Neutron Scattering Study of the Dynamics of $(KCN)_{0.5}(KBr)_{0.5}$

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Our earlier measurements on pure KCN and $(KCN)_{0.25}(KBr)_{0.75}$ have been extended to mixed crystals of $(KCN)_{0.5}(KBr)_{0.5}$. From a comparison of the observed neutron scattering line shapes to those predicted by a simple extension of the theory used to describe pure KCN, it is concluded that this theory does not describe the mixed systems correctly. This Letter suggests that the current results may be indicative of the formation of a "glass" phase at low temperatures in these mixed systems.

In earlier work,[1] the results of neutron scattering measurements of the dynamical behavior of the coupled rotational-vibrational modes which lead to a first-order phase transition in KCN at 168 K have been presented. Reported[2] also are similar studies of a mixed crystal of $(KCN)_{0.25}$-$(KBr)_{0.75}$ in which there is no observable crystallographic phase transition for temperatures as low as 4 K. In the present communication, we extend this work to include $(KCN_{0.5})(KBr)_{0.5}$ in which there is no observable crystallographic phase transition for temperatures as low as 2 K. The earlier results on pure KCN were well described by the theory of Michel and Naudts,[3] in which a linear coupling between reorientational motions of the $(CN)^-$ ion and certain phonon branches was derived from the repulsive interactions between the $(K)^+$ and $(CN)^-$ ions. The theory described the temperature dependence of both the elastic constants C_{44} and C_{11} and the detailed neutron-scattering line shapes. In addition, it gave a good description to the momentum-transfer dependence of the neutron-scattering line shapes. In contrast, the mixed-crystal results do not agree well with the theory. We suggest that they are indicative of the formation of a low-temperature "glass" phase.

Following the experimental observation that for mixed crystals of KCN and KBr, the frequency of the "soft mode" first decreased with temperature, then increased,[2,4] Michel, Naudts, and deRaedt[5] proposed in 1978 an extension of the earlier model which seemed to explain the experimental results. In order to further test the proposed model, the present work on $(KCN)_{0.5}$-$(KBr)_{0.5}$ was undertaken. The crystal, which was grown from the melt by a technique similar to that used earlier[6] for KCN, had a volume of approximately 5 cm^3. The mosaic spread of the sample before thermal cycling was less than 0.25°; after several cycles to 13 K, evidence of damage to the crystal could be observed by neutron diffraction. The neutron inelastic scattering was measured at the National Bureau of Standards reactor under various experimental conditions. A typical spectrometer configuration used an incident energy of 5 meV with collimation of 40-20-20-40 minutes of arc before and after the monochromator and analyzer.

Since there is no observable crystallographic phase transformation for x less than 0.75 in $(KCN)_x(KBr)_{1-x}$,[4] the neutron-scattering line shapes were measured for temperatures between 13 K and 295 K. Although measurements were made for many directions in the crystal, the phonons of interest in the present communication are those propagating along a cube edge with polarization perpendicular to the propagation direction, i.e., [100] TA. In Fig. 1, the neutron scattering observed at a wave vector of (2, 1.9, 0) is shown as a function of energy for various temperatures. This wave vector corresponds to a reduced wave vector of 1/10 the distance to the Brillouin-zone boundary along a [100] direction. As can be seen from the figure, the energy of the phonon peak decreases as temperature is decreased from 295 to 150 K. At 150 K a small peak at zero energy transfer also appears. This peak grows and the energy of the phonon mode decreases down to 90 K, where the phonon is in fact overdamped, then at ~50 K the phonon energy increases while the "elastic" peak also grows in intensity. The intensity at zero energy transfer has essentially the shape of the resolution function from the time that it is first observed down to the lowest temperatures measured.

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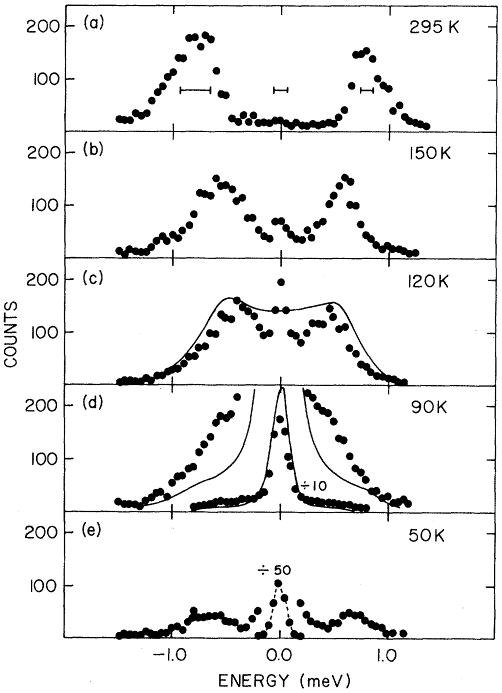

FIG. 1. Neutron–inelastic-scattering line shapes for $(KCN)_{0.5}(KBr)_{0.5}$ at $q = (2.0, 1.9, 0)$ in units of $2\pi/a$, where a is the lattice parameter. The reduced wave vector q is 1/10 the way to the Brillouin-zone boundary. Resolution is shown for three energies in (a). Solid curves shown in (c) and (d) are the predictions of Ref. 5 with relative normalization given by the theory. The comparison at 120 K is typical of those for 110 and 130 K. Dashed line at 50 K is only a guide to the eye.

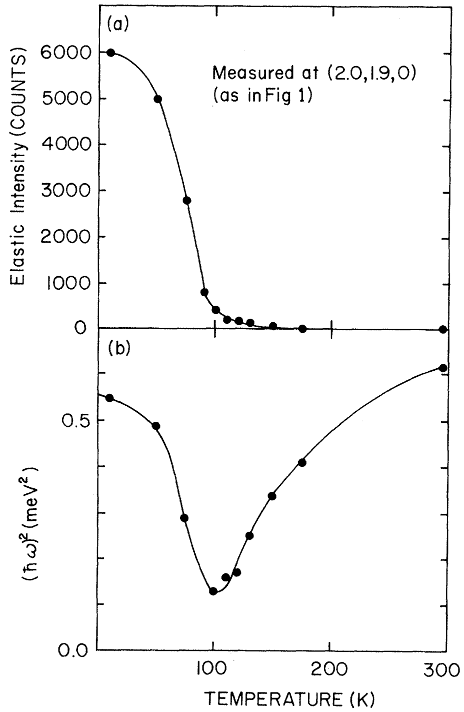

FIG. 2. (a) The intensity at zero energy transfer for the same momentum transfer as Fig. 1. Lines are a guide to the eye. (b) The square of the energy of the phonon peak at the momentum transfer of Fig. 1. Lines are a guide to the eye.

The behavior of the scattering at this wave vector is summarized in Fig. 2, where the inverse elastic intensity and the phonon energy are plotted against temperature. Note that at 90 K, no energy could be assigned. These results should also be compared with the Brillouin-scattering data of Satija and Wang,[4] which probe the phonon energy at smaller wave vector, but do not, of course, probe the "central peak" (zero-energy-transfer) intensity. The light-scattering results for several KBr concentrations show the characteristic behavior observed in Fig. 2(b), namely a decrease in energy of the phonon mode down to some characteristic temperature (which is a function of KBr concentration) followed by an increase in energy as the temperature is further lowered.

This behavior was suggestive of the behavior predicted by theory[3,7,8] as the reorientation rate changes from being fast with respect to the unperturbed phonon frequency to being slow with respect to the phonon frequency. In this case, theory predicts that a central peak should appear, and grow larger in intensity as reorientations slow down, and that the phonon energies should then increase again when reorientations become slower than the phonon frequency. This mechanism was suggested by Rowe and Rush[2] and by Satija and Wang[4] to explain their data, and Michel, Naudts, and deRaedt[5] proposed a simple extension of the earlier theory which seemed to explain the results. In Fig. 1, we show the predictions of the theory of Michel, Naudts, and deRaedt[5] for 120 and 90 K for a concentration of 0.5. Both curves have the same normalization, as the theory includes the temperature dependence. Clearly, the theory does *not* explain the results (this is equally true for other temperatures between 100 and 140 K). The width of the observed elastic peak is, within error, that of the resolution function, i.e., 0.16 meV. Further, the theory predicts an overdamped peak for $T = 90–110$ K, while the data show such behavior only at 90 K, but not at 100 or 110 K. The theory also predicts a phase transition near 90 K, so that it is inapplicable below that temperature. Thus, the present results cannot be explained by this model, and we must look elsewhere for an explanation. However, we *do* have evidence that the elastic scattering does result from the interaction proposed by Michel, Naudts, and deRaedt and this is shown in Fig. 3. The lines shown are equal-intensity contours around the (2, 2, 0) reciprocal-lattice point. These contours have the same overall symmetry as the elastic interaction proposed, but note that they are *not* quite symmetric in reduced wave vector about (2, 2, 0). This asymmetry is predicted by the theory[3,5] and is a reflection of the bilinear coupling between reorientations and phonons which leads to a mixed displacement-rotation correlation function that is odd in the reduced wave vector. Since the observed intensity is the sum of displacement-displacement and rotation-rotation correlations which are even in reduced wave vector and the displacement-rotation correlations which are odd in the reduced wave vector, there is the observed asymmetry.

The results in Figs. 1 and 2 are suggestive of a phase transition near 90 K. From light-scattering studies of Satija and Wang, one would estimate a temperature somewhat lower than that suggested from Fig. 2(b), but there is at least qualitative agreement (this discrepancy might be due to the very different wave vector at which the measurements were made). However, neutron diffraction measurements[9] show that there is no long-range order in these crystals. Thus, if there is a cooperative transition, it is to a phase in which the dipoles order locally, but there is no long-range order—i.e., a "dipole glass" in analogy to the quadropolar glass proposed by Sullivan *et al.*[10] and simulated by Klenin.[11] Such a transition is also consistent with the observations and discussion of Diaz-Gongora and Lüty[12] on Kerr effect and birefringence in alkali halides containing $(CN)^-$ defects. Fischer and Klein[13] proposed the existence of phase transitions to dipolar glasses in alkali halides with dilute concentrations of tunnelling electric dipoles. In a recent paper,[14] the same authors allude to such a phase transition in alkali halides containing $(CN)^-$ impurities interacting via a strain mechanism. Although $(CN)^-$ has a weak electric dipole moment, it is clear from the neutron scattering data that the mechanism involved here is associated with strain. If one accepts this proposed explanation for the experimental results on $(KCN)_x(KBr)_{1-x}$, then the following associations can be made. First, the order parameter, reflecting local orientations, will be related to the elastic intensity (Fig. 2) through the static coupling of strain and orientation. Second, the elastic constant C_{44} will be related to the orientational susceptibility as was shown, e.g., for pure KCN in Eq. (6.4) of the paper by Michel and Naudts.[15] A more quantitative discussion of these effects is dependent upon the formulation of a realistic theoretical model of such transitions.

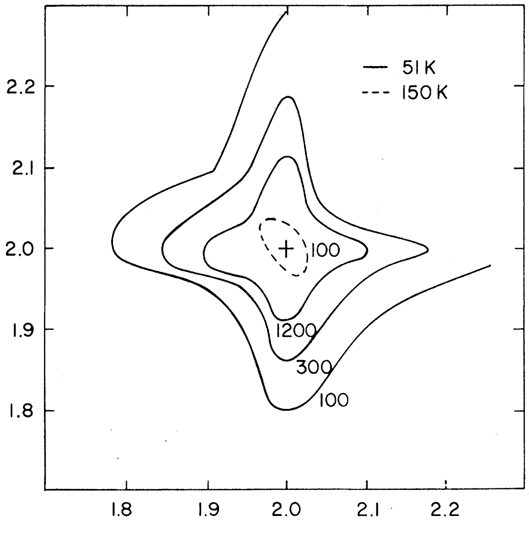

FIG. 3. The contours represent the intensity measured at zero energy transfer near the (2, 2, 0) reciprocal-lattice point at two temperatures. Note the asymmetry for (1.8, 2.0, 0) and (2.2, 2.0, 0) which shows the effect of the translation-rotation correlation function which is odd in reduced wave vector. The dashed line represents the 100-count contour at 150 K.

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Small-Angle-Scattering Evidence of Voids in Hydrogenated Amorphous Silicon

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The observation of extensive small-angle x-ray scattering from hydrogenated *a*-Si indicates that the void distribution in this material is very similar to that for evaporated *a*-Si. Thus the improved electrical properties of the hydrogenated material are not due to this material having a homogeneous structure.

The doping of crystalline semiconductors with substitutional impurities for the purpose of controlling electronic properties is a most important feature of modern solid-state electronics. Prior to 1969, attempts to control the properties of amorphous tetrahedrally coordinated semiconductors in a similar manner were unsuccessful. The main reason for this failure was the high level of the localized-state density found in the mobility gap of evaporated or sputtered *a*-Si (Spear[1]) and *a*-Ge. These states were thought to be related to microvoids and point defects.

It was demonstrated[2] in 1969 that *a*-Si prepared by the glow-discharge decomposition of silane with about 200 ppm of phosphine could lead to a hundred-fold increase in specimen conductivities. Subsequent investigations of electrical properties,[3,4] optical properties,[5,6] and the distribution of localized states[1,7] have been undertaken on specimens of *a*-Si prepared from the gas-phase decomposition of silane in a rf glow discharge. These studies indicate that the gap-state densities are remarkably low in such specimens when deposited at relatively high substrate temperature (500–600 °K). Samples prepared in such a manner may contain from 18 to 50 at.% hydrogen,[8] and are, thus, called hydrogenated *a*-Si.

This paper reports a study of the small-angle x-ray scattering (SAXS) from a 10-μm sample of *a*-Si fabricated by the glow-discharge decomposition of silane onto a 20-μm Al substrate. It contains 15 at.% hydrogen. The objective was to determine whether a sample so prepared was free from microvoids that are normally associated with a high level of localized-state density. The observed SAXS, however, is very similar to that observed for evaporated *a*-Si.[9] This indicates that samples produced from the glow discharge of silane contain a distribution of voids or holes containing an undetermined amount of hydrogen (x rays are only weakly scattered by the hydrogen relative to the Si atoms) similar to that found in evaporated samples. Thus the improved electrical properties of the hydrogenated *a*-Si are not the result of the material being free from microregions of low electron density.

The scattering of x rays is sensitive to the fluctuations in the electron density in the sample. The SAXS is determined by such fluctuations or inhomogeneities in regions measuring about 6 Å or more in size. These inhomogeneities may be due to voids or phase-separated regions dispersed in an approximately homogeneous medium. In the approximation that the inhomogeneities are widely dispersed and the approximate law of Guinier holds, the scattering is proportional to[10]

$$I_c(s) \propto \sum_{R_0} M(R_0) R_0^3 \exp(-R_0^2 s^2/3), \tag{1}$$

where $I_c(s)$ is the calculated intensity, $M(R_0)$ is the volume fraction of the inhomogeneities with radius of gyration R_0, and s is the scattering vector ($s = 4\pi \sin\theta/\lambda$). For a spherical particle $R_0^2 = 0.6R^2$, where R is the radius of a sphere. An instrumental resolution function, $P(s)$, may be defined, the convolution of which with $I(s)$

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