
0.25	0.20	32.4	-44.0	5.05	2.0
0.50	0.49	71.8	-138.0	5.40	
0.60	0.57	86.2	-136.0	4.95	
0.80	0.76	118.2	-146.0	4.66	
1		153.3	-212.0	5.08	

somewhat with  $x$  for  $c_{44}$  and decrease with increasing  $x$  for  $c_{11}$ . The coefficient of the anharmonic term  $\alpha_{11}$  seems to become smaller for higher CN concentrations. For  $\alpha_{44}$  it is difficult to separate the weak temperature dependence due to this term from the much stronger one caused by the third term in Eq. (1). The fits are not much worse with  $\alpha_{44}=0$ . The  $T$  dependence of  $c_{44}$  is much stronger than that of  $c_{11}$ . Note that  $c_{11}$  is a linear combination of the two symmetry modes, the bulk module ( $A_{1g}$ ), and the  $(c_{11}-c_{12})/2$  ( $E_g$ ) mode. We have shown previously (for  $x=0.04$ ) that it is only the  $E_g$  component of  $c_{11}$  that is affected by the reorientations of the CN system, while the  $A_{1g}$  component is insensitive. This fact and the slightly lower coupling coefficients  $T_c$  and  $T_c + g^2$  of  $c_{11}$  explains why the anomalous behavior of  $c_{11}$  is less dramatic than that of  $c_{44}$ .

#### COMMENTS ON THE FREEZING PROCESS

At lower temperatures the elastic constants deviate more and more from the extrapolated paraelastic behavior. They pass through a minimum at a temperature  $T_F(x)$  and stiffen again for  $T \rightarrow 0$ , though they do not reach the background values  $c_0$ . A detailed analysis of  $c_{44}$  around  $T_F$  is handicapped by the heavy damping of the transverse sound waves, which leads to a loss of the echoes in the ultrasonic experiment. Nevertheless, the results support the view that there is a common freezing temperature  $T_F$  (Refs. 13 and 14) of  $c_{11}$  and  $c_{44}$  for a given  $x$ . We thus inspect  $c_{11}$  more closely. Despite the fact that while well away from  $T_F$  the elastic constant  $c_{11}$  is independent of the measuring fre-

quency, there are clear dispersion effects around  $T_F$ . Higher frequencies lead to shallower minima, as documented in Figs. 3 and 4, a fact which reminds us very much of the behavior of the dielectric constant of the same system.<sup>17</sup> A slight shift of  $T_F$  to higher values for higher frequencies is evident for  $x=0.035$  (Fig. 4). The difference of  $T_F$  between the 10- and 50-MHz data is nearly 1 K. (For  $x=0.008$  the relative scatter of the data is too large for a quantitative analysis.) Referring to our recent work on the frequency dependence of  $T_F$  (Refs. 16 and 17), we note that the overall Arrhenius law, which was proposed there on the basis of dielectric, ultrasonic, and neutron data, covering a frequency range from  $10^2$  to  $10^{12}$  Hz, does not strictly hold within the ultrasonic regime. The overall Arrhenius law predicts a shift of  $T_F$  between 10 and 50 MHz of about 2 K for  $x=0.035$ . According to recent theoretical work<sup>21,22</sup> on the sound propagation in spin-glasses, the frequency-dependent part of the elastic constant  $\Delta c(\nu)$  at  $T=T_F$  should be proportional to the square root of the frequency. The experimental results on  $c_{11}(\nu)$  for  $x=0.008$  and 0.035 at the corresponding freezing temperatures are shown in Fig. 6 on a linear scale. The solid lines are the best fits to a square-root behavior. For the lower concentration the  $\nu^{1/2}$  dependence is well realized. For the higher concentration, where only three data points exist, the confirmation of this law is less convincing.

Another interesting detail of the glass transition is shown by the comparison between the ultrasonic and the neutron results on  $c_{44}$ . For the concentrations  $x=0.16$  and 0.20, one observes the presently well-established effect that the minima of the high-

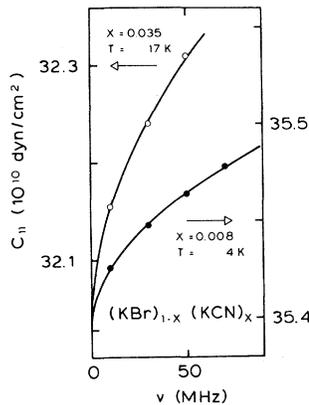


FIG. 6. Frequency dependence of the minimum of the elastic constant  $c_{11}$  at  $T_F \approx 4$  K for the concentration  $x=0.008$ , and for  $x=0.0035$  at  $T_F \approx 17$  K, respectively. The solid lines are the best fits to a  $\nu^{1/2}$  behavior.

frequency neutron data are less deep, and occur at higher temperatures, than in the corresponding ultrasonic experiment. For the low concentration  $x=0.008$ , however, the neutron data completely fail to reproduce the  $T$  dependence of the ultrasonic  $c_{44}$ . Presumably, this result can be explained by the crossover from a situation of slow to one of fast relaxation.<sup>4</sup> Let us introduce a characteristic relaxation time  $\tau$  for the CN reorientations in a Debye-type quadrupolar susceptibility. With the measuring frequencies  $\omega_{us}$  and  $\omega_n$  for the ultrasonic and the neutron experiment, we propose that the relation  $\omega_n, \omega_{us} < 1/\tau$  holds for  $x=0.16$  and  $0.20$ ,

whereas  $\omega_n > 1/\tau > \omega_{us}$  is obeyed for  $x=0.008$ . A more detailed support for this view will be given in a planned future publication of neutron results.

## SUMMARY

In this paper detailed ultrasonic results on the elastic properties of mixed crystals  $(\text{KBr})_{1-x}(\text{KCN})_x$  have been reported. Both modes of propagation, longitudinal and transverse, along [100] show similar behavior of the elastic constants as a function of temperature with a characteristic minimum at the freezing temperature  $T_F$ , which signals the onset of a reorientational glass state for  $x < 0.5$ . Well above  $T_F$  a coupled-mode model for the elastic constants is appropriate. At  $T_F$  the frequency dependence of the elastic constant follows approximately a  $\nu^{1/2}$  law, as was observed from the longitudinal waves at frequencies between 10 and 70 MHz. Another feature of the dynamical properties of the glass phase became obvious from comparing ultrasonic and neutron scattering experiments, where we were able to observe the transition from the fast to the slow relaxation regime.

## ACKNOWLEDGMENTS

Two of us (R.F. and A.L.) thank the members of the Physics department Risø, Denmark, for their kind hospitality. This work was supported by the Bundesministerium für Forschung und Technologie of the Federal Republic of Germany.

- <sup>1</sup>S. Haussühl, *Solid State Commun.* **13**, 147 (1973).
- <sup>2</sup>J. M. Rowe, D. G. Hinks, D. L. Price, and S. Susman, *J. Chem. Phys.* **58**, 2039 (1973).
- <sup>3</sup>W. Dultz, *Solid State Commun.* **15**, 595 (1974).
- <sup>4</sup>K. H. Michel, J. Naudts, and B. DeRaedt, *Phys. Rev.* **18**, 648 (1978).
- <sup>5</sup>J. M. Rowe, J. J. Rush, N. J. Chessier, K. H. Michel, and J. Naudts, *Phys. Rev. Lett.* **40**, 455 (1978).
- <sup>6</sup>D. Durand (unpublished).
- <sup>7</sup>A. Loidl, K. Knorr, J. Daubert, W. Dultz, and W. J. Fitzgerald, *Z. Phys. B* **38**, 153 (1980).
- <sup>8</sup>J. Z. Kwiecien, R. C. Leung, and C. W. Garland, *Phys. Rev. B* **23**, 4419 (1981).
- <sup>9</sup>S. K. Satija and C. H. Wang, *Solid State Commun.* **28**, 617 (1978).
- <sup>10</sup>C. W. Garland, J. Z. Kwiecien, and J. C. Damien, *Phys. Rev. B* **25**, 5818 (1982).
- <sup>11</sup>J. M. Rowe, J. J. Rush, D. J. Hinks, and S. Susman, *Phys. Rev. Lett.* **43**, 1148 (1979).
- <sup>12</sup>K. H. Michel and J. M. Rowe, *Phys. Rev. B* **22**, 1417

- (1980).
- <sup>13</sup>A. Loidl, R. Feile, and K. Knorr, *Z. Phys. B* **42**, 143 (1981).
- <sup>14</sup>A. Loidl, R. Feile, and K. Knorr, *Phys. Rev. Lett.* **48**, 1263 (1982).
- <sup>15</sup>S. Bhattacharya, Sr. Nagel, L. Fleishman, and S. Susman, *Phys. Rev. Lett.* **48**, 1267 (1982).
- <sup>16</sup>A. Loidl, R. Feile, K. Knorr, B. Renker, J. Daubert, D. Durand, and J. B. Suck, *Z. Phys. B* **38**, 253 (1980).
- <sup>17</sup>K. Knorr and A. Loidl, *Z. Phys. B* **46**, 219 (1982).
- <sup>18</sup>Matec, Inc., Warwick, Rhode Island.
- <sup>19</sup>E. P. Papadakis, in *Physical Acoustics XII*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1976).
- <sup>20</sup>*Handbook of Physics and Chemistry*, edited by R. C. Weasnd, 60th ed. (Chemical Rubber Company, Boca Raton, 1979).
- <sup>21</sup>J. A. Hertz, A. Khurana, and R. A. Klemm, *Phys. Rev. Lett.* **46**, 496 (1981).
- <sup>22</sup>K. H. Fischer, *Z. Phys. B* **43**, 291 (1981).