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Brillouin-scattering investigation of the mixed system $KBr_{1-x}(CN)_x$

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Phonon linewidths and frequencies of the mixed crystals $KBr_{1-x}(CN)_x$, $0.00<x<0.57$, are presented as a function of temperature for the T_{2g} symmetry mode and an off-symmetry mode in backscattering geometry using Brillouin spectroscopy. At the higher concentrations a "glass" transition can be observed: The scattering intensity and phonon linewidth increase sharply at the transition and the phonon frequency goes through a minimum. The increase in scattering intensity near the transition temperature is allied to the decreasing phonon frequency, but the changes in linewidth and frequency cannot be completely understood at the present time.

INTRODUCTION

The disordered system $KBr_{1-x}(CN)_x$ has been studied extensively in the recent past, using low-temperature specific-heat and thermal conductivity measurements,[1,2] light scattering,[3,4] inelastic neutron scattering,[1,5,6] and dielectric measurements.[7-9] In addition, several theoretical models have been proposed.[10-13]

For $0.1<x<0.57$, $KBr_{1-x}(CN)_x$ crystals exhibit low-temperature thermal properties similar to those found in glasses. Upon cooling from room temperature, a transition takes place from a disordered to an orientational glass state, at a temperature which depends on CN^- concentration and the frequency of the measuring probe. The transition is probably caused by interactions between the CN^- dipoles and is analogous to the spin glass transition in magnetic systems. The CN^- ion has a small electric dipole moment but a much larger elastic dipole moment in the alkali halides, and consequently the elastic dipole interaction is dominant.[14]

Near the transition temperature the T_{2g} symmetry phonon lifetime decreases dramatically and the self-energy is found to decrease sharply; however, for $x<0.57$ it never reaches zero, but recovers as the temperature is lowered further.[3,4]

In addition, extra modes have been observed which appear to be a result of the decrease in the tunnel splitting of the CN^- ion due to its interactions with other CN^-. These results have been reported.[15] The present work does not discuss them in detail but instead deals with the phonons. It reports results for the phonon lifetime, and also extends previously published[3,4] results for the temperature dependence of the phonon frequency to include different symmetries.

The CN^- ion implanted in an alkali halide host lattice is believed to have preferential orientations along the [111] axes. Tunneling and librational energy states are present in addition to rotational energy levels. Phonons interact with the CN^- impurities, the extent of interaction obviously dependent on the concentration of the dopant. In addition, as the CN^- concentration increases, the effect of dipole-dipole interactions between the CN^- becomes evident. The effect of individual CN^- and coupled CN^- on the phonons can be described qualitatively.

At and above room temperature the dipole-dipole interaction has little effect on the almost freely rotating CN^- ions. The orientational relaxation frequency[12] is also considerably higher than the phonon frequency. However, as the temperature is lowered this frequency decreases and the interaction between neighboring dipoles further decreases the relaxation frequency. At some critical temperature the relaxation and phonon frequencies will be comparable and the effect of the interaction between T_{2g} phonons and the dipoles is at its maximum. As the temperature decreases further the relaxation rate decreases, and eventually the dipole is effectively static as far as the phonon is concerned. It is then decoupled from the phonons.

Michel *et al.*[12,16] have developed a microscopic dynamic theory of coupled interactions in molecular crystals which has direct application to the KBr-CN system. The relevant quantity for interpretation of inelastic neutron or Brillouin experiments in this theory is the relaxation function $\Phi(\omega)$, the resonances of which are obtained by setting its denominator to zero, yielding (for details see Ref. 12)

$$\omega^2-[\Omega_1^2+\omega^2\beta_1^2/(\omega^2+\delta\lambda_1^2)]+i\omega\lambda_1\beta_1^2/(\omega^2+\lambda_1^2)=0\ , \quad (1)$$

where $\Omega_1^2=\omega_1^2-A/T$, $\beta_1^2=A/T$, and $\lambda_1=BT$. Parameter $A=\omega_1^2 x\delta y(T)$ and parameter $B=\Lambda/y(T)$, where x is the CN^- concentration, $y(T)$ varies slightly with temperature, Λ is a transport coefficient, assumed constant, and δ is an element of the effective interaction matrix. λ_1 is the orientational relaxation frequency for the dipoles. Finally, ω_1 is the phonon frequency of pure KBr. This expression is a gross simplification but is that used in Michel *et al.*[12] Unfortunately while this expression yields a minimum in the velocity of sound, it does not yield a corresponding maximum in the attenuation, and cannot account for the experimental results.

Finally, the differential scattering cross section per unit volume for Brillouin scattering[17] is given as

$$(1/V)d\sigma/d\Omega=k_B T\omega^4(32\pi^2c^4\rho v_q^2)^{-1}$$
$$\times(n_s/n_i)(\epsilon_s\cdot\overleftrightarrow{\mathrm{P}}\cdot\epsilon_i)^2\ , \quad (2)$$

where c is the speed of light, ρ is the crystal density, ω is the light frequency, v_q is the phonon velocity, n_s and n_i are refractive indices, ϵ_i and ϵ_s are incident and scattered light polarization vectors, and $\overleftrightarrow{P}$ is the Pockel's matrix. For pure T_{2g} symmetry phonons the scattering intensity will be primarily a function of T and v_q. Using the Brillouin equation defining phonon frequency $\Delta\nu = 2v_q\omega n/c \sin\theta/2$, one obtains

$$(1/V)d\sigma/d\Omega \propto T/(\Delta\nu)^2 \ . \tag{3}$$

EXPERIMENT

An argon ion laser in conjunction with a temperature-controlled etalon provided single-frequency light at a maximum power of $\simeq$700 mW. The 5145-Å line was used for all of the experiments. Conventional optical elements focused the beam in the sample space and collected scattered light over a limited solid angle as well as directing the light into the photomultiplier.

The heart of our system is the tandem Fabry-Perot interferometer designed by Sandercock.[18] The key features of this instrument are its common translation stage which permits dynamic synchronization of the two etalons and the capacitance feedback circuit which provides linear ramping of the translation stage. Figure 1 illustrates the vernier-like effect on the output spectra. In effect, the free spectral range of this tandem Fabry-Perot is 20 times larger than that of the single Fabry-Perot. The principal advantage of a tandem is the elimination of overlapping orders. In these experiments a 4-pass arrangement was used, the beam passing through each etalon twice.

A unique feature of our system is the computer-controlled scanning and alignment of the Fabry-Perot. A 4-MHz programmable clock signal is sent to an on-board 10-bit counter whose output then goes to a digital-to-analog converter (DAC) which produces the low-voltage ramp signal. The five alignment parameters of the tandem Fabry-Perot (two tilt adjustments for each etalon and one for spectral overlap) are adjustable manually by varying 10-turn potentiometers and, following initial alignment, are controlled by a minicomputer via an eight-channel DAC located in the interface module.

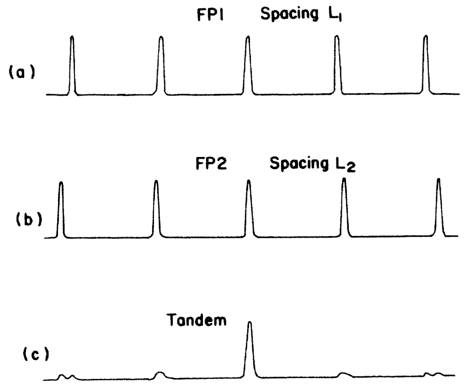

FIG. 1. (a) Successive orders transmitted through Fabry-Perot 1 with plate separation L_1. (b) Transmission through Fabry-Perot 2 with a slightly smaller spacing L_2. (c) Net transmission from tandem Fabry-Perot showing one central order with adjacent ghost peaks.

The basis of the feedback system for alignment control is an integration over the upper portion of the Rayleigh peak, the value of which is monitored continuously. When this drops below a prescribed percentage of an optimized initial value, a sequence of test and correction steps is initiated adjusting all parameters until the height of the Rayleigh peak is maximized, indicating that alignment is restored. The same computer accumulates spectra and can analyze previously accumulated results simultaneously. Data are stored permanently on floppy diskettes.

Samples were mounted in a conventional optical cryostat and cooled by conduction from liquid N_2 or He baths. To attain temperatures around 60–77 K, pumped liquid N_2 was used. For temperatures in the range 120–294 K, a nitrogen-flow cryostat was employed. A resistance heater aided in maintaining a steady temperature. Temperature measurements were made by a Si diode at $T<20$ K and by a copper-constantan thermocouple for $T>20$ K.

It should be pointed out that the temperature measurement must of necessity be the outside crystal temperature. Even at the lowest practical laser power localized heating takes place in the scattering volume. It is possible to estimate the degree of self-heating by reducing the laser power until the phonon frequency ceases to shift. This ranged from 1 to 5 K, depending on the thermal conductivity of the crystals.

The crystals all originated from the Crystal Growth Lab of the University of Utah. The CN concentrations were measured to within $\pm 1\%$ by chemical analysis.

RESULTS AND DISCUSSION

Experiments were first conducted in the backscattering geometry with the samples oriented such that the angle of incidence ϕ was 15° off the [100] axis. Selection rules for crystals of cubic symmetry[19] prohibit light scattering in the case of the transverse phonon at $\phi = 0°$ when $\theta \simeq 180°$. The choice of crystal orientation is consistent with our previous work on KCl-CN.[20]

Figure 2 shows the frequency response of the transverse T_{2g} symmetry phonon (mixed), observed in the backscattering geometry as a function of temperature for various concentrations of CN^-. The phonon frequency which first decreases as the temperature is lowered begins to increase when the temperature decreases beyond a critical temperature T_g. This is the point at which the CN^- dipoles enter the orientational glass state, referred to earlier in this paper. The value of T_g increases as the CN^- concentration, and hence, as the dipole-dipole interaction increases. Frequency measurements are accurate to roughly $\pm 5\%$. In Fig. 3 the associated linewidths of the same phonons are shown as a function of temperature. The linewidth reaches a maximum at the same temperature as the frequency has its minimum for each concentration of CN^-; that is, maximum phonon attenuation also occurs at T_g. These and other linewidths were measured by obtaining a best fit for a Lorentzian phonon profile using the Rayleigh peak as the resolution function. For spectra just below T_g some complications were en-

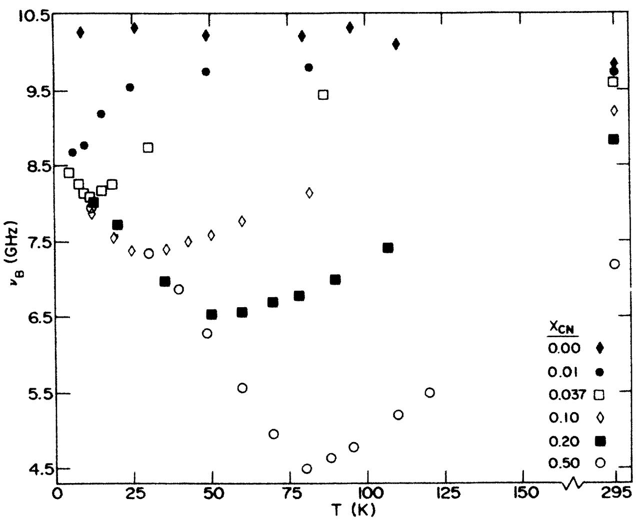

FIG. 2. Frequency shifts of the transverse mixed mode phonon in $KBr_{1-x}(CN)_x$ are plotted against temperature for various concentrations of CN^-. Using a backscattering configuration scattered light was collected at 15° off the [100] crystal axis.

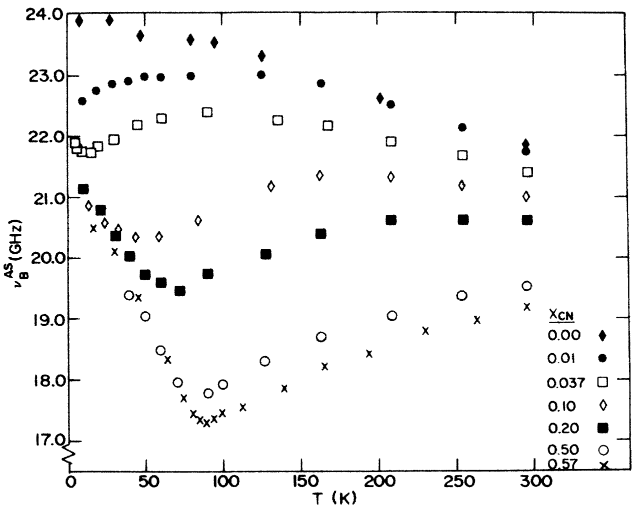

FIG. 4. Frequency shifts of the longitudinal mixed mode phonon in $KBr_{1-x}(CN)_x$ are plotted against temperature for various concentrations of CN^-. The scattered geometry is identical to that used to study the mixed transverse mode phonons.

countered because of the asymmetric background and hence linewidth values are only accurate to approximately ±15%. Aperture broadening effects are negligible in these experiments.

Similar results for the mixed longitudinal phonon, also in backscattering geometry, are presented in Figs. 4 and 5, with the inclusion of a higher concentration $x=0.57$. The asymmetry in the linewidth peaks for the higher concentrations arises from the presence of extra modes at and below T_g. These will be discussed below.

Experiments were also performed in 90° scattering geometry. In this case a pure T_{2g} symmetry phonon traveling in the [110] direction and polarized along $[1\bar{1}0]$ is in-

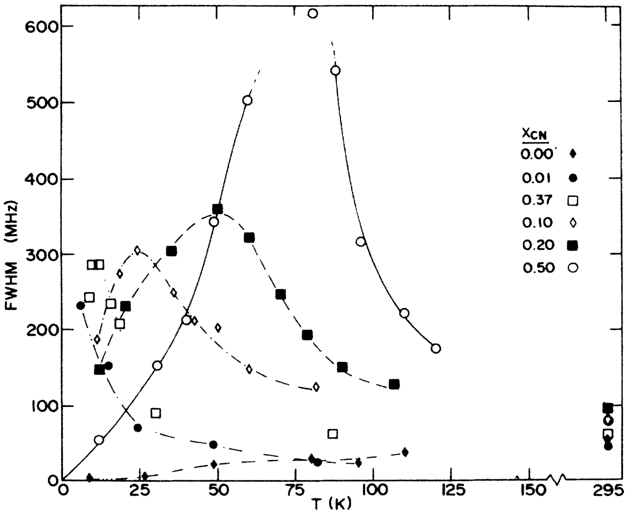

FIG. 3. Full widths at half-maximum (FWHM) of the transverse mixed mode phonon in $KBr_{1-x}(CN)_x$ are given as a function of temperature for various CN^- concentrations. Scattered light was collected at 15° off the [100] axis. Connecting lines are guides to the eye.

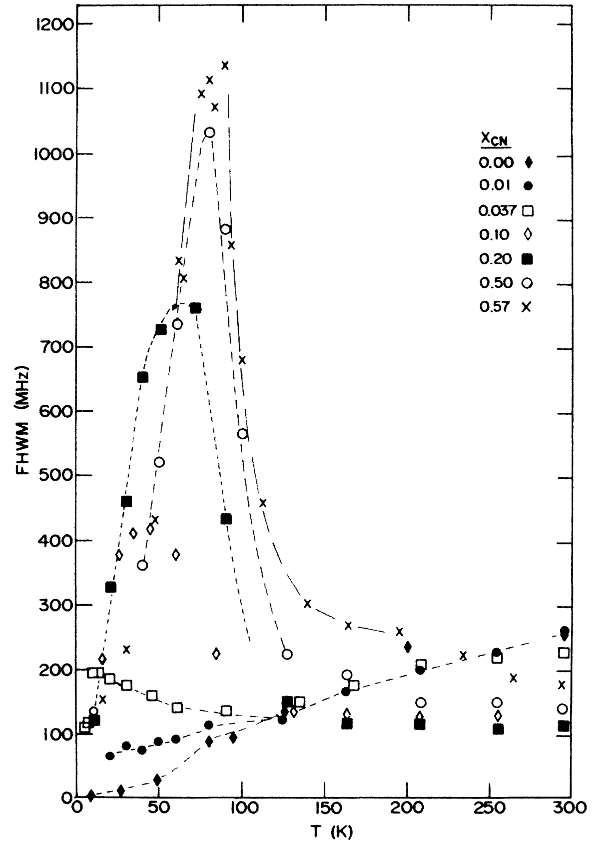

FIG. 5. Full widths at half-maximum (FWHM) of the longitudinal mixed mode phonon in $KBr_{1-x}(CN)_x$ vs temperature for different CN^- concentrations. Collecting angle is again 15° off the [100] crystal axis. Connecting lines are guides to the eye.

volved. The frequency of this phonon as a function of temperature is shown in Fig. 6 for various CN^- concentrations. The relative changes in frequencies are greater than those of the mixed transverse phonon, although the magnitude of the changes is less.

The critical temperatures, i.e., the temperature at which the frequency is a minimum, or the attenuation a maximum, are essentially the same for each respective concentration for all the results, with two exceptions: the T_{2g} mixed phonon in the backscattering geometry for $x=0.10$ and 0.20. In these instances T_g is about 20 K lower. This is too large to be an experimental error, but no explanation can be offered for this discrepancy at the present time. The curves in Figs. 2–6 can be compared to the results of Satija and Wang[3] whose work differs from the present results mainly in the lower-temperature regime. There is good overall agreement within experimental error between our data and those obtained by Satija and Wang.[3,4]

Their results for $x=0.20$ indicate that T_g is 50 K for both longitudinal and transverse phonons. This agrees with our "anomalous" value for the T_{2g} mixed phonon, but again is 20 K below T_g for the longitudinal mixed and the T_{2g} mode observed in 90° scattering. Figure 7 repeats the higher-concentration data of Fig. 6 along with theoretical curves from the microscopic dynamic formulation of Michel mentioned previously. As outlined in the Introduction, the equation to be solved was simplified to a form requiring two parameters, A and B. Using $x=0.57$, two experimental points were chosen and values of A and B at these points were determined by a fitting program. Simple interpolation and extrapolation gives all values of A and B for $x=0.57$. Curves for other concentrations are simply obtained because of the linear dependence of A on concentration. This means of determining the two parameters in no way fixes the theoretical critical temperature values. One can see from Fig. 7 that the fit ranges from good for $x=0.57$ to poor for $x=0.35$. This should not be surprising since the Michel theory was formulated for high-CN-concentration systems.

A sample linewidth curve for the pure T_{2g} symmetry phonon, for $x=0.5$, is given in Fig. 8. Once again the slopes of the curve in the vicinity of T_g are considerably greater than those of the associated frequency plot. Note also that the linewidth peak is asymmetric, similar to those in Figs. 3 and 5. As indicated in the Introduction it proved impossible to even approximate the linewidth results with the Michel theory.

Evidence for scattering from extra modes in the vicinity of T_g in samples with concentrations of $CN^- x \geq 0.35$ was first observed as an increase in the background between the Brillouin peak and the Rayleigh peak. Comparison of spectra of phonons of roughly equal frequency and linewidth on either side of the critical temperature for a

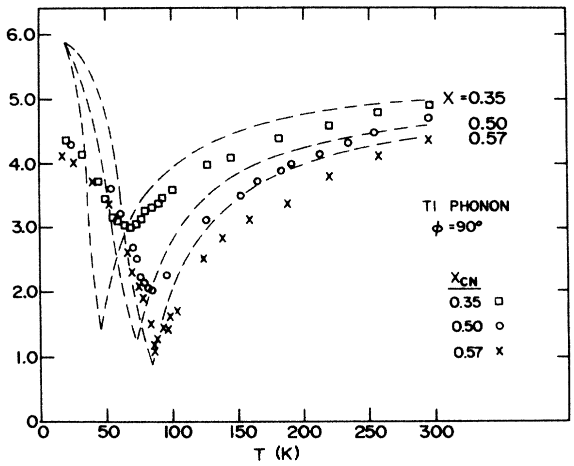

FIG. 7. For CN^- concentrations $x=0.35$, 0.50, and 0.57, frequency shifts of T_{2g} symmetry phonons are compared to their respective theoretical fits employing the dynamic theory of Michel *et al.* (Refs. 12 and 16).

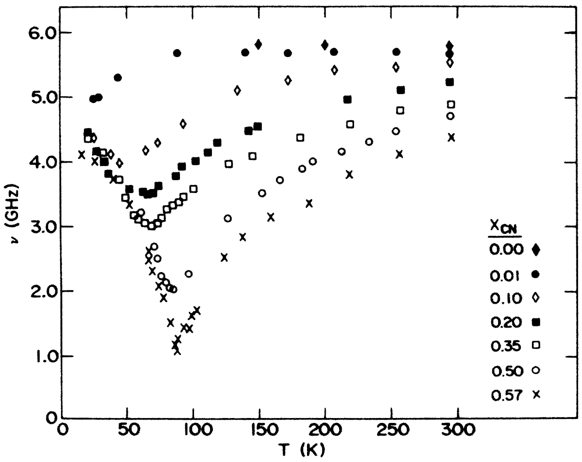

FIG. 6. Frequency shifts of the pure transverse mode phonon with T_{2g} symmetry in $KBr_{1-x}(CN)_x$ against temperature for various CN^- concentrations. 90° scattering geometry was employed.

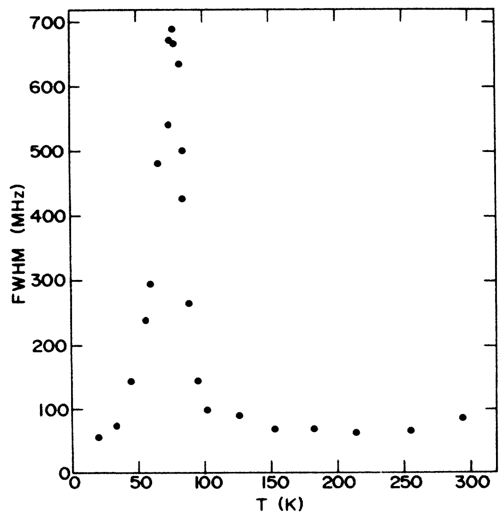

FIG. 8. Full width at half-maximum of the pure transverse mode phonon in $KBr_{0.5}(CN)_{0.5}$ is plotted against temperature.

given CN$^-$ concentration clearly demonstrates that the effect is not simply due to an overlap with the tail of the Rayleigh peak. In Fig. 9 differences in background levels on the low- and high-frequency sides of the Brillouin peaks normalized to Brillouin peak intensity are plotted for two concentrations. Note that in both instances the maximum difference occurs 3–5 K below T_g. This difference in background is predicted by the Michel *et al.* theory.[12]

Further examination of the background revealed that it actually consisted of a superposition of many extra peaks whose strengths were time dependent as well as being temperature and CN$^-$ concentration dependent. The observation of these extra modes has been presented elsewhere[15] and a complete discussion is forthcoming.[21]

For both the pure and mixed transverse mode the Brillouin count rate was found to increase considerably when approaching T_g from room temperature. The effect was most pronounced at CN$^-$ concentrations of 0.50 and 0.57. A quantitative study is difficult because of the variability introduced by slight differences in Fabry-Perot alignment. However, a rough measure can be obtained by integrating the Brillouin peaks over a fixed range and normalizing to the integrated peak value at room temperature. The result for the pure T_{2g} symmetry phonon with CN$^-$ concentration of 0.50 is shown in Fig. 10. This is a result of the decreasing phonon frequency: The triangles are a plot of Eq. (3).

The approximate maximum Brillouin count rate for T_{2g} mode phonons as a function of CN$^-$ concentration is shown in Fig. 11 for room temperature. The integrated Brillouin peaks have been normalized to the integrated peak value of pure KBr. The dipole moment of the CN is larger than that of Br so the increasing concentration increases the polarizability of the medium. As the CN$^-$ concentration changes, the contribution to the Pockel's photoelastic constant by KBr and KCN can be determined by weighting their respective concentrations. Therefore the differential cross section for the mixed system may be written as

$$d\sigma/d\Omega \propto [xP_{44\mathrm{KCN}}+(1-x)P_{44\mathrm{KBr}}]^2/(\Delta\nu_{\mathrm{mix}})^2 \ . \quad (4)$$

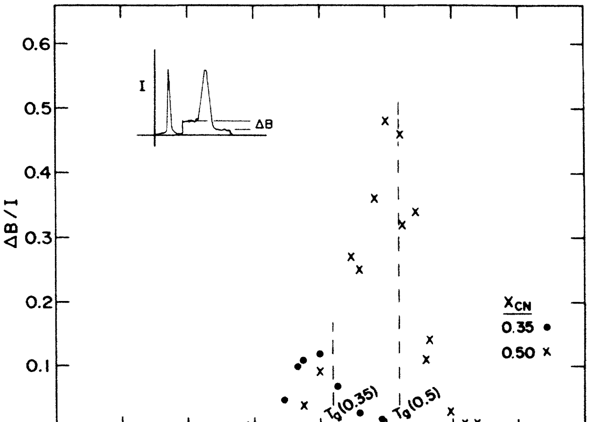

FIG. 9. Difference in background ΔB between the low-frequency and high-frequency sides of the Brillouin peak normalized to the Brillouin peak intensity is plotted as a function of temperature for CN$^-$ concentrations 0.35 and 0.50. The respective critical temperatures T_g are indicated. Phonon symmetry is T_{2g}.

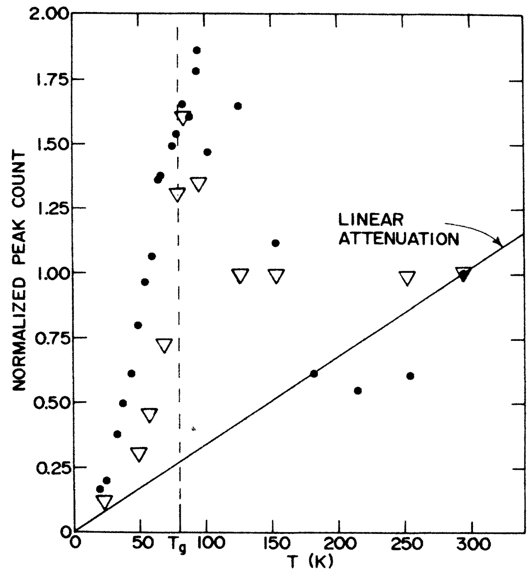

FIG. 10. Integrated Brillouin peak counts for the T_{2g} symmetry phonon as a function of temperature for $(\mathrm{KBr})_{0.5}(\mathrm{KCN})_{0.5}$ normalized to the integrated peak count at room temperature are indicated by solid circles. The triangles represent the calculated values of the differential cross-section equation. The solid line indicates $1/T$ dependence; T_g is the critical temperature.

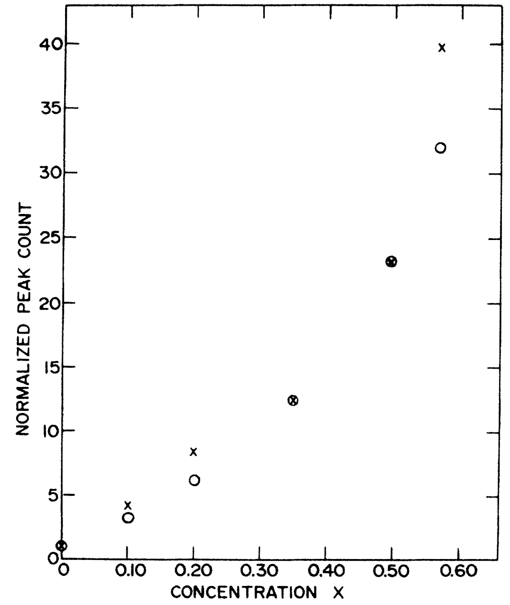

FIG. 11. Integrated Brillouin peak counts for T_{2g} symmetry phonons as a function of CN$^-$ concentration normalized to the integrated peak count of KBr are indicated by crosses. The open circles are the calculated values of the differential cross-section equation. All measurements are at room temperature.

Taking the ratio of differential cross section between the mixed and pure crystal, and fitting this ratio to the experimental data for $(KBr)_{0.5}(KCN)_{0.5}$ at room temperature with $P_{44}=-0.026$ for KBr, we get $P_{44}=-0.74$ for KCN. Thus we deduce that the absolute value of P_{44} in KCN is seven times larger than that for KBr. Using $P_{44\text{KCN}}$ and phonon frequencies in Fig. 7 at room temperature, the theoretical intensities are obtained versus concentration and are plotted in Fig. 11.

CONCLUSIONS

We have studied the transition of CN^- dipoles in mixed crystals $KBr_{1-x}(CN)_x$ from a disordered to an orientational glass state. The transition or critical temperature T_g is independent of phonon mode or symmetry but is, however, strongly dependent on the CN^- concentration. Qualitatively these results may be understood as the result of phonon frequency approximating the frequency of CN^- orientational relaxation. However, an adequate theoretical description is not available at present.

ACKNOWLEDGMENTS

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