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Soft-mode transition in the ferroelastic crystal $K_2Hg(CN)_4$

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Inelastic neutron scattering techniques have been used to investigate the structural transition from the paraelastic to the ferroelastic phase in $K_2Hg(CN)_4$. Several low-frequency phonon branches were measured along the high-symmetry directions and found to be almost independent of temperature. However, a particular low-lying branch along [111] was found to show a strong temperature dependence. The structure factor for this mode shows it to be a longitudinal, librational mode whose eigenvector specifies antiphase rotation of adjacent rigid cyanotetrahedra. This is in agreement with the change in the crystal structure observed at the transition by diffraction measurements. The frequency of this branch at the zone-boundary L point tended to zero at ≈ 101 K, thus showing the paraelastic to ferroelastic transition in this cyanospinel is a soft-mode transition.

I. INTRODUCTION

The complex metal cyanides with chemical composition $A_2M(\mathrm{CN})_4$, where A is K or Rb and M is Zn, Cd, or Hg, have phase transitions as a function of temperature or pressure from a high-temperature paraelastic structure to a low-temperature ferroelastic structure. The crystal structures of these compounds were first investigated at room temperature by x-ray diffraction.[1] The space group was identified as $Fd\bar{3}m$ and, although the structure could not be solved in detail, it was found to be of the spinel type. As a result the compounds became known as "cyanospinels." The existence of a phase transition in the particular cyanospinel $K_2Hg(CN)_4$ was first indicated by nuclear quadrupole resonance measurements.[2] Subsequent experiments[3] showed the transition to occur at 111 K and result in a lower-symmetry structure with two crystallographically nonequivalent cyanide ions. Measurements of the elastic constants and of the thermoelastic constants ($T_{ij} = d\ \ln C_{ij}/dT$) of the potassium cyanospinels by ultrasonic methods[4] showed that, compared with the Cd and Zn cyanides, $K_2Hg(CN)_4$ exhibits anomalous behavior as a function of temperature. All three elastic constants decrease as the temperature is lowered to the transition while two of the thermoelastic constants change sign and all three reach large values as the transition is approached. This behavior was confirmed by Brillouin measurements.[5] The third-order elastic constants and the pressure derivatives of the second-order elastic constants were also found to be anomalous.[6] They have values very different from those of alkali halides and alkali cyanides. The response to mechanical stress[7] of the analogous compound $Rb_2Hg(CN)_4$ established that its room-temperature phase was ferroelastic,[8] while a transition to a cubic spinel structure was found at ≈ 400 K.[9] The properties of the mixed crystals $(Rb_xK_{1-x})Hg(CN)_4$ as a function of concentration, x,[10] suggest that $K_2Hg(CN)_4$ is analogous to the rubidium compound despite the enormous difference in their transition temperatures.

Despite the extensive data now available on the cyanospinels, their dynamics and phase transitions are not understood in any detail. Librational motion of the $M(\mathrm{CN})_4$ tetrahedra is thought to play a role in the transition,[10] but one that is different from the reorientation of the cyanide ions in the alkali cyanides.[4] Several Raman and infrared measurements of vibrational modes have been made,[11-13] but it is not clear whether phonons play any part in the transitions. Even the order of the transitions is in dispute.[13,14]

By means of neutron powder diffraction methods[15] we have measured the temperature dependence of the crystal structure of $K_2Hg(CN)_4$. This study established that the low-temperature phase is trigonal (space group $R\bar{3}c$) and that at the transition an antiphase rotation occurs of $Hg(CN)_4$ tetrahedra adjacent along [111]. From comparison with the structural characteristics of other cyanospinels it was argued that the transition could not be due to static interactions, but must have its origin in the lattice dynamics.

In the present paper we report coherent, inelastic neutron scattering measurements of the temperature dependence of phonons in the cubic, high-temperature phase of $K_2Hg(CN)_4$. A search was made for a mode whose eigenvector is that of the displacement pattern found at the transition.[15] This mode was observed and its frequency was found to soften to zero at the transition, thus showing the transition is of soft-mode character. The experimental details of the measurements are given in Sec. II and the results are presented in Sec. III. The conclusions are discussed in Sec. IV. A preliminary report on these results has been presented previously.[16]

II. EXPERIMENTAL DETAILS

The single crystal of $K_2Hg(CN)_4$ had a volume of ≈ 5 cm^3 and was mounted in a variable-temperature cryostat. Two specimen orientations were used for the measurements. Dispersion curves for the three high-symmetry directions were measured with the specimen in the conventional $[1\bar{1}0]$ orientation. To observe a particular L-point librational mode the $(1\bar{2}1)$ plane containing the $[111]$ and $[\bar{1}01]$ directions was oriented in the horizontal scattering plane of the spectrometer. In this orientation, measurements were made of a particular $[111]$ optical branch of the dispersion relation as a function of temperature. The measurements were made on the C5 triple-axis spectrometer at the NRU reactor, Chalk River, at temperatures of 298 and 120 K. Monochromators were Ge(111) and Si(111), respectively, while graphite (0002) was used as the analyzer in both cases. Collimations before and after the specimen were 0.6°, and 5 cm of sapphire was used as a filter before the monochromator. The majority of measurements were made with analyzing frequencies of 3 or 2.5 THz and the resolution (FWHM of the incoherent scattering from vanadium) was then 0.2 THz or 0.14 THz, respectively.

III. RESULTS

The detailed changes in the crystal structure of $K_2Hg(CN)_4$ at the phase transition consist of an antiphase rotation of rigid cyanotetrahedra adjacent along $[111]$, accompanied by a small shift in one of the potassium positions.[15] A view of the crystal structure along the $[111]$ direction is shown in Fig. 1. If we neglect the small potassium shift then we can postulate that the dominant characteristic of the transition, the antiphase rotation, is the eigenvector of a longitudinal, librational phonon mode propagating along $[111]$. The one-phonon structure factor, $|F|^2$ of such a mode, is given by

$$F \propto A_k \left[\sum_{k=1}^{4} \exp[i\mathbf{B}\cdot\mathbf{r}(k)] \right] - A_{k'} \left[\sum_{k'=1}^{4} \exp[i\mathbf{B}\cdot\mathbf{r}(k')] \right] ,$$

where

$$\begin{aligned} A_k = {} & Q_x \sin[b(Q_z - Q_y)] \exp(-ibQ_x) \\ & + Q_y \sin[b(Q_x - Q_z)] \exp(-ibQ_y) \\ & + Q_z \sin[b(Q_y - Q_x)] \exp(-ibQ_z) , \\ A_{k'} = {} & Q_x \sin[b(Q_z - Q_y)] \exp(ibQ_x) \\ & + Q_y \sin[b(Q_x - Q_z)] \exp(ibQ_y) \\ & + Q_z \sin[b(Q_y - Q_x)] \exp(ibQ_z) . \end{aligned}$$

The atomic positions are specified by origin choice 1 of space group $Fd\bar{3}m$, $b = (\frac{1}{4} - u)$, where u is a *mean* fractional atomic coordinate for the CN ion and has the value 0.37; $\mathbf{B}$ is a reciprocal-lattice vector; $\mathbf{Q} \equiv (Q_x, Q_y, Q_z)$ is the wave-vector transfer; $\mathbf{r}(k)$ and $\mathbf{r}(k')$ are the position vectors of Hg(k) and Hg(k'); respectively, which define the centers of mass of tetrahedra k, k'; k designates the four Hg sites derived from (000) by the face-centering operations; and k' designates the four Hg sites derived from $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ by the same operations. This intensity vanishes for reciprocal-lattice points with $h = k$ and is strong for reciprocal-lattice points such as (024), (135) with $h \neq k \neq l$. The crystal was oriented with $(1\bar{2}1)$ as the scattering plane to search for this postulated mode at such lattice points and along the $[111]$ directions passing through these points.

At both (024) and (135) (Γ points of the Brillouin zone), a strong, well-defined neutron group was observed with a frequency at 298 K of 0.52(3) THz. For propagation vectors along $[111]$, neutron groups could be observed out to the zone boundary L point (0.5,2.5,4.5). Typical neutron groups are shown in Fig. 2. An analytic line shape was assumed to describe the inelastic peak due to the mode and this was convoluted with a simple Gaussian resolution function before fitting the resulting line shape to the observed distribution. The elastic component of the distribution was assumed to be Gaussian. Both Gaussian and Lorentzian line shapes were investigated for the inelastic component and the latter gave

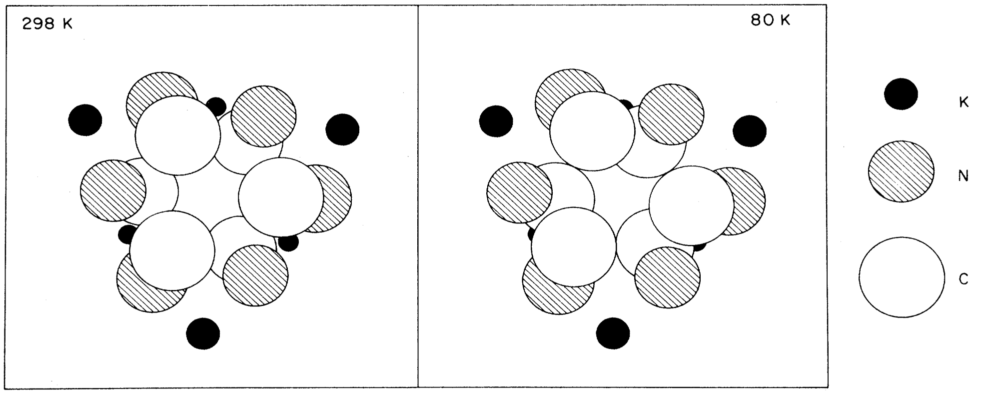

FIG. 1. The projection of the cyanotetrahedra along the [111] direction. The (CN) ion and Hg atom which lie on [111] have been omitted for clarity. At 298 K the tetrahedra have a staggered configuration. At 80 K adjacent tetrahedra have rotated about [111] in antiphase.

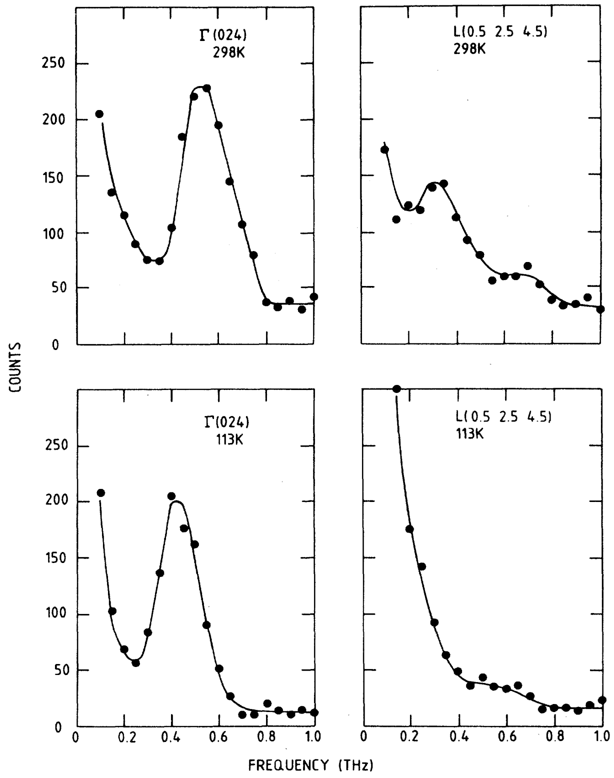

FIG. 2. Scattered neutron distributions observed at the Γ(024) and $L(0.5,2.5,4.5)$ points at temperatures of 298 and 113 K.

somewhat better fits overall. The frequency, width, and intensity of the mode were adjustable parameters in the fitting procedure.

The dispersion curve measured from (024) to (0.5,2.5,4.5) is shown at 298 K in Fig. 3. On the basis of the structure-factor calculations we interpret this curve as the dispersion curve of the postulated antiphase librational mode propagating along [111]. As the temperature is lowered to the transition the entire branch softens. But, at 113 K, while a well-defined neutron group is still observed at Γ with a frequency which has softened by $\approx 20\%$, the corresponding mode at L can be detected only as a broadening of the elastic incoherent peak (Fig. 2). As shown in Fig. 3, when the temperature is lowered to the transition the frequency of the mode at L decreases to zero and the atomic displacement pattern specified by its eigenvector becomes frozen in, thus driving the observed structural transition. The new Bragg peaks which appear at the L points are the superlattice peaks observed in the low-temperature diffraction profile,[15] e.g., the L point (0.5,2.5,4.5) in the cubic spinel phase becomes the reciprocal-lattice point (456) in the trigonal phase. The observed temperature dependences of the L-point and Γ-point mode frequencies are shown in Fig. 4.

The frequencies at the L point were fitted to an expression of the form,

$$\omega^2=c(T-T_c)^\gamma ,$$

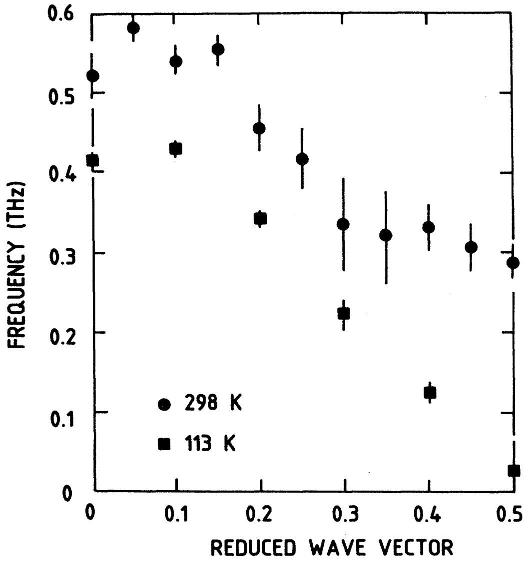

FIG. 3. Experimental dispersion curves at 298 and 113 K of the [111] longitudinal antiphase librational mode.

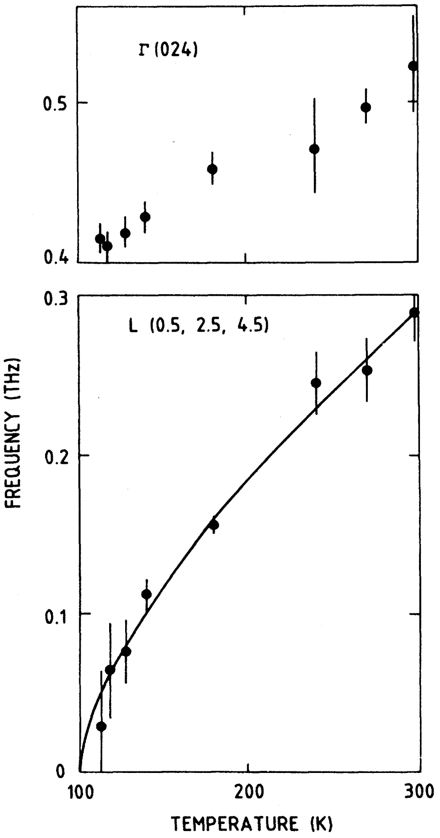

FIG. 4. Temperature dependence of the Γ-point and L-point mode frequencies for the dispersion curves of Fig. 3.

where T_c is the transition temperature and c is a constant. The "best-fit" values of the parameters are as follows: $T_c = 101 \pm 11$ K, $\gamma = 1.30 \pm 0.20$, and the solid line in Fig. 4 is calculated with these parameters. The transition temperature is lower than that measured previously,[3] although the two agree within the present experimental error. The exponent γ is correspondingly large. The apparently low T_c is probably due to the difficulty in measuring the inelastic peak as its frequency tends to zero in the presence of a strong incoherent elastic peak.

The transition is of the soft-mode type[17] and, in mean-field theory, such a transition for spatial dimension $d = 3$ has an exponent $\gamma = 1$.[18] Measurements were not made for $T < T_c$ due to fears of cracking the single crystal.[4] Consequently, it is not established experimentally whether or not the transition is continuous, and hence second order. Further, the temperature dependence of the order parameter is not known in sufficient detail to be definitive on this question. The ordering wave vector for the transition is from the class $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ and there are four independent wave vectors within the star of this vector. Since the soft mode is of longitudinal character, there is only one soft-mode eigenvector associated with each of the ordering wave vectors. Thus, the dimensionality of the order parameter is four, and modern theories of phase transitions[19] suggest that such a transition might be of second-order character, and predict the exponent γ to be 1.39.

Since the ordering wave vector is a zone-boundary wave vector, there can be no bilinear term in the free energy which couples the order parameter and the elastic strain. Consequently, the observed decrease in the elastic constants from 473 K to the transition[4] is not due to a direct coupling to the soft mode. However, to investigate the possible temperature dependence of other modes, several phonon dispersion curves were measured for the high-symmetry directions. Since the $(1\bar{2}1)$ plane in which the soft mode was observed is rather sparsely populated with reciprocal-lattice points, the crystal was reoriented to the conventional $[1\bar{1}0]$ orientation for the phonon measurements. The structure factor for the soft mode is zero in this plane.

In the spinel structure there are eight formula units in the cubic unit cell and hence two units in the primitive cell. If we assume that the Hg(CN)$_4$ ions are rigid units, there will be 24 branches of the dispersion relation for a general propagation vector. The higher symmetry for propagation vectors along [001] and [111] will reduce this, but the number of branches is still sufficiently large that a detailed lattice-dynamical model is necessary to interpret completely the inelastic neutron scattering distributions. Consequently we measured only the low-frequency branches of the dispersion relation up to a frequency of ≈2 THz. Typical neutron groups are shown in Fig. 5. The results for temperatures of 298 and 120 K are shown in Figs. 6(a) and 6(b) where the solid lines show the assumed connectivity of the points. The dashed lines through the origin show the velocity of sound calculated from the experimental elastic constants.[4] The neutron data evidently agree very well with these lines. It is clear that none of the observed modes propagating along these high-symmetry directions shows any great temperature dependence. Indeed, they are remarkably independent of temperature. The behavior of $K_2Hg(CN)_4$ is thus similar to that of many other solids with soft-mode transitions, in which the soft mode and those coupled to it are the only modes which exhibit any substantial temperature dependence.

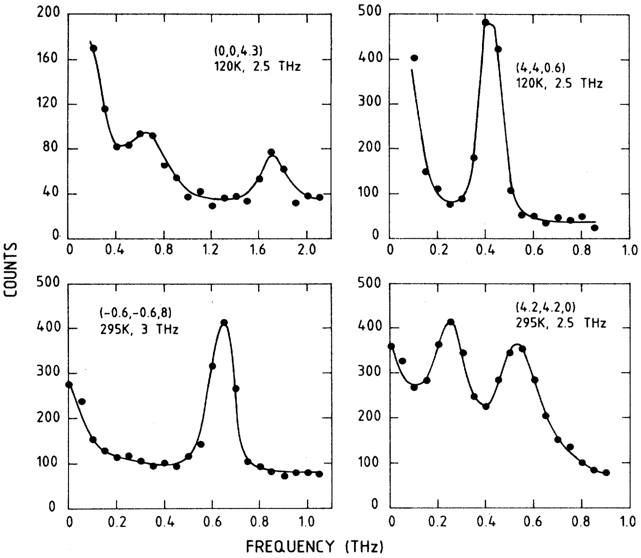

FIG. 5. Scattered neutron distributions observed with the high-symmetry $[1\bar{1}0]$ orientation.

IV. DISCUSSION

We have shown that the cubic (paraelastic) to trigonal (ferroelastic) phase transition in $K_2Hg(CN)_4$ is a dynamic effect, as suggested in the measurement of the crystal structure.[15] It is a soft-mode transition, driven by a low-lying L-point librational mode whose eigenvector is predominantly antiphase rotation of adjacent, rigid Hg(CN)$_4$ tetrahedra. An analogous transition has been observed in the antifluorite crystal K_2OsCl_6.[20] There, the soft mode is a Γ-point mode and the softening was shown to arise from the near cancellation of a particular combination of short-range force constants. Since the soft mode is at Γ, a bilinear coupling can exist between the order parameter and the elastic strains. It was suggested that this could lead to anomalous behavior of the elastic constants at the transition.[20] The anomalous temperature dependence of the elastic constants[4] in the cubic phase of $K_2Hg(CN)_4$ cannot be due to an analogous coupling term. Since the cyanospinels, $K_2M(CN)_4$, with $M =$ Zn or Cd do not exhibit transitions at zero pressure, it is of interest to consider what might be the microscopic interactions responsible for the transition in the $K_2Hg(CN)_4$. The great similarity in unit-cell dimensions and interatomic distances in the different cyanospinels has been pointed out previously[15] but the charge distributions of the $M(CN)_4$ tetrahedra will depend strongly on

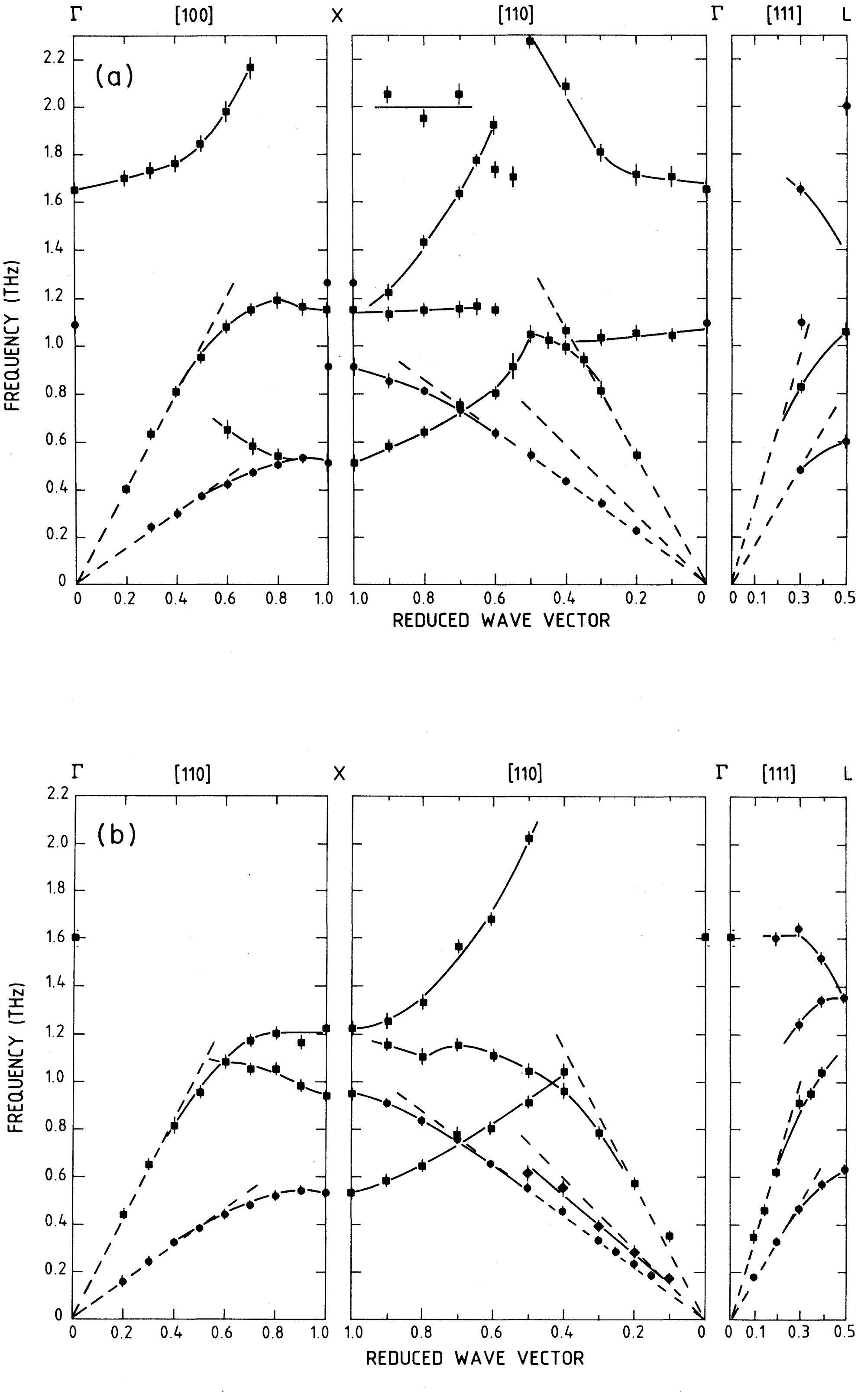

FIG. 6. Experimental dispersion curves for modes propagating along the high-symmetry directions: (a) $T = 120$ K, (b) $T = 298$ K. The solid lines are hand drawn to show the assumed connectivity. The symbols ■ (●) identify modes with predominantly longitudinal (transverse) character.

M and hence may be very different for different cyanospinels.

In the cubic phase, tetrahedra adjacent along [111] have their cyanide ions in a staggered configuration (Fig. 1). However, in view of the complex charge distribution of the $M(\mathrm{CN})_4$ tetrahedra, several energy minima may exist for different relative orientations of adjacent tetrahedra. The staggered orientation observed at high temperatures may then be a dynamically averaged orientation, resulting from the librational amplitude of the tetrahedra sampling several minima. As the temperature is lowered the librational amplitude decreases and at some critical temperature, T_c, the tetrahedra can no longer overcome the potential barrier between energy minima. The relative orientation thus changes from the dynamically averaged configuration to that of a local energy minimum, i.e., a phase transition occurs at T_c in which the relative orientations of adjacent tetrahedra change from the staggered configuration.

The thermal parameters, B, derived in the structure determination[15] show a pronounced decrease between 298 K and T_c. If we use the values of B at 298 K from Table II of Ref. 15 and assume the difference between $B(\mathrm{CN})$ and $B(\mathrm{Hg})$ is entirely due to librational motion of the tetrahedra about a [111] direction, then the librational amplitude is $\approx 2.5°$. At T_c the measured rotation for each tetrahedron is $\approx 3.5°$. Although clearly oversimplified, the consistency between the librational amplitudes lends support to the view of the phase transition described herein. A detailed interatomic force model with a realistic charge distribution for the cyanotetrahedra will be necessary to provide a more quantitative test.

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[1] R. G. Dickenson, J. Am. Chem. Soc. **44**, 774 (1922).

[2] R. Ikeda, D. Nakamura, and M. Kubo, J. Phys. Chem. **72**, 2982 (1968).

[3] S. Saruwatari, R. Ikeda, D. Nakamura, and M. Kubo, J. Magn. Reson. **9**, 503 (1973).

[4] S. Haussühl, Acta Crystallogr. **A32**, 160 (1976).

[5] W. Krasser and S. Haussühl, Solid State Commun. **20**, 191 (1976).

[6] S. Haussühl, D. Bunthoff, and W. Michaelis, Solid State Commun. **34**, 764 (1980).

[7] S. Haussühl, Acta Crystallogr. **A34**, 965 (1978).

[8] V. Wadhawan, Mater. Sci. Forum **3**, 91 (1985).

[9] P. Klüfers, H. Fuess, and S. Haussühl, Z. Kristallogr. **156**, 255 (1981).

[10] L. Wiehl and S. Haussühl, Z. Kristallogr. **156**, 117 (1981).

[11] D. M. Adams and R. E. Christopher, Inorg. Chem. **12**, 1609 (1973).

[12] L. H. Jones, Inorg. Chem. **13**, 2289 (1974).

[13] P. Preu and S. Haussühl, J. Phys. Chem. Solids **46**, 265 (1985).

[14] D. M. Adams, M. E. Gerrard, and P. D. Hatton, Solid State Commun. **39**, 229 (1981).

[15] P. N. Gerlach and B. M. Powell, J. Chem. Phys. **85**, 6004 (1986).

[16] B. M. Powell and P. N. Gerlach, Mater. Sci. Forum **27-28**, 99 (1988).

[17] A. D. Bruce and R. A. Cowley, *Structural Phase Transitions* (Taylor and Francis, London, 1981).

[18] L. P. Kadanoff, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 5A, p. 1.

[19] D. Mukamel, Phys. Rev. Lett. **34**, 481 (1975); D. Mukamel and S. Krinsky, Phys. Rev. B **13**, 5065 (1976); **13**, 5078 (1976); P. Bak and D. Mukamel, *ibid.* **13**, 5086 (1976).

[20] D. Mintz, R. L. Armstrong, B. M. Powell, and W. J. L. Buyers, Phys. Rev. B **19**, 448 (1979); M. Sutton, R. L. Armstrong, B. M. Powell, and W. J. L. Buyers, *ibid.* **27**, 380 (1983).