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High-Pressure Brillouin Scattering Study of the Order-Disorder Transition in KCN†

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Pressure and temperature dependences of the Brillouin spectra for KCN are shown for pressures of 0 to 7 kbar and temperatures of 178 to 295 K. It is shown that multiphonon interactions are the dominant anharmonic effect, and it is suggested that the phase transition at 168 K comes from a ferroelastic ordering of CN^- dipoles strongly coupled anharmonically to the phonons.

Crystalline KCN displays many interesting properties which arise from the molecular character of the CN^- ion. Of interest in this Letter is the phase transition[1] occurring at 168 K at pressures of 1 bar, in which KCN transforms from a high-temperature fcc structure with CN^- directional disorder to a lower-temperature orthorhombic structure with directional order but head-to-tail randomness. The transition temperature, T_c, is strongly pressure dependent, increasing 2 K per kbar of hydrostatic pressure.[2]

The phase transition is seen clearly in the elastic constants, which have been studied by two different techniques. Haussühl[3] used 15-MHz ultrasonic measurements to show that C_{44} softens very markedly, tending to zero at a temperature T_0 about 14 K below T_c, and therefore concluded that C_{44} was directly involved in the phase transition. Brillouin scattering studies were doen by Krasser, Buchenau, and Haussühl[4] in order to study the temperature dependence of C_{44} at GHz frequencies, where CN^- orientational motion might be reflected in C_{44} and therefore involved in the phase transition.

In this Letter we report both the pressure[5] and temperature dependences of C_{44} obtained by Brillouin spectroscopy. It will be shown that C_{44} and T_0 are independent of pressure and that the softening of C_{44} is *not* the driving mechanism for the phase transition, as suggested by Rowe *et al.*[6] Instead, the TA mode associated with C_{44} will be seen to be strongly anharmonic, with a large multiphonon contribution to the self-energy near T_c. It will be suggested that the phase transition comes about because of a strong elastic dipole interaction of the type discussed by Julian and Lüty.[7]

Our results are in contradistinction to the case of soft-optic-mode ferroelectrics and incipient ferroelectrics. In those cases, even though higher-order anharmonicities are strong and couple the soft mode to other phonons,[8] the soft mode *drives* the phase transition. Our results show that KCN is not a soft-mode system in the same sense as the softening of C_{44} is the *result* of the phase transition and *not* the cause.

KCN single crystals of very high optical, mechanical, and chemical quality were provided by Professor Franz Rosenberger of the University of Utah. Brillouin spectra were analyzed by using a piezoelectrically scanned, electronically stabilized, triple-pass Fabry-Perot interferometer, preceded by an interference filter. The observed Brillouin spectra are from TA and LA phonons propagating in the (110) direction, with velocities given by C_{44} and $C' = \frac{1}{2}(C_{11}+C_{12}+2C_{44})$, respectively.

We have calculated the pressure and temperature dependence of the elastic constants C_{44} and C', using the relation between the measured Brillouin shifts, ν_B, and sound velocity, v_s,

$$\nu_B = \pm(2nv_s/\lambda_0)\sin(\Theta/2). \tag{1}$$

Here, n is the index of refraction, λ_0 is the wavelength of the incident light, and Θ is the scattering angle. In order to obtain the pressure and temperature dependences of the elastic constants we must know the pressure and temperature dependence of the index of refraction, n, and the density, ρ. The temperature dependence of ρ is given by Haussühl; and from the bulk modulus, one can calculate the pressure dependence of ρ. With these data and the room-temperature value of n at 1 bar we can calculate the pressure and temperature dependence of n by assuming constancy of the specific refraction, r, given by

$$r = (n^2-1)/\rho(n^2+2). \tag{2}$$

In doing this we have neglected changes in the refractive index because of the change in the polarizability with pressure and temperature. This is justified in the case of molecular crystals where these corrections[9] are of the order of one part in 10^4.

Figure 1 shows the temperature dependence of C_{44} at 56 bar, 3.8 and 7.0 kbar determined from our Brillouin shifts for the TA phonon. As can be seen the data coincide for all pressures. The top curve is a least-squares fit to Haussühl's 15-MHz ultrasonic values for C_{44} at 1 bar, while curve 2 is a least-squares fit to our values for C_{44}, determined at about at about 3 GHz and 56 bar. Although the two curves do not coincide, the error in our measurements is of the order of the distance between the curves, and thus we cannot conclude that C_{44} shows dispersion. Curves 3 and 4 are calculated temperature dependences of C_{44} at pressures of 3.8 and 7.0 kbar using the relation determined by Haussühl from his data,

$$C_{44} = a\ln(T/T_0), \tag{3}$$

with the assumption that T_0 has the same pres-

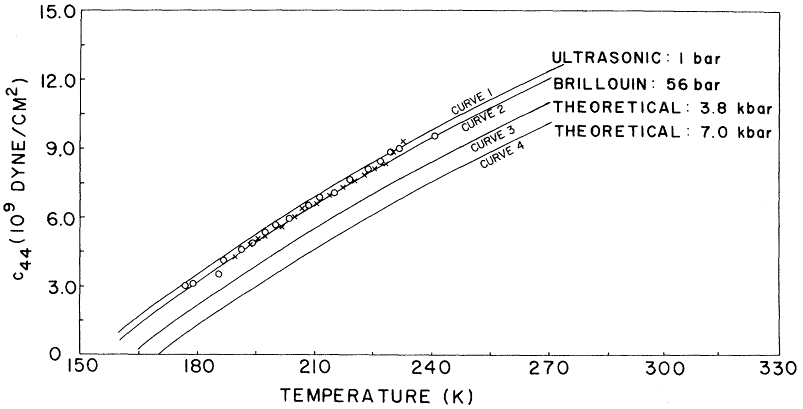

FIG. 1. Isobaric temperature dependence of C_{44}. Theoretical curves, $C_{44}=a\ln[T/(T_0)_P]$ with $a = 21.9\times10^9$ dyn/cm^2 and $(T_0)_P = (T_0)_{1\,\mathrm{bar}} + (\partial T_\lambda/\partial P)_T P$. $(T_0)_{1\,\mathrm{bar}} = 155.9$ K, $(\partial T_\lambda/\partial P)_T = 2$ K/kbar. Circles, values of C_{44} determined from Brillouin shifts at 3.8 kbar; crosses, values of C_{44} determined from Brillouin shifts at 7.0 kbar. Curve 1, least-squares fit to the ultrasonic data of Haussühl (Ref. 3); curve 2, least-squares fit to the values of C_{44} determined from Brillouin shifts at 56 bar.

TABLE I. Pressure dependence of T_0, the temperature where $C_{44}=0$, and the constant a in Eq. (3).

	Pressure (kbar)	T_0 (K)	a (10^9 dyn/cm^2)
Ultrasonic (Ref. 3)	0.001	153.7	21.9
Brillouin	0.056	155.9 ± 2.4%	23.1 ± 1.2%
Brillouin	3.8	156.3 ± 3.4%	22.4 ± 1.7%
Brillouin	7.0	157.1 ± 4.7%	22.7 ± 2.3%

sure dependence as T_c, namely 2 K per kbar. Clearly, neither of these curves reproduces our data, suggesting that T_0 does not have a pressure dependence as large as that of T_c.

This point can be made more explicit by a consideration of Table I, where we have listed the values of a and T_0 for pressures of 56 bar, 3.8 and 7.0 kbar, obtained by a least-squares application of Eq. (3) to our data. It is obvious that within the errors of our experiment *both a and T_0 are constants,* independent of pressure, and our high-pressure values agree well with Haussühl's zero-pressure values. It must be borne in mind that at a pressure of 7 kbar the transition temperature, T_c, has been moved upward 14 K, while the same pressure has not moved T_0 by any significant amount. From this we conclude that, while the softening of C_{44} is a manifestation of the phase transition, it is certainly not the cause of the transition.

The Brillouin shifts, and hence the TA and LA frequencies, have been seen to vary with temperature and pressure. One can relate the pressure and temperature dependence by the relation

$$\left(\frac{\partial \ln\omega_i}{\partial T}\right)_P = -\frac{\beta}{\kappa_T}\left(\frac{\partial \ln\omega_i}{\partial P}\right)_T + \left(\frac{\partial \ln\omega_i}{\partial T}\right)_V, \qquad (4)$$

where ω_i is the phonon frequency, β is the volume thermal expansion coefficient, and κ_T is the isothermal compressibility. The term on the left-hand side of Eq. (4) is what one measures in a temperature-dependence experiment done at constant pressure, while the first term on the right-hand side of Eq. (4) is measured in a pressure-dependence experiment done at constant temperature. Both of these terms are therefore available from our data, allowing calculation of the second term on the right-hand side of Eq. (4). It is the terms on the right-hand side of Eq. (4) which have been shown by Maradudin and Fein[10] and by Cowley[11] to be related to the anharmonic frequency shifts of the real part of the phonon self-energy. The first term can be related to the "thermal-expansion" shift (i.e., a pure volume effect), while the second term can be related to the frequency shifts arising from three- and four-phonon multiphonon interactions. Table II lists the magnitude of the two terms on the right-hand side of Eq. (4) for the TA and LA zone-center phonons at 188 and 295 K.

For the LA mode, one sees that the thermal-expansion and multiphonon terms are of about the same size. However the multiphonon term is positive, indicating strong four-phonon interactions. The TA mode is dramatically different, with the multiphonon term being 27 times larger than the thermal-expansion term at room temperature and 200 times larger at 188 K, near the phase transition. The multiphonon term is also positive for the TA phonon. This enormous in-

TABLE II. Values obtained by fitting Eq. (4) to the temperature and pressure dependence of the Brillouin peaks. Note that $(\partial \ln\omega_i/\partial T)_P = -(\beta/\kappa_T)(\partial \ln\omega_i/\partial P)_T + (\partial \ln\omega_i/\partial T)_V$.

	T (K)	ω_i (GHz)	$\frac{1}{\kappa_T}\left[\frac{\partial \ln\omega_i}{\partial P}\right]_T$	$\left[\frac{\partial \ln\omega_i}{\partial T}\right]_P$ (10^{-5}/K)	$-\frac{\beta}{\kappa_T}\left[\frac{\partial \ln\omega_i}{\partial P}\right]_T$ (10^{-5}/K)	$\left[\frac{\partial \ln\omega_i}{\partial T}\right]_V$ (10^{-5}/K)
TA	295	3.73	−0.82 ± 0.10	340.7	+12.3	328.4
	188	2.12	−1.09 ± 0.16	3500.0	+17.2	3482.8
LA	295	12.96	1.50 ± 0.03	13.9	−22.5	36.4
	188	12.48	1.95 ± 0.07	33.5	−30.8	64.3

crease in multiphonon interaction strength, seen also to a lesser degree for the LA phonon, is clearly the dominant anharmonic effect for the zone-center acoustic phonons.

Our direct observation of strong multiphonon interactions provides a justification for the conclusions of Rowe *et al.*[6] Their inelastic neutron scattering experiments on KCN and NaCN failed to show any clearly assignable optic-phonon peaks. They attributed this to multiphonon scattering and other inelastic scattering involving hindered rotations of the CN$^-$ ions. They also argued that the phonon lifetimes could be significantly reduced through interaction of the translational modes (phonons) with large-amplitude rotational motions of the CN$^-$ ions. Moreover, Bill, Jex, and Müllner[12] did a shell-model treatment of the neutron results of Rowe *et al.*,[6] using a bilinear phonon-rotation interation (i.e., an interaction energy of the form $u\varphi$, where u is a phonon coordinate and φ is a rotational coordinate). This gives a linear relation between C_{44} and the φ force constant.[12] Their results failed to reproduce the TA branch by as much as 40% and gave a librational frequency which was a factor of 5 to 9 too high. Clearly, multiphonon interactions are important in KCN. However, the exact relation between C_{44} and φ is not clear from our data since quartic anharmonicities are strong enough to be larger than cubic anharmonicities, but we cannot tell how large the cubic anharmonicities are.

Julian and Lüty[7] have done temperature-dependent dielectric measurements on KCN_x:KCl_{1-x}, for x ranging from 0 to 1. Their data are consistent with the interpretation that the 168-K phase transition involves a "ferroelastic" ordering of the CN$^-$ elastic dipoles, but they did suggest that a purely dipole ordering was not a sufficient explanation.

One can extend the ideas of Julian and Lüty as follows. The interaction energy between two dipoles of equal moment, m, can be shown to be given by $U \sim m^2/l^3$ for the electric dipoles, where l is the dipole spacing. The same qualitative form should hold for elastic dipoles. If the order parameter for this phase transition obeys a Curie-Weiss law, $C/(T-T_c)$, then a molecular-field treatment allows one to relate T_c to the interaction energy. The result is $T_c \propto 1/l^3 = 1/V$, or $T_c \propto P$, where P is the pressure. Thus the observed linear dependence of the transition temperature on pressure provides further support for the idea of an elastic dipole interaction.

We summarize by pointing out that the data of Rowe *et al.*,[6] Julian and Lüty,[7] Haussühl,[3] Krasser, Buchenau, and Haussühl[4] and our measurements can be synthesized with the following picture of the phase transition at 168 K. At high temperatures the rapidly reorienting CN$^-$ ions are disordered but interact through an elastic dipole interaction. The dipoles are not unhindered rotors seeing only energy barriers due to the lattice structure. The rotational motion is strongly coupled anharmonically to the lattice modes, so strongly as to reduce sharply the lifetimes of some of the lattice modes, particularly the optic phonons. The phase transition occurs because of a "ferroelastic" ordering of these anharmonically coupled dipoles and is seen through anharmonic effects in the lattice modes. In particular, the elastic constant softening is not the cause but is the effect of the phase transition and the coupling of the CN$^-$ rotation to the phonons.

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