Nature of the Phase Transition in KCN at 168 K

J. M. Rowe and J. J. Rush
Institute of Materials Research, National Bureau of Standards, Washington, D. C. 20234

and

N. J. Chesser
Energetic Materials Division, Large Caliber Weapon Systems Laboratory, U. S. Army Armament Research and Development Command, Dover, New Jersey 07801

and

K. H. Michel[a] and J. Naudts
Natuurkunde, Universiteit Antwerpen, 2610 Wilrijk, Belgium
(Received 9 August 1977)

Neutron inelastic scattering line shapes for [100] TA phonons in KCN have been measured for temperatures between 169 and 300 K. The results are compared to the predictions of a model incorporating a strong *indirect* $(CN)^-$-$(CN)^-$ ion interaction mediated by elastic strains. The present experiments confirm the essential features of the model and elucidate the nature of the mode softening which leads to the phase transition at 168 K. In particular, the softening is shown to exist even for wave vectors one-half the distance to the Brillouin zone boundary.

Potassium cyanide (KCN) undergoes two successive phase transitions[1] as the temperature is lowered from just below the freezing point. In the highest temperature phase the crystal structure is of the NaCl type, with the linear $(CN)^-$ ions reorienting among equivalent orientations[2,3] to give effective cubic symmetry. At approximately 168 K, there is a first-order phase transition to an orthorhombic structure in which the $(CN)^-$ ions are oriented with their long axes along the b direction[4] but with their sense (i.e., electric dipole) disordered. At approximately 83 K, there is an order-disorder phase transition at which the sense of the $(CN)^-$ ions begins to order. These successive phase transitions have been a subject of intense recent interest,[5-8] especially since the observation by Haussühl[5] that the elastic constant C_{44} (related to shear strains along cube faces which tend to distort the cubic cell towards the orthorhombic structure) softens markedly with temperature so that it would extrapolate to zero at a temperature T_0 of 154 K, about 14 K below the actual phase transition temperature T_c of 168 K. In the present Letter we present neutron scattering data taken for the transverse acoustic mode propagating along a cube edge, for which C_{44} determines the initial slope. We compare these data to an extension of a model proposed[9] by Michel and Naudts to explain the elastic-constant data.[5] We show that this model can explain the neutron scattering results over a wide range of phonon frequencies, thus verifying the form of the model-predicted scattering law as a function of phonon frequency. We further demonstrate that the softening of acoustic phonons persists for wave vectors one-half the distance to the Brillouin zone.

The neutron scattering data were collected on a triple-axis crystal spectrometer at the National Bureau of Standards reactor using an incident energy of 5.08 meV with a beryllium filter (Fig. 1) or a fixed final energy of 14.7 meV with a pyrolitic graphite filter (Fig. 2). The monochromator and analyzer crystals were pyrolitic graphite with 40′ mosaic spreads while the collimation angles were 45′, 46′, 42′, and 72′. The sample was the same crystal[10] used for an earlier study[11,12] of the dynamics of KCN. The results of measurements of the [100] TA mode near the reciprocal-lattice point (2,2,0) at a reduced wave vector $q = 0.1$ are shown in Fig. 1. The present results are not in agreement with those of Daubert *et al.*[13] We have been informed that the authors of Ref. 13 have repeated their measurements under more appropriate experimental conditions and that they were able to reproduce the results shown here. The solid line shown in Fig. 1 represents a fit by the model discussed below. It should be noted that there is no "central peak" (i.e., scattering at $\Delta E = 0$) for temperatures down to 1 K above T_c.

The model fitted to the data of Fig. 1 is an extension of an earlier static theory[9] and is analogous to, but more general than, that used[14] to explain the neutron scattering data[15] on ND_4Br. In

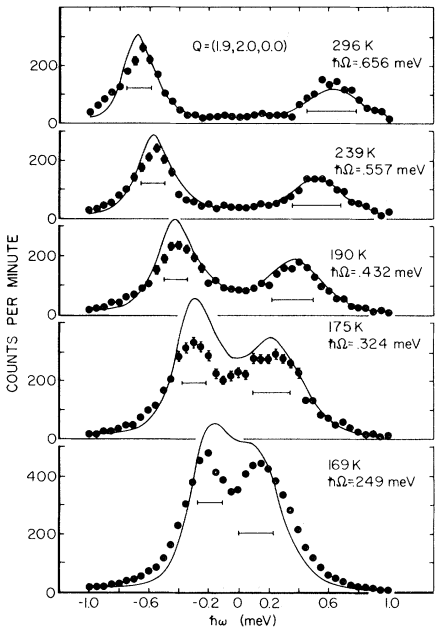

FIG. 1. A comparison of neutron line shapes for KCN for a transverse acoustic mode with wave vector q equal to $\frac{1}{10}$ of the Brillouin zone distance in the [100] direction with the model described in the text. The horizontal bars represent calculated resolution widths for a planar dispersion surface. The only parameter varied is the energy of the mode. The data are not corrected for spectrometer efficiency; rather, the theory is converted to the spectrometer representation. The discrepancies for $T = 175$ and 169 K are believed to be due to the inadequacy of the resolution correction used. Note that although the mode softens (this mode is related to C_{44} as $q \to 0$), there is *no* "central peak" —i.e., scattering at $\hbar\omega = 0$.

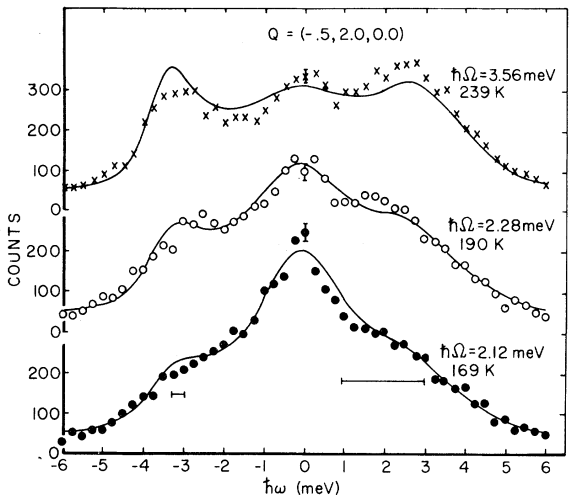

FIG. 2. Comparison of neutron scattering line shapes for the same branch as in Fig. 1 to the model described in the text for wave vector $q = 0.5$ ($\frac{1}{2}$ the distance to the Brillouin zone). Note that here $\hbar\omega_0$ is about 3 meV, and thus is comparable to the orientational relaxation parameter $\hbar\lambda = 3.0$ meV. As the temperature is lowered towards 168 K, the behavior is quite different from that in Fig. 1. In this figure, there are no spectrometer efficiency corrections as the data were taken with fixed final energy. The peaks broaden and the intensity at $\hbar\omega = 0$ increases, confirming the different behavior of the theory and experiment for $\hbar\omega_0 \ll \hbar\lambda$ and $\hbar\omega_0 \sim \hbar\lambda$.

this theory, the static and dynamic behavior of an orientationally disordered crystal is described in terms of an effective orientational interaction between ions arising from the strong rotational-translational coupling which is a consequence of the nonspherical nature of the ions involved. This is an *effective* $(CN)^-$-$(CN)^-$ ion coupling which is mediated by elastic strains. It should be noted that we explicitly do *not* postulate $(CN)^-$ ion librations—rather the reorientation motion is diffusive in nature. The dynamical equations for the correlation functions needed to obtain neutron scattering cross sections are derived[16] in the spirit of Mori's projection-operator techniques[17] by choosing appropriate forms for the damping and restoring forces. In particular, the form chosen for the damping forces is appropriate to the hydrodynamic regime—that is, we assume exponential decay of the rotational correlation functions. With these assumptions (in analogy with those in Ref. 14) the neutron cross section becomes

$$d^2\sigma/d\Omega\, d\omega = -A\,[1 - \exp(-\hbar\omega/kT)]^{-1}\omega\Phi'', \quad (1)$$

where A is a constant representing instrumental and sample volume details,

$$\Phi'' = -[\eta + \beta^2 f(\omega)]/\{[\omega^2 - \Omega^2 - \omega^2\beta^2 f(\omega)/\lambda]^2 + \omega^2[\eta + \beta^2 f(\omega)]^2\}, \quad (2)$$

η is a term representing phonon-phonon damping, $\beta^2 = \omega_0^2 - \Omega^2$, Ω is the phonon frequency with rotational interactions, ω_0 is the phonon frequency without rotational interactions, λ^{-1} is the relaxation time for orientational correlations, and $f(\omega) = \lambda/(\omega^2 + \lambda^2)$.

By analysis of the form of Eq. (2) we can derive limiting cases in accord with those found in Ref. 14. For $\lambda \gg \omega_0$, we obtain two peaks centered at $\omega = \pm\Omega$ and no central peak. As shown in Refs. 14 and 16 this can lead to a softening of a normal mode (in the present case C_{44}). For $\lambda \ll \omega_0$ we get a three-peak

structure with response at $\omega = \pm \omega_0$ and 0. According to our theory, λ remains finite at T_c. As can be seen from the data in Fig. 1, there is no central peak and the phonon frequencies soften. This shows that λ remains finite at T_c and hence that there is no long-range critical slowing down of $(CN)^-$ reorientations at the phase transition, in accord with the neutron diffraction results.[3]

We have fitted the model to the data for various values of phonon wave vector and total momentum transfer at temperatures between 169 and 300 K. We have allowed all parameters to vary and have found that we can get satisfactory fits (the solid lines in Figs. 1, 2) for $\eta = 0$, $\hbar\lambda = 3.0$ meV for all data. Physically, this implies that λ is almost temperature independent in this range, and that phonon-phonon damping is negligible compared to the damping due to phonon-reorientation coupling. It should be noted that the data shown cover the range $\omega_0 \ll \lambda$ to $\omega_0 \sim \lambda$, so that this is the first case in which the predictions of Eq. (2) could be tested over a range of values where the qualitative behavior changes. It also should be noted that even when all terms (including η) were allowed to vary, $\hbar\lambda$ was never less than 2.0, thus strengthening the qualitative conclusion from Fig. 1 that the orientations do not order.

In Ref. 7, the authors observed that the phase transition temperature T_c increased by 2 K per kilobar of applied pressure, while T_0, the temperature at which C_{44} would extrapolate to zero, hardly changed for pressures up to 7 kbar. However, their conclusion that the strain associated with C_{44} is "the result" of the phase transition rather than "the cause" cannot be correct. Rather, we believe that the phase transition in KCN should be considered as analogous to the cooperative Jahn-Teller effect, as discussed by Gehring and Gehring.[18] The interesting observation in Ref. 7 that T_0 is unaffected by pressure has strong consequences for testing the microscopic origin of the interactions responsible for the softening of C_{44}. We are presently investigating this phenomenon.

Finally, it should be emphasized that the theory used here to describe the phase transition does not invoke small rotational motions about equilibrium position (librations) as does a recent model[19] of Bill, Jex, and Müllner. This latter model *cannot* be applied to KCN or NaCN since, as was pointed out in Ref. 12, there are no well-defined librations or optic modes in KCN.

The present theory provides a unified explanation of the ultrasonic data,[5] of the *atmospheric pressure* Brillouin scattering data,[6,7] and of the small-wave-vector neutron data. However, problems remain, especially in our understanding of the *high-pressure* Brillouin scattering data. The essential result is that the relaxation time for orientational correlations induced by the indirect interactions of $(CN)^-$ ions through elastic strains is short compared to the period of the phonon going soft. This is the opposite extreme of the behavior found[15] in ND_4Br, where the flipping rate was slow compared to the phonon of interest, leading to critical scattering and to an order-disorder phase transition. Since the phonon period decreases as the wave vector increases, the interesting possibility of observing the transition from one type of behavior to the other exists with neutron scattering. In the results for $q = 0.5$ shown in Fig. 2, the small "central peak" growing in the data as $T \to T_c$ should be noted. However, since $C_{44} \to 0$ before the angular correlations become infinite, one cannot see critical behavior. In this case $\hbar\omega_0 = 3.8$ meV while $\hbar\lambda \sim 3.0$ meV, and the neutron line shape has the characteristic shape of an overdamped oscillator. At even larger values of q, the interaction becomes weaker, i.e., $\beta^2 \to 0$, so that there is little effect on the frequency or line shape.

In summary, we have observed the neutron scattering line shapes for phonons in KCN as the phase transition at 168 K is approached from above, and compared the data to an extension of the static model of Michel and Naudts.[9] From this comparison, we conclude that the reorientational motions of the $(CN)^-$ ions couple strongly to the translations to decrease C_{44} as the temperature is decreased, and that this leads to the phase transition.

We acknowledge the assistance of many colleagues, including D. G. Hinks, S. Susman, D. L. Price, N. Vagelatos, R. C. Casella, and C. J. Glinka.

---

[a] Present address: Theoretische Physik des Universitat des Saarlandes, 6600 Saarbrücken, W. Germany.

[1] H. Suga, T. Matsuo, and S. Seki, Bull. Chem. Soc. Jpn. 38, 1115 (1965).

[2] D. L. Price, J. M. Rowe, J. J. Rush, E. Prince, D. G. Hinks, and S. Susman, J. Chem. Phys. 56, 3697 (1972).

[3] J. M. Rowe, D. G. Hinks, D. L. Price, S. Susman,

and J. J. Rush, J. Chem. Phys. 58, 2039 (1973).
[4]J. M. Rowe, E. Prince, and J. J. Rush, J. Chem. Phys. 66, 5147 (1977).
[5]S. Haussühl, Solid State Commun. 13, 147 (1973).
[6]W. Krasser, U. Buchenau, and S. Haussühl, Solid State Commun. 18, 287 (1976).
[7]H. D. Hochheimer, W. F. Love, and C. T. Walker, Phys. Rev. Lett. 38, 832 (1977).
[8]W. F. Love, H. D. Hochheimer, M. W. Anderson, R. N. Work, and C. T. Walker, Solid State Commun. 23, 365 (1977).
[9]K. H. Michel and J. Naudts, Phys. Rev. Lett. 39, 212 (1977), and J. Chem. Phys. 67, 547 (1977).
[10]D. G. Hinks, D. L. Price, J. M. Rowe, and S. Susman, J. Cryst. Growth 15, 227 (1972).
[11]J. M. Rowe, J. J. Rush, N. Vagelatos, D. L. Price, D. C. Hinks, and S. Susman, J. Chem. Phys. 62, 4551 (1975).
[12]J. M. Rowe, J. J. Rush, E. Prince, and N. J. Chesser, to be published.
[13]J. Daubert, K. Knorr, W. Dultz, H. Jex, and R. Currat, J. Phys. C 9, L389 (1976).
[14]Y. Yamada, H. Takatera, and D. L. Huber, J. Phys. Soc. Jpn. 36, 641 (1974).
[15]Y. Yamada, Y. Noda, J. D. Axe, and G. Shirane, Phys. Rev. B 9, 4429 (1974).
[16]K. H. Michel and J. Naudts, to be published.
[17]H. Mori, Prog. Theor. Phys. 33, 424 (1965).
[18]G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. 38, 1 (1975).
[19]C. J. Bill, H. Jex, and M. Müllner, Phys. Lett. 56A, 320 (1976).

Plastic Deformation of bcc ^{4}He

D. J. Sanders, H. Kwun, A. Hikata, and C. Elbaum
Metals Research Laboratory and Department of Physics, Brown University, Providence, Rhode Island 02912
(Received 12 December 1977)

Measurements have been made of the stress-strain relations and the changes in ultrasonic attenuation during plastic deformation of free-standing and constrained crystals of bcc ^{4}He. Comparison is made with measurements for hcp ^{4}He. During plastic deformation, bcc crystals are found to behave much like a viscous liquid. The results suggest a large concentration of highly mobile vacancies in the bcc phase.

We report here the first studies of the plastic deformation of bcc solid ^{4}He. While plastic deformation in solid helium has been the subject of several investigations,[1-7] these have all been confined to the hcp phase of ^{4}He. Since the discovery of the bcc phase in 1961,[8] many of its properties have been measured, including its specific heat,[9,10] thermal conductivity,[11] and elastic constants.[12] However, the information to be gained from these measurements, especially with regard to the nature, concentration, and behavior of crystal defects, is severly limited by the small temperature range of about 50 mK over which the bcc phase exists. This is in contrast to solid ^{3}He for which extensive specific-heat measurements,[13] along with x-ray[14] and NMR studies,[15] have demonstrated that there is a much larger concentration of vacancies in the bcc phase than in the hcp phase. So far, the limited NMR data[16,17] and specific-heat analysis[12] have been insufficient to show if this is also the case in solid ^{4}He. If a large concentration of vacancies does exist in bcc ^{4}He, one might expect this to be reflected in its behavior during plastic deformation.

In a previous report,[7] we outlined a method for producing and deforming free-standing single crystals of solid helium. We also pointed out the importance of using free-standing crystals for measurements of the stress-strain relations. In the present experiments, we have extended these investigations to the bcc phase of solid ^{4}He, and have found significant, qualitative differences in the behaviors of the two phases.

The experimental apparatus has been described previously.[7] A large ballast volume of 44 liters was added to the high-pressure system at room temperature to aid in maintaining a constant pressure during crystal growth and deformation Crystals of bcc ^{4}He were grown at a pressure of 27.6 atm, corresponding to a freezing temperature of 1.65 K and a molar volume of 21.0 cm^3/mole,[10,18] by slowly reducing the bath temperature from 1.67 to 1.63 K over the course of about $\frac{1}{2}$ h. In growing crystals from liquid He II, it was found that the heat leak due to the superfluid was sufficient to keep the fill line open without the use of the fill-line heater.

The completed crystal filled the sample cell, 16 mm×16 mm in cross section, and 28 mm between the cell bottom and the movable piston. Crystal growth and quality were monitored by ultrasonic waves (pulse-echo method) generated