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THE ELASTIC ANOMALY OF KCN AT 168 K

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Résumé. — Nous avons mesuré la largeur Brillouin de phonons longitudinaux ($q /\!/ e /\!/ [1, 0, 0]$) et de phonons transverses mous ($q /\!/ [1, 1, 0]$; $e /\!/ [0, 0, 1]$) dans la phase cubique, au-dessus de la transition de phase élastique. Une théorie semi-phénoménologique est proposée pour décrire la variation de ces largeurs ainsi que celles des constantes élastiques avec la température. On explique en particulier pourquoi il n'apparaît aucun effet spectaculaire sur la largeur des phonons transverses, quoique la constante élastique correspondante tende vers zéro.

Abstract. — The Brillouin linewidths of longitudinal phonons ($q /\!/ e /\!/ [1, 0, 0]$) and soft transverse phonons ($q /\!/ [1, 1, 0]$; $e /\!/ [0, 0, 1]$) have been measured for the first time in KCN in its cubic phase above the elastic phase transition temperature. We propose a semi phenomenological model which explains the temperature variation of both these linewidths and of the related elastic constants, and, in particular, the absence of any spectacular variation of the transverse phonon linewidth close to the transition in spite of the soft character of the related elastic constant.

1. **Introduction.** — At room temperature, Potassium cyanide possesses the rock salt structure. Nevertheless, the C_∞ symmetry of the CN^- molecule is not compatible with the cubic symmetry of its site, which implies a certain degree of disorder in the crystal. Indeed, neutron elastic scattering [1] has shown that the cyanide molecules preferentially point in one of the 8 equivalent [1, 1, 1] directions.

This crystal transforms at 168 K into an orthorhombic structure [2] (D_{2h}^{25}) characterized by the elongation of a [1, 1, 0] diagonal, and the decrease of the corresponding [1, $\bar{1}$, 0] diagonal. In this structure, the CN^- molecules are parallel to the long diagonal with a residual head to tail disorder.

The study of these two phases and of the transition between them has been made by various techniques including NMR [3], heat capacity measurements [4], and light scattering [5-6]. Inelastic neutron studies of the high temperature phase have also been performed [7-8]. Nevertheless, the most important information concerning the phase transition has been obtained by ultrasonic [9] and Brillouin scattering [10] measurements. Those have revealed that :

— The C_{44} elastic constant, which has the same order of magnitude as $\frac{C_{11} - C_{12}}{2}$ at room temperature, decreases by one order of magnitude at the phase transition. This elastic constant seems thus to be the *soft mode* associated with the transition.

— The transition is of first order, as the extrapolation of $C_{44}(T)$ leads to its vanishing at $T_c^* = 154$ K compared to the actual (168 K) value of T_c.

— No dispersion of $C_{44}(\omega)$ is revealed between the ultrasonic and Brillouin scattering measurements.

In order to get more information on this phase transition we have repeated Buchenau and Krasser's Brillouin scattering experiment [10] but we have included the measurement of the signal linewidth, for some longitudinal and transverse phonons. In the next section we shall discuss our experimental results, which confirm the values obtained in [10] but also reveal a moderate increase of the phonon linewidths for both the transverse and longitudinal cases. In the third section, we shall briefly discuss a semi-phenomenological model which allows a quantitative description of our data to be given. Some implications of the model and of its relationship with other experimental data, including some very recent Brillouin measurements under hydrostatic pressure [11], will

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be given in the last section of this paper. A second paper will deal with the case of NaCN which presents the same succession of phases, and the same type of problems.

2. **Experimental technique and results.** — For the study of the Brillouin spectra, we used a device described previously [12]. The light source is a single-frequency argon ion laser with an output power of about 800 mW for each of the two wavelengths $\lambda_1 = 4\,880$ Å and $\lambda_2 = 5\,145$ Å. In order to achieve both a high contrast and a high resolution, the double-passed plane Fabry-Pérot interferometer, used as a monochromator, is followed by a confocal Fabry-Pérot interferometer of 50, 100 or 250 mm thickness. Fast repetitive scans are performed, in order to avoid a distorsion of the profile due to the frequency drift of the laser. The maximum resolving power of this device is equal to 10^8 (corresponding to a bandwidth of about 10 MHz), with a contrast greater than 10^7. The high resolving power allows measurement of both the frequency shifts and the linewidths of Brillouin lines to be made. Furthermore, the contrast of this spectrometer enables us to study Brillouin spectra in samples of poor optical quality and to perform backscattering experiments, where a strong parasitic laser line cannot be avoided.

Samples of different origins were used. One of the KCN samples was grown from aqueous solution [13]. The others were grown at the Département de Recherches Physiques by the Bridgman method. The faces of the crystals were parallel to the [1, 0, 0], [0, 1, 0] and [0, 0, 1] planes respectively. The c_{11} elastic constant was obtained by measurement of the longitudinal Brillouin frequency shift in backscattering (longitudinal acoustic wave propagating along $\mathbf{q} = [1, 0, 0]$). The velocity of this wave is $v_L = (c_{11}/\rho)^{1/2}$. In right-angle scattering experiments, with the same sample, the acoustic waves responsible for the Brillouin scattering propagate with $\mathbf{q} = (1/\sqrt{2})\ [1, 1, 0]$. The measurement of the frequency shift of the transverse component gives the value of the c_{44} elastic constant and of the corresponding velocity $v_T = (c_{44}/\rho)^{1/2}$. The mixture $c' = \frac{1}{2}(c_{11} + c_{12} + 2\,c_{44})$ can be deduced from the frequency shift of the longitudinal Brillouin component.

From the relation :

$$\delta\nu_B/\nu_0 = 2\,n(v/c)\sin(\theta/2)\,, \qquad (1)$$

where ν_B is the Brillouin frequency shift, ν_0 the frequency of the incident light, n the index of refraction, v the sound velocity, c the light velocity and θ the scattering angle, it can be seen that, for a given scattering geometry, variations of v with temperature leads to variations of the frequency. Therefore, the temperature dependence of the velocity is studied at variable frequency, but at constant wave vector $\mathbf{q}$.

The temperature dependence of both the density and the refractive index must be taken into account in the calculation of the elastic constants. The density was taken from [9]. The temperature variations of the refractive index were obtained from the relation

$$(n^2 - 1)/\rho(n^2 + 2) = \text{const.} \qquad (2)$$

Our measurement of v_T as a function of temperature is in good agreement with that of Krasser *et al.* [10]. These results, as well as the longitudinal velocities v_L are plotted vs temperature in figures 1 and 2 ; they agree with the ultrasonic values [9] to within experimental accuracy.

The measurements of the Brillouin linewidths Γ are shown in figure 3. All the curves show an increase of Γ with decreasing temperature. As this increase could be due to various possible parasitic effects, we have tried to test the influence of the most important ones, as discussed below.

The sample heating by the laser could produce differences in temperature between elementary scattering volumes, leading to a line broadening increasing near the phase transition. This effect can be ruled out as no differences have been found between experiments performed at different incident powers. Another origin of broadening could be the strain field in the crystal, whose amplitude increases near the transition

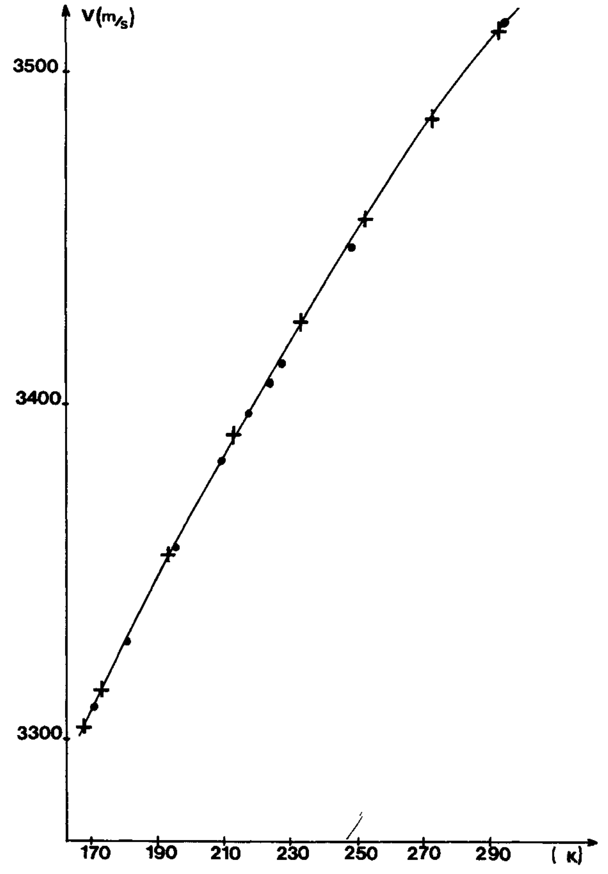

FIG. 1. — The longitudinal sound velocity $v_L = \sqrt{\frac{c_{11}}{\rho}}$ as a function of temperature. × ref. [10] • our measurements —— theory.

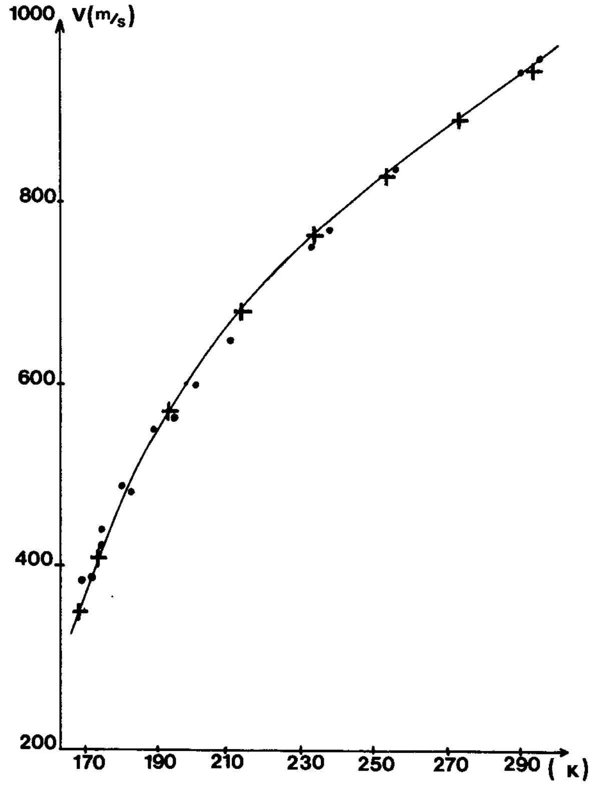

FIG. 2. — The transverse sound velocity $v_T = \sqrt{\frac{c_{44}}{\rho}}$ as a function of temperature. X ref. [10] ● our measurements —— theory.

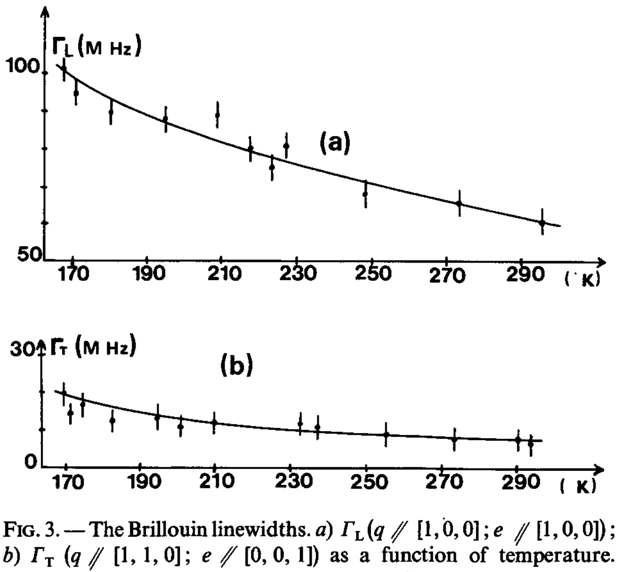

FIG. 3. — The Brillouin linewidths. *a*) Γ_L ($q /\!/ [1,0,0]$; $e /\!/ [1,0,0]$) ; *b*) Γ_T ($q /\!/ [1,1,0]$; $e /\!/ [0,0,1]$) as a function of temperature. ● our measurements —— theory.

temperature. We have tried to observe the influence of strains on the velocity by applying uniaxial pressures of about 100 kg.cm^{-2} the sample. These pressures did not lead to a noticeable change in the elastic constants, so that the corresponding broadening can be neglected. Furthermore, the strain field strongly depends on the origin of the crystal, the samples grown from solutions being nearly free of strains while those obtained by the Bridgman method are strongly strained. The same measurements, performed on the two samples, lead to similar results, showing that the influence of strains is not the origin of the increase of the linewidth. We have therefore concluded that the observed increase of Γ near the transition temperature is of intrinsic origin. This effect nevertheless does not exceed a factor of three, while the room temperature value of the linewidth is smaller than 200 MHz. In the next section, we shall propose a model for the temperature variation of both the elastic constants and the linewidths ; we shall then show that this model correctly fits our data.

3. **Discussion.** — The preceding results can be explained by a simple model which takes into account the ferroelastic nature of the transition. We shall first briefly describe this model, then use it to interpret our results.

3.1 A MODEL FOR THE FERROELASTIC TRANSITION OF NaCN AND KCN. — The ordering of molecules in plastic crystals is often described with the help of an Ising spin model where the spin variables label the different available orientations of the molecule. Such a description is not valid here as the available orientations differ between the two phases (see introduction).

Nevertheless, a more realistic description of the probability distribution function of the molecular orientation provides an alternative way of exhibiting variables which, in the vicinity of a phase transition, have the same thermodynamics as the previous variables.

Let us describe the long range orientational order of the molecules at a temperature T by

$$P(\theta, \varphi) = 1 + \sum_{J,k} \lambda_J^k F_J^k(\theta, \varphi) \qquad (3)$$

where :

— $P(\theta, \varphi)$ is the probability of finding a molecule with angular variables θ, φ ;

— $F_J^k(\theta, \varphi)$ is the complete set of surface harmonics related to the O_h group [14] ;

— J is an integer ;

— k a composite index with $2J + 1$ values, which describes at the same time :

- the irreducible representation of the cubic point group under which $F_J^k(\theta, \varphi)$ transforms ;
- the dimensionality of this representation ;
- the number of times this representation is included in the $2J + 1$ surface harmonics with index J.

In order for (3) to represent the crystal probability distribution of the molecules, λ_J^k must clearly be zero if k does not belong to the unity representation of the cubic point group.

Nevertheless, if the reorientation time of the molecules is fast enough with respect to some local deformations of the environment of the molecules, the other λ_J^k coefficients can serve as a basis for the expansion of a local, slowly varying probability

$$P(\theta_R, \varphi_R) = \sum_{J,k} \lambda_J^k(R)\, F_J^k(\theta_R, \varphi_R)\,, \tag{4}$$

where R labels a crystal site.

The space Fourier transform of the corresponding variables $\lambda_J^k(q)$ can then serve as a basis for the expansion of the corresponding energy and entropy.

In particular, in the vicinity of a phase transition, it can be shown [15] that these deformations add to the free energy a term of the form

$$F = \sum_{\substack{J,J'\\ k,k'\\ q}} \lambda_J^k(q)\, \lambda_{J'}^{k'}(-q)\, [TS_{JJ'}^{kk'}(q) - E_{JJ'}^{kk'}(q)]\,. \tag{5}$$

In this expression, T is the temperature and $\bar{\bar{S}}$ and $\bar{\bar{E}}$ are two (infinite) square matrices describing respectively the entropy and the energy related to a change in the probability distribution function of the molecule, while q is a vector of the first Brillouin zone.

The free energy F and, in particular, the tensorial sets $S_{JJ'}^{kk'}(0)$ and $E_{JJ'}^{kk'}(0)$, corresponding to the long wavelength limit ($q \to 0$) must be invariant under the symmetry operations of the crystal point group; $S_{JJ'}^{kk'}(0)$ and $E_{JJ'}^{kk'}(0)$ transform according to the product of the two representations implied by the index k and k'. As such a product contains the unity representation only if the two involved representations are equivalent, the only non zero coefficients $S_{JJ'}^{kk'}(0)$ and $E_{JJ'}^{kk'}(0)$ will be those for which k and k' belong to the same irreducible representation of the crystal point group O_h.

We can summarize this discussion by stating that, in the long wavelength limit, which is the case we are interested in here, there always exists additional, slowly time varying variables, coupled by symmetry arguments, and that linear combination of these variables can play the same role as a pseudo spin variable in a Landau type description of the thermodynamics of a phase transition. Finally, local fluctuations of non conserved quantities usually follow rate equations in the long time limit. We shall make this assumption here, which is also valid for the $q \to 0$ limit of their spatial Fourier transform.

In the rest of this paper, we shall thus be entitled to use a pseudo spin formalism, quite analogous to the one used for example by Yamada *et al.* [16] in the case of NH_4Br, to describe the phase transition of KCN.

3.2 PHASE TRANSITION AND THE ELASTIC CONSTANT C_{44}. — As the phase transition is characterized by the vanishing of C_{44}, and the corresponding deformation transform as the irreducible F_{2g} representation, it is natural to couple to this deformation a pseudo spin variable which belongs to the same representation. We shall write it λ^i ($i = 1, 2, 3$), and the part of the free energy which we need to consider here may be written, in the elastic limit up to second order as

$$\begin{aligned} F_1 = {} & F_0(T) + \tfrac{1}{2} c_{11}(e_1^2 + e_2^2 + e_3^2) + \\ & + c_{12}(e_1 e_2 + e_2 e_3 + e_3 e_1) + \tfrac{1}{2} c_{44}(e_4^2 + e_5^2 + e_6^2) \\ & + g(e_4 \lambda^1 + e_5 \lambda^2 + e_6 \lambda^3) \\ & + \tfrac{1}{2} J(T - T_0)\, [(\lambda^1)^2 + (\lambda^2)^2 + (\lambda^3)^2]\,. \end{aligned} \tag{6}$$

In this expression, g represents the linear coupling between the elastic deformations e_4, e_5 or e_6 with the λ variables, while $J(T - T_0)$ represents the entropy and energy associated, in the vicinity of the transition temperature, with the same pseudo spin variables.

If we consider only those acoustic transverse phonons which propagate with $q /\!/ [1, 1, 0]$ and $e /\!/ [0, 0, 1]$, the same free energy may conversely be written as

$$F_1 = F_0(T) + \sum_q \times \left[\frac{Mv^2 q^2}{2} Q^2 + gqQ\Lambda + \frac{1}{2} J(T - T_0)\, \Lambda^2 \right] \tag{7}$$

where

$$\Lambda = \frac{1}{\sqrt{2}}(\lambda^1 + \lambda^2)\,; \quad v^2 = \frac{c_{44}}{M}$$

M being the mass of an elementary cell, and Q the amplitude of the phonon mode.

Equation (7) is just the free energy associated with a coupled spin phonon system, and its dynamics and thermodynamics can thus be obtained by methods identical to those of [16].

If the pseudo spins are assumed to have a diffusive dynamics, one easily obtains the coupled system of equations

$$\begin{aligned} Mv^2 q^2 Q + gq\Lambda - M\omega^2 Q &= i\bar{\gamma} q^2 \omega Q \\ J(T - T_0)\, \Lambda + gqQ &= i\gamma\omega\Lambda \end{aligned} \tag{8}$$

where γ represents a relaxation associated to the individual pseudo spin, while the usual damping of the acoustical phonons is written the form $\bar{\gamma} q^2 \omega Q$ in order to take into account the fact that the experiments are performed at constant $\| q \|$, but that it is a time response function which is actually obtained.

If one assumes that the light is scattered only by the modulation of the dielectric tensor by the lattice deformation, the Brillouin intensity is just proportional to the imaginary part of the deformation Green's function, which is easily obtained by eliminating Λ between the two equations (8). The Brillouin intensity is thus proportional to :

$$I_m \left\{ \frac{1}{q^2 \left[v^2 - \dfrac{g^2}{MJ(T - T_0)} - i\Gamma\omega \right] - \omega^2} \right\} \tag{9}$$

where

$$\Gamma = \frac{1}{2M}\left[\bar{\gamma} + \frac{g^2\,\gamma}{J^2(T - T_0)^2}\right] \qquad (10)$$

and where it has been taken into account that

$$\frac{\gamma\omega}{J(T - T_0)} \ll 1 \,.$$

This last inequality expresses the fact that the pseudo spin relaxation time is short with respect to the time evolution of the long wavelength probability fluctuation described by the variable Λ. (Note that this inequality is implied by the absence of dispersion between Haussuhl's result [9] and ours.)

The implications of (9) and (10) are threefold.

a) The phase transition (which is accompanied by an alignment of the CN$^-$ molecules in the [1, 1, 0] direction) does not take place at T_0, but at a value T_c^* such

$$c_{44} = M\left[v^2 - \frac{g^2}{MJ(T_c^* - T_0)}\right] = 0 \qquad (11)$$

(see also section IV, *a*)).

b) The phonon linewidth, at constant q, is given by (10). Formulae (10) and (11) have been used to fit our data for the c_{44} phonons.

We find that, in the region 168-273 K, the elastic constant c_{44} can be represented by (see Fig. 1)

$$c_{44} = c_{44}^0 - \frac{b_{44}^2}{T - T_0}$$

with

$$c_{44}^0 = 0.372 \times 10^{11}\ \text{dyn./cm}^2$$
$$b_{44}^2 = 89 \times 10^{11}\ \text{dyn./cm}^2/^0$$
$$T_0 = -\,86\ \text{K} \Rightarrow T_c^* = 154\ \text{K}\,.$$

The negative value for T_0 means that in the absence of important coupling to the elastic constant, the λ fluctuations would never condense at any positive temperature. (Note that, in this formula, the thermal expansion of the crystal, which should also affect the temperature variation of the elastic constant of the crystal, has not been taken into account, and that the same effect has been also neglected in the rest of the discussion.)

Using the above value for T_0, the corresponding Brillouin linewidth can be represented in accordance with (10) by

$$\Gamma_{44} = \Gamma_{44}^0 + \frac{\gamma_{44}^2}{(T - T_0)^2} \qquad (12)$$

with

$$\Gamma_{44}^0 = 10\ \text{MHz}$$
$$\gamma_{44}^2 = 10^6\ \text{MHz}/(^0)^2$$

and the corresponding fit is shown on figure 3*b*.

c) Phase transition and the elastic constant c_{11}. — Another coupling mechanism between the λ variables and the longitudinal phonons must be used to explain both the temperature dependence and the linewidth of the longitudinal phonons propagating along the [1, 0, 0] direction. Indeed, this coupling cannot be a linear one, as the corresponding deformation is of the A_{1g} or the E_g representation, while the λ variables are of the F_{2g} representation. Such a problem is very usual in phase transitions, and has been treated in the case of the antiferroelastic transitions by Pytte [17]. As the product $F_{2g} \otimes F_{2g}$ contains both representations, one sees that the fluctuations of the λ variables can easily couple to longitudinal phonons, through an energy term (where only those longitudinal phonons have been taken into account) of the form

$$F = F_1 + \sum_q \left\{ \frac{Mv^2}{2} q^2 e^2 + \right.$$
$$\left. + \, qe[d_1(\lambda^1)^2 + d_2((\lambda^2)^2 + (\lambda^3)^2)] \right\}. \qquad (13)$$

The influence of the fluctuations of the λ^2 variables on the elastic constant c_{11} and on the linewidth of the longitudinal phonons can be easily obtained from Pytte's results when one notes that the diffusive dynamics assumed for the pseudo spins should give the same results as that of the overdamped phonons considered by Pytte, and that, furthermore, the dispersion of the diffusive mode must have cubic symmetry. One then obtains

$$c_{11} = c_{11}^0 - \frac{b_{11}^2}{(T - T_0)^{1/2}} \qquad (14a)$$

$$\Gamma_{11} = \Gamma_{11}^0 + \frac{\gamma_{11}^2}{(T - T_0)^{1/2}}\,. \qquad (14b)$$

Our experimental data can be well fitted by (14*a*) and (14*b*) (see Figs 2 and 3*a*) with

$$c_{11}^0 = 2.74 \times 10^{11}\ \text{dyn./cm}^2$$
$$\Gamma_{11}^0 = 13.5\ \text{MHz}$$
$$b_{11}^2 = 1.6 \times 10^{11}\ \text{dyn./cm}^2\,(^0)^{1/2}$$
$$\gamma_{11}^2 = 3.5 \times 10^5\ \text{MHz}/(^0)^{3/2}\,.$$

4. **Final remarks.** — We conclude this paper with a few remarks on the proposed model which was based on our measurements.

4.1 ORDER OF THE TRANSITION. — In order to describe the phase transition of KCN from the cubic phase I to the orthorhombic phase II, we have used a Landau type free energy in which the *soft mode* is of the F_{2g} representation. Nevertheless, for obtaining the order of this transition, the free energy must be expanded up to higher orders in the corresponding variables. When this is done, it is found [18] that, when an elastic constant c_{44} goes to zero, as the symmetrized cube of F_{2g} contains the unity representation, the transition is always of first order. This seems to agree with the experiment, as we have found that T_c^* is equal to 154 K while the actual transition takes place at $T_c = 168$ K, for a still finite value of c_{44}.

Nevertheless, this does not account for the present situation because this first order transition should bring the crystal into a rhombohedral symmetry D_{3d} (see [18]), while the transition is actually to D_{2h} symmetry. The terms of order 4 and 6 in the soft mode variables must thus be taken into account to explain the first order character of the transition. In such a case the exact value of T_c has no analytical expression in terms of the coefficients of the free energy expansion, and cannot be easily discussed. We believe that the role of these coefficients, and of their pressure dependence can also explain the very recent experiments under hydrostatic pressure of Hocheimer *et al.* [11]. They find that T_c increases with pressure while the actual value of c_{44} at any temperature is very little affected by the pressure variation. As is seen from equation (11), the value of c_{44} in the high temperature phase depends only on the temperature (and pressure) variation of $J(T - T_0)$, the second order term in λ in the free energy (equation (6)). On the other hand, the actual T_c depends in a precise manner on the value of the higher order coefficients. The pressure results can thus be explained by assuming that the high order coefficients have a greater pressure dependence than $J(T - T_0)$, an assumption which is not in contradiction with the conclusions of ref. [11].

4.2 MOLECULAR PROBABILITY FUNCTION AND PHASE TRANSITION. — The discussion given above implies that, below T_c, the probability distribution function $P(\theta, \varphi)$ contains some components λ which transform as F_{2g}, while, above T_c, the same components represent a diffusive excitation in the crystal. Following the reference given in [14], the two lowest variables transforming as F_{2g} are associated with surface harmonics with $J = 2$ and $J = 4$ respectively.

However, if one assumes that, in Raman scattering experiments on both cyanides, the principal light scattering mechanism is the rigid rotation of the CN^- molecules, it is easily shown [19] that the low frequency F_{2g} spectrum exactly represents the time Fourier transform of the correlation function $\langle \lambda_2^i(t)\, \lambda_2^i(0) \rangle$ where as in equation (1) the subscript 2 stands for the corresponding value of J while the superscript $i = 1, 2, 3$ labels the three components of this F_{2g} type variable.

This F_{2g} spectrum has been measured as a function of the temperature [5], and can be correlated with our description of the phase transition. If we again use equation (9) in the low frequency region ($10\ \text{cm}^{-1} < \omega < 30\ \text{cm}^{-1}$), we find that the intensity at fixed frequency ω is proportional to $J(T - T_0)$ (the coupling with the sound waves being negligibly small at this frequency). A plot of this intensity versus temperature is given in figure 4. Though there is a small scatter in the data, this intensity is clearly constant with temperature. This means that the *order parameter* λ does not contain any $J = 2$ contribution and that any realistic microscopic model will have to take into account the fact that the order parameter contains only contributions from surface harmonics with $J \geqslant 4$.

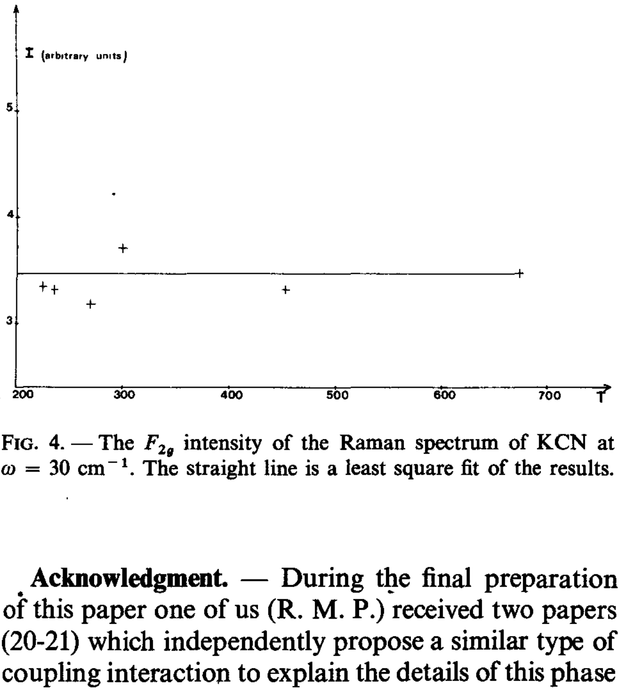

FIG. 4. — The F_{2g} intensity of the Raman spectrum of KCN at $\omega = 30\ \text{cm}^{-1}$. The straight line is a least square fit of the results.

Acknowledgment. — During the final preparation of this paper one of us (R. M. P.) received two papers (20-21) which independently propose a similar type of coupling interaction to explain the details of this phase transition. Nevertheless, both the methods and the emphasis are quite different in each case giving rise to significant differences in the calculated results.

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[13] This crystal was kindly given to us by Prof. S. Haussuhl.

[14] The surface harmonics are linear combinations of the spherical harmonics with the same value of J which transform as the eigen vectors of some irreducible representation of some point group. An extensive table of these surface harmonics can be found, in particular for the cubic group O_h in e.g.

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