Low-Temperature Acoustic Properties of $(KBr)_{1-x}(KCN)_x$ in the Orientationally Disordered State

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The attenuation and the variation of the phase velocity of high-frequency ultrasonic waves have been measured in $(KBr)_{1-x}(KCN)_x$ crystals for $x=0.25$ and 0.50 in the temperature range 0.1 to 8 K. For both crystals we observe the low-temperature acoustic anomalies characteristic of structural glasses. The results are interpreted in terms of a tunneling model with a broad spectrum of energy splittings and relaxation times. Spectral density and phonon-coupling constants are determined and discussed with respect to their dependence on x.

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During the last years the cubic mixed crystal system $(KBr)_{1-x}(KCN)_x$ has been studied extensively with respect to an orientationally disordered state observed in the range $0.03 < x < 0.60$.[1] It was suggested that the interacting CN^- molecules are characterized by a wide distribution of relaxation times which gives rise to a gradual freezing of the CN^- reorientations as the temperature is lowered.[2] At low temperatures the CN^- dumbbells are considered to be frozen in an orientational glass state. Measurements of the specific heat and the thermal conductivity below 10 K have shown that such a disordered system possesses all of the anomalous low-temperature thermal properties of structural glasses.[3,4] According to the tunneling model for amorphous solids,[5,6] these results can be understood by the existence of a broad spectrum of two-level systems (TLS) in $(KBr)_{1-x}(KCN)_x$ in the orientationally disordered state.

In a recent paper[7] it was shown that for $(KBr)_{0.5}(KCN)_{0.5}$ a spectral density of tunneling centers $\bar{P}=0.8\times10^{45}$ J^{-1} m^{-3} can be deduced from the logarithmic time dependence of the specific heat on a time scale of 100 μsec $< t_{exp} <$ 10 sec and in the temperature range 50 mK $< T <$ 0.5 K. In addition, the average TLS coupling constant to phonons $\bar{\gamma}=0.18$ eV has been determined from the T^2 dependence of the thermal conductivity. It has been pointed out in Ref. 7 that $\bar{\gamma}$ is the same as the coupling constant of isolated CN^- ions in KBr. This suggests that the TLS in $(KBr)_{1-x}(KCN)_x$ may be some CN^- molecules which have retained their rotational mobility.

In this Letter we report ultrasonic measurements of two $(KBr)_{1-x}(KCN)_x$ crystals with $x=0.25$ and 0.50 in the temperature range $0.1 < T < 8$ K. Our measurements of the attenuation and the variation of the phase velocity of acoustic waves provide conclusive evidence on the glassy behavior for both mixed crystals. In contrast, such effects are not observed in $(KBr)_{0.95}(KCN)_{0.05}$ on which we studied the phase velocity of the longitudinal mode only. We analyze our acoustic measurements with use of the tunneling model developed for glasses,[8] which allows us to determine for the first time, independently, the values of the spectral density $\bar{P}$ of TLS and their coupling constants to phonons γ_l and γ_t.

The attentuation and relative velocity change have been measured for both longitudinal and transverse acoustic waves of frequencies around 400 MHz propagating along a fourfold axis. The samples (from the same batch as used in Ref. 7) were cleaved and stuck to a quartz delay line with silicone grease.[9] The variations of the sound velocities $\Delta v/v$ are shown in Fig. 1. The data for both the $x=0.25$ and $x=0.50$ samples and for both polarizations exhibit the logarithmic temperature dependence characteristic of glasses at low temperatures. At $T\approx1$ K $\Delta v/v$ passes through a maximum and then decreases with increasing temperature. Such a behavior is not observed for a $(KBr)_{0.95}(KCN)_{0.05}$ crystal where the phase velocity of

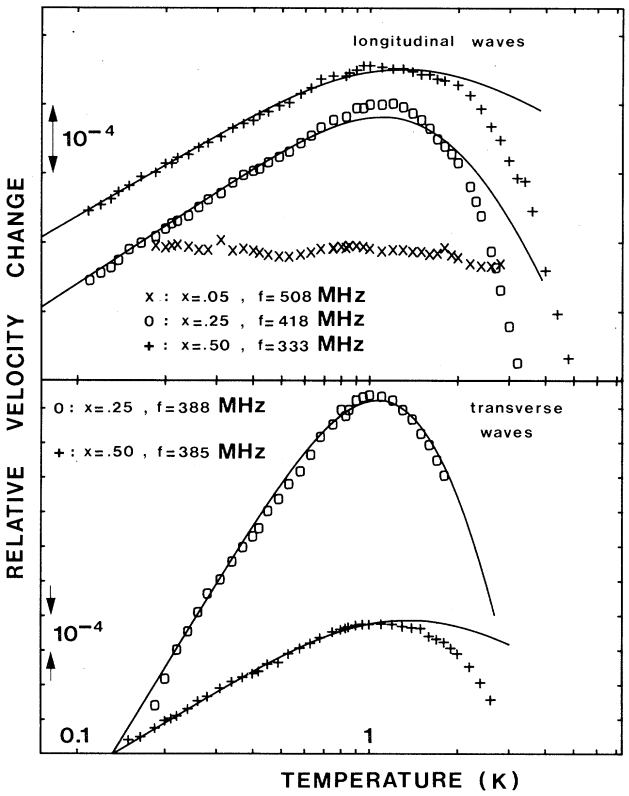

FIG. 1. Relative variation of ultrasonic phase velocity for longitudinal and transverse waves propagating along the (001) axis in $(KBr)_{1-x}(KCN)_x$. Solid lines are calculated according to the tunneling model with use of the parameters listed in Table I. The different sets of data are arbitrarily shifted relative to each other.

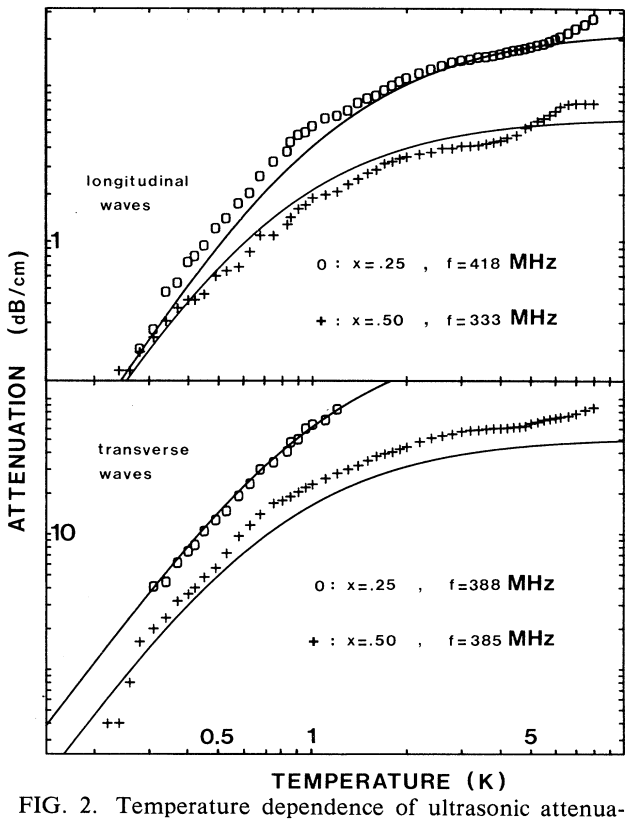

FIG. 2. Temperature dependence of ultrasonic attenuation for longitudinal and transverse waves propagating along the (001) axis in $(KBr)_{1-x}(KCN)_x$. Solid lines are calculated according to the tunneling model with use of the parameters listed in Table I.

longitudinal waves is nearly temperature independent between $T \simeq 0.2$ and 3 K. Figure 2 exhibits the ultrasonic attenuation α measured for the $x=0.25$ and 0.50 samples. The characteristic behavior of glasses is observed too: A T^3 increase at low temperatures is followed by a plateau. Because of the strong absorption for the transverse mode in the $x=0.25$ sample the signal is lost for temperatures $T > 1$ K.

We analyze our acoustic data according to the tunneling picture, using a TLS distribution function[9] in energy splitting E and normalized relaxation rate r as $P(E,r) = (\bar{P}/2) r^{-1}(1-r)^{\mu-1/2}$, where μ is a parameter which is zero in the standard model[8] and takes into account discrepancies often observed in the analysis of the $\Delta v/v$ and α data. Subsequently, the total absorption and velocity changes can be calculated[9] as the sum of resonant and relaxational contributions.[10] The resonant interaction of TLS with phonons results in a saturable absorption[11] and a velocity change

$$(\Delta v/v)_{l,t} = [C_{l,t}/(1+2\mu)] \ln(T/T_0),$$

where T_0 is a reference temperature and

$$C_{l,t} = \bar{P}(\gamma_{l,t})^2/\rho(v_{l,t})^2,$$

with ρ as mass density and $v_{l,t}$ the longitudinal and transverse phase velocities. The relaxational contribution to the absorption and velocity changes can only be derived by numerical integration. At low temperatures, the absorption shows an asymptotic behavior to

$$\alpha_{l,t} = \pi^4 C_{l,t} K_3 T^3/32(3+2\mu) v_{l,t},$$

where

$$K_3 = (\gamma_l^2/v_l^5 + 2\gamma_t^2/v_t^5) 4k_B^3/\pi\rho\hbar^4,$$

and the velocity change gives negligible contributions compared to the resonant part. At higher temperatures, $\alpha_{l,t}$ becomes constant and $(\Delta v/v)_{l,t}$ dominates the total with a negative contribution as the temperature increases (both quantities are scaled by the parameter $C_{l,t}$).

By treating C_l, C_t, and K_3 as independent parameters, we fitted the data in Figs. 1 and 2 with the calculated total absorption and velocity changes. With

respect to the remaining parameter μ, which diminishes the standard distribution function at $r \simeq 1$, we find a value $\mu = 0.25$ for the $x = 0.50$ sample, whereas we obtain $\mu = 1.38$ for the $x = 0.25$ sample. In Figs. 1 and 2 the solid lines are best fits with use of the model parameters listed in Table I. We note that our fits to the attenuation data are satisfying in the whole temperature range for both polarizations with use of the same values of μ and K_3. For the velocity changes the agreement is very good up to the maximum. A discrepancy above the maximum is usually observed in glasses and often referred to the onset of thermal-activated relaxational processes.[8]

Since ultrasonic experiments, like thermal measurements, are testing TLS of energy splitting of about $k_B T$, a comparison between the present work and the thermal results of Ref. 7 should provide a crucial check of the tunneling model. From the experimentally determined values of $\bar{P}(\gamma_{l,t})^2$, $v_{l,t}$, and μ we calculate the thermal conductivities $K(T,x)$ employing no free parameters. In the temperature range of resonant interaction we obtain $K(T,x) = A(x)T^2$ where $A = 0.07$ and 0.14 W m^{-1} K^{-3} for $(KBr)_{0.75}(KCN)_{0.25}$ and $(KBr)_{0.5}(KCN)_{0.5}$, respectively. These values agree reasonably well (within 20%) with the actual experimental findings of Ref. 7. In addition, the values of the coupling constants listed in Table I are in accord with former results on the average $\bar{\gamma} \simeq 0.15$ eV, which is close to the strain coupling of an isolated CN^- ion in diluted KBr:CN.[12] Our values of $\bar{P}(x)$ are larger by factors $\simeq 7.5$ and $\simeq 4$ for the $x = 0.25$ and $x = 0.50$ samples, respectively, than those derived from the logarithmic time dependence of the specific heat.[7] It should be pointed out that the time-resolved specific-heat technique tests the coupling of TLS to phonons on a 0.1-msec to 10-sec time scale, whereas the present acoustic measurements probe faster-relaxing TLS. As in our model the value of the spectral density depends on the form of the distribution function, the above discrepancies should not be overestimated.[13]

Turning now to the concentration dependence $\bar{P}(x)$, our results confirm the former observations[4,7] that the number of effective TLS increases with decreasing cyanide concentration. While in structural glasses no drastic variation of $\bar{P}$ can be achieved by the varying of chemical compositions,[14] we observe in $(KBr)_{1-x}(KCN)_x$ a ratio $\bar{P}(x=0.25)/\bar{P}(x=0.50) \simeq 10$. Moreover, the absence of the acoustic anomaly in $(KBr)_{0.95}(KCN)_{0.05}$ shows that the tunneling picture is no longer appropriate for the low-concentration limit of the orientationally disordered state. A similar conclusion has been made from specific heat and thermal conductivity measurements in the concentration range $0.03 \leq x \leq 0.10$ where the tunneling model was unable to fit the thermal data.[4,15] Although we cannot assign any physical meaning to the parameter μ introduced into the distribution function to weight TLS with larger asymmetries,[9] it should be emphasized that for $(KBr)_{0.5}(KCN)_{0.5}$ a value $\mu = 0.25$ indicates only a slight modification of the original distribution function[5] which was proposed to be uniform in asymmetries and tunneling parameters. For $(KBr)_{0.75}(KCN)_{0.25}$ the parameter $\mu = 1.38$ can be interpreted as evidence that the number of TLS with long relaxation times is increased as the CN^- concentration is reduced from $x = 0.50$ to 0.25. Consequently, we conclude that the form of the distribution function and the spectral density of TLS change significantly in the concentration range where orientational disorder is observed,[1] and that any microscopic model of the KBr:KCN system should verify this remarkable behavior.

Very recently Sethna and Chow[16] developed a mean-field theory for $(KBr)_{1-x}(KCN)_x$ and identified microscopic tunneling centers with cyanide ions which are weakly coupled to the mean field and reorient in 180° flips within the experimental time scale. By use of a Gaussian distribution of barrier heights, which hinder the CN^- reorientations, it is shown that the low-energy tail contains (within a factor of 2) the right number of tunneling centers which contribute to the specific heat below 1 K. As the mean-field interaction scales with the CN^- concentration, the maximum and the width of the Gaussian distribution are shifted to the lower energy with decreasing x. This shift corresponds to an enhancement of the low-energy tail and, consequently, increases the number of effective TLS.

TABLE I. Values of the parameters used to fit the present acoustic data for $(KBr)_{1-x}(KCN)_x$ with the tunneling model (see text).

x	ρ[a] (kg m^{-3})	v_l[b] (10^3 m sec^{-1})	v_t[b]	γ_l (eV)	γ_t	μ	$\bar{P}$ (10^{45} J^{-1} m^{-3})
0.25	2500	3.47	1.11	0.13	0.09	1.38	30
0.50	2180	3.61	1.05	0.24	0.10	0.25	3

[a]From Ref. 7.

[b]Measured at $T_0 \simeq 110$ mK.

We interpret the drastically increased value of $\bar{P}$ and the deviation from the standard tunneling-model distribution function found for $(KBr)_{0.75}(KCN)_{0.25}$ as an experimental observation which supports the above microscopic model[17]

In summary, we have shown that in $(KBr)_{1-x}(KCN)_x$ for $x=0.25$ and 0.50 the presence of tunneling systems gives rise to low-temperature acoustic properties analogous to those observed in structural glasses. From an analysis of the ultrasonic phase velocity and attenuation on the basis of the tunneling model we deduce the spectral densities $\bar{P}(x)$ and the phonon coupling constants $\gamma_{l,t}(x)$. The variation of the model parameters with CN^- concentration should provide a quantitative test of a new microscopic model[16] which links the TLS with reorientations of isolated CN^- ions hindered by a Gaussian distribution of potential barriers.

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[10]For simplicity, we consider the cubic $(KBr)_{1-x}(KCN)_x$ crystals as being elastically isotropic.

[11]With the ultrasonic frequencies used this effect is only observable below 0.1 K and with weak acoustic intensities.

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[17]It should be pointed out that our ultrasonic measurements probe the (elastic) quadrupolar susceptibility whereas the distribution function of Sethna and Chow is based on dielectric measurements (see Ref. 2) probing the electric dipole moment only.