Local properties in orientationally disordered crystals with translation-rotation coupling

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In orientationally disordered crystals, the translation-rotation coupling affects both collective and local properties near ferroelastic phase transitions. The anomalous temperature behavior of the static mean-square displacements is investigated. The single-particle orientational distribution function in a deformable lattice is calculated and it is shown that molecular symmetry plays an essential role in addition to site symmetry. The theory is applied to a quantitative study of the alkali cyanides in the disordered phase and leads to an understanding of experimental results.

I. INTRODUCTION

The coupling of orientational motion to lattice vibrations is most apparent at structural phase transitions where the occurrence of orientational order is accompanied by a change in lattice structure. The alkali cyanides constitute a model system for the study of translation-rotation (T-R) coupling.[1] In addition to drastic anomalies in static and dynamic collective properties,[2,3] one finds unusual behavior in local properties. As examples, we mention exceptionally large mean-square translational displacements[4−6] and the temperature dependence of the single-particle orientational distribution function.[7]

It is the purpose of the present paper to study the influence of the bilinear T-R coupling on local properties and to show the mutual relation between local and collective properties. From the theory of bilinear T-R coupling in orientationally disordered crystals, it is well known that the local orientational susceptibility influences the softening of the elastic constants.[8] On the other hand, the single-particle properties are themselves dependent on a modification of the single-particle potential due to T-R coupling.[9]

The single-particle orientational distribution function is directly accessible to neutron and x-ray scattering. The corresponding structure factor in orientationally disordered crystals is most conveniently expanded in terms of symmetry-adapted functions.[7,10,11] The coefficients of such an expansion, which are found to be temperature dependent, are treated as experimental parameters.[7,11,12] The calculation of these coefficients from a microscopic theory has been an open question and it has been suggested that such a calculation should include the effect of T-R coupling.[13]

Molecular dynamics simulations have contributed substantially to our present understanding of T-R coupling.[14] The interaction of the charge distribution of the CN^- ion with the alkali atoms in the alkali cyanides was first studied by molecular dynamics. Subsequently, it was shown in an extension of the analytic theory that short-range

repulsions and Coulomb forces act in an opposite sense.[15] The computer simulations take into account the asymmetry of the CN^- ion, but so far the deviations from centrosymmetry have been ignored in the theoretical analysis.[8,15] In a preceding paper,[16] we have studied the T-R coupling from a general point of view of molecular symmetry. In the following we shall show that the deviations of the CN^- ion from centrosymmetry play an important role.

The content of the present paper is as follows. We first (Sec. II) consider the formal relations between collective and single-particle susceptibilities in the presence of bilinear T-R coupling. The self-interaction of the molecule with the lattice is calculated by including even and odd l rotational modes in the bilinear T-R coupling. In Sec. III the modified single-particle potential is used to calculate the single-particle orientational probability distribution function. Next, (Sec. IV) local displacement-displacement correlation functions are calculated and their anomalous temperature behavior is obtained. In Sec. V we present a detailed numerical application to KCN on the basis of microscopic interaction potentials.

II. DISPLACIVE AND ORIENTATIONAL CORRELATIONS

We start from a model of a crystal with bilinear T-R coupling which was originally derived in Ref. 8. Here we use a generalization of the model as it was given in our previous paper[16] hereafter referred to as I. We consider a potential of the form

$$V = V^{TT} + V^{TR} + V^{RR} + V^{R} . \quad (2.1)$$

The harmonic lattice part reads

$$V^{TT} = \frac{1}{2} \sum_k u_\rho(-k) M_{\rho\sigma}(k) u_\sigma(k) , \quad (2.2a)$$

where $u_\rho(k)$ are the Fourier-transformed lattice displacements and $\overline{M}(k)$ denotes the bare dynamical matrix. The index ρ labels the particles in the primitive cell and indicates the Cartesian components. The bilinear translation-

rotation coupling reads

$$V^{TR} = \sum_{\mathbf{k}} v_{\lambda\rho}(\mathbf{k}) Y_\lambda(-\mathbf{k}) u_\rho(\mathbf{k}) . \qquad (2.2b)$$

Here, $Y_\lambda(\mathbf{k})$ are the Fourier-transformed orientational coordinates in the form of symmetry-adapted functions, $\lambda \equiv \{\Gamma, l, \alpha\}$ labels the representation Γ of the static site, l is the angular momentum number, and α denotes the column (row) within the representation. The bilinear interaction coefficients have also been specified in terms of basic atomic potentials. The direct orientational interaction is of the form

$$V^{RR} = \tfrac{1}{2} \sum_{\mathbf{k}} J_{\lambda\lambda'}(\mathbf{k}) Y_\lambda(\mathbf{k}) Y_{\lambda'}(-\mathbf{k}) , \qquad (2.2c)$$

where $J_{\lambda\lambda'}$ represents, for instance, an electrostatic multipole interaction.[15] Finally, the single-particle orientational potential reads

$$V^R = \sum_{\mathbf{n}} \sum_{\lambda_0} \alpha_{\lambda_0} Y_{\lambda_0}(\Omega(\mathbf{n})) , \qquad (2.2d)$$

where $\mathbf{n}$ refers to the nth molecule (or molecular ion) in the lattice. We recall that λ_0 denotes those values of l and Γ which refer to the unit representation of the site point group.

As has been shown in I, the potential (2.1) can be replaced by an effective orientational potential where the translations have been eliminated:

$$V = W^{RR} + V^{RR} + \sum_{\mathbf{n}} W^R(\mathbf{n}) , \qquad (2.3)$$

where

$$W^{RR} = -\tfrac{1}{2} \sum_{\mathbf{k}} [C_{\lambda\lambda'}(\mathbf{k}) - C_{\lambda\lambda}^s \delta_{\lambda\lambda'}] Y_\lambda(\mathbf{k}) Y_{\lambda'}(-\mathbf{k}) \qquad (2.4a)$$

and

$$W^R(\mathbf{n}) = \sum_{\lambda_0} \alpha_{\lambda_0} Y_{\lambda_0}(\mathbf{n}) - \tfrac{1}{2} \sum_\lambda C_{\lambda\lambda}^s [Y_\lambda(\mathbf{n})]^2 . \qquad (2.4b)$$

Here, W^{RR} represents the effective-lattice-mediated interaction with

$$\overline{C}(\mathbf{k}) = \overline{v}(\mathbf{k}) \overline{M}^{-1}(\mathbf{k}) \overline{v}^\tau(-\mathbf{k}) , \qquad (2.5)$$

and $\overline{C}^s$ is the self-interaction which is due to the Onsager[17,18] reaction field

$$\overline{C}^s = \frac{1}{N} \sum_{\mathbf{k}} \overline{C}(\mathbf{k}) . \qquad (2.6)$$

From the interaction (2.3), we can directly obtain the orientational susceptibility

$$\chi_{\lambda\lambda'}(\mathbf{k}) = \beta \langle Y_\lambda(\mathbf{k}) Y_{\lambda'}(-\mathbf{k}) \rangle . \qquad (2.7)$$

Here, $\beta = (k_B T)^{-1}$ and the brackets $\langle \ \rangle$ denote a statistical average with respect to the potential (2.3). Using methods of molecular-field theory, we obtain[9]

$$\chi_{\lambda\lambda'}(\mathbf{k}) = \chi_{\lambda\lambda}^0 [\overline{1} - (\overline{C}(\mathbf{k}) - \overline{C}^s - \overline{J}(\mathbf{k})) \overline{\chi}^0]^{-1}_{\lambda\lambda'} . \qquad (2.8)$$

We recall that $\overline{C}^s$ is a diagonal matrix, as is also the case for the single-particle susceptibility

$$\chi_{\lambda\lambda}^0 = \beta Z_0^{-1} \int d\Omega \, Y_\lambda^2(\Omega) \exp[-\beta W^R(\Omega)] , \qquad (2.9a)$$

$$Z_0 = \int d\Omega \exp[-\beta W^R(\Omega)] . \qquad (2.9b)$$

A second-order phase transition occurs at the highest temperature where $\chi_{\lambda\lambda'}(\mathbf{k})$ becomes divergent. This corresponds to the largest eigenvalue of

$$\overline{K}(\mathbf{k}) = (\overline{C}(k) - \overline{C}^s - \overline{J}(\mathbf{k})) \overline{\chi}^0 \beta^{-1} . \qquad (2.10)$$

As has been shown previously, in case of a bilinear T-R coupling, there exists an exact relation between the collective orientational susceptibility and the collective displacement-displacement susceptibility[8]

$$[D^{-1}(\mathbf{k})]_{\rho\sigma} \equiv \beta \langle u_\rho(\mathbf{k}) u_\sigma(-\mathbf{k}) \rangle , \qquad (2.11a)$$

$$\overline{D}^{-1}(\mathbf{k}) = \overline{M}^{-1}(\mathbf{k})[\overline{1} + \overline{v}^\tau(-\mathbf{k}) \overline{\chi}(\mathbf{k}) \overline{v}(\mathbf{k}) \overline{M}^{-1}(\mathbf{k})] . \qquad (2.11b)$$

Both Eqs. (2.8) and (2.11b) are obtained from a same free energy (see Appendix). A divergence in $\overline{\chi}(\mathbf{k})$ leads to a divergence of the displacement-displacement susceptibility, or equivalently, to a softening of the corresponding displacive restoring forces.

In the alkali cyanides we mention the anomalous behavior of the shear elastic constants or of the transverse acoustic phonons. The instability is of T_{2g} symmetry, and for $\mathbf{k} \to 0$ and perpendicular to one of the crystal axes,[19,20] we obtain T_c from Eq. (2.10) as a solution of

$$T_c = \left[\frac{2B^2}{ac_{44}^0} - C_f^s - J_f \right] y_f(T) . \qquad (2.12)$$

Here the potential parameter B represents the interaction of an $l = 2, T_{2g} \equiv f$ orientational mode with the deformation of the surrounding lattice [see Eq. (4.20) of I]. The elastic constants c_{44}^0 are obtained from the bare dynamical matrix $\overline{M}_\rho$, a denotes half the cubic lattic constant ($a = 3.26$ Å for KCN).

The single-particle expectation value y_f reads

$$y_f = Z_0^{-1} \int d\Omega [Y_{2,1}^f(\Omega)]^2 \exp[-W^R(\Omega)] , \qquad (2.13)$$

where the function $y_{2,1}^f$ is defined by Eq. (A4a) of I. The self-interaction C^s and the single-particle potential W^R will be studied in detail in the next section. The elastic constants are obtained from Eq. (2.11b) in the long wavelength limit.[8] In particular, we obtain with the present potential

$$c_{44} = c_{44}^0 \left[\frac{T - T_c(T)}{T + (C_f^s + J_f) y_f(T)} \right] . \qquad (2.14)$$

Expressions (2.12) and (2.14) constitute a generalization of previous results in several respects. In comparison with Ref. 8, the self-interaction C^s and the direct orientational coupling is taken into account. In comparison with Refs. 2b and 21, the orientational motion is treated as a continuous process and no restriction is made to a few orientations of the CN ion as is done in discrete tunneling models. Expression (2.14) also differs from Eq. (5.23) of Ref. 15, the reason being that there the collective orientational susceptibility is calculated without the lattice-

mediated interaction $C(\mathbf{k})$ and without C^s. Such an approximation does not lead to a simultaneous divergence of $\bar{X}(\mathbf{k})$ and $\bar{D}^{-1}(\mathbf{k})$ as one should expect from a bilinear interaction.

From Eqs. (2.8), (2.9a), and (2.9b) it is obvious that the self-interaction $\bar{C}^s$ influences both the collective and the local properties at orientational phase transitions. It is known, mainly from the study of Jahn-Teller systems,[22] that $\bar{C}^s$ leads essentially to a change of T_c in the collective quantities such as the orientational and displacive susceptibilities $\bar{X}(\mathbf{k})$ and $\bar{D}^{-1}(\mathbf{k})$. We notice that in Eq. (2.8) only those elements of $\bar{C}^s$, of which the index $\lambda \equiv (\Gamma, l, \alpha)$ refers to the same representation Γ as the order parameter, are relevant. In particular, this property is also seen in Eq. (2.12). On the other hand, the single-particle potential W^R, Eq. (2.4b) contains a summation over the whole set $\{\Gamma, l, \alpha\}$. It is therefore to be expected that the self-interaction plays an important role in determining the single-particle orientational behavior.

III. SELF-INTERACTION AND ORIENTATIONAL DISTRIBUTION

Here we want to study the self-interaction contribution to the single-particle potential. Since for fixed l and Γ, all members α of $C^s_{\lambda\lambda}$ with $\lambda \equiv (l, \Gamma, \alpha)$ are equal, we can write

$$\frac{1}{2} \sum_\lambda C^s_{\lambda\lambda} [Y_\lambda(\Omega)]^2 = \frac{1}{2} \sum_{l,\Gamma} C^s_{(l,\Gamma)} \sum_\alpha [Y^\Gamma_{l,\alpha}(\Omega)]^2 . \quad (3.1)$$

Using the generalized Unsöld theorem[23]

$$\sum_\alpha [Y^\Gamma_{l,\alpha}(\Omega)]^2 = \sum_{\lambda_0} \beta^{(\Gamma,l)}_{\lambda_0} Y_{\lambda_0}(\Omega) , \quad (3.2)$$

where $\lambda_0 \equiv (\Gamma_0, l_0, 1)$ refers to the unit representation of the molecular site group, we rewrite Eq. (3.1) as

$$\frac{1}{2} \sum_\lambda C^s_{\lambda\lambda} [Y_\lambda(\Omega)]^2 = \sum_{\lambda_0} \alpha^s_{\lambda_0} Y_{\lambda_0} , \quad (3.3a)$$

with the definition

$$\alpha^s_{\lambda_0} = \frac{1}{2} \sum_{l,\Gamma} C^s_{(l,\Gamma)} \beta^{(\Gamma,l)}_{\lambda_0} . \quad (3.3b)$$

The total single-particle potential W^R, Eq. (2.4b), then reads

$$W^R(\mathbf{n}) = \sum_{\lambda_0} (\alpha_{\lambda_0} - \alpha^s_{\lambda_0}) Y_{\lambda_0}(\mathbf{n}) , \quad (3.4)$$

where $(\mathbf{n})$ stands for $\Omega(\mathbf{n})$. The coefficients $\alpha^s_{\lambda_0}$ measure the contribution of the self-interaction to the single-particle potential; they constitute the Onsager reaction field[17] on the molecule in the lattice. Our procedure of evaluating the self-interaction coefficients $\alpha^s_{\lambda_0}$ consists in calculating first the coefficients $\beta^{(\Gamma,l)}_{\lambda_0}$ from Eq. (3.2) of a given representation Γ and a given l. Then we calculate the matrix elements $C^s_{(l,\Gamma)}$ for the same (Γ, l). Explicitly, for fixed l and Γ, where the representation Γ has dimension α_s, all α elements, $\alpha \in \{1 - \alpha_s\}$, of the diagonal matrix $C^{s(\Gamma,l)}_{\alpha\alpha}$ are equal. We therefore write for such elements (for fixed α)

$$C^s_{(\Gamma,l)} = \frac{1}{N} \sum_{\mathbf{k}} v^{(\Gamma,l)}_{\alpha\rho}(\mathbf{k}) (M^{-1}(\mathbf{k}))_{\rho\alpha} v^{(\Gamma,l)}_{\sigma\alpha}(-\mathbf{k}) . \quad (3.5)$$

This expression corresponds to Eq. (2.6) for given (Γ, l).

Although the present considerations, since they are based on group theory, are general and not restricted to any given system, we shall now apply them to the case of the alkali cyanides in the orientationally disordered cubic phase. We consider first the representations of E_g and T_{2g} symmetry of which the functions $Y^e_{2,\alpha}$, $\alpha = 1, 2$ and $Y^f_{2,\alpha}$, $\alpha = 1, 2, 3$ form a basis. Here we use the notation introduced in Sec. II of I. Application of Eq. (3.2) yields

$$\sum_{\alpha=1}^2 [Y^e_{2,\alpha}(\Omega)]^2 = -\sum_{\alpha=1}^3 [Y^f_{2,\alpha}(\Omega)]^2 = \left[\frac{3}{7\pi}\right]^{1/2} K_{41}(\Omega) . \quad (3.6)$$

On the right-hand side of Eq. (3.6) we have dropped irrelevant constants. The function K_{41} denotes the cubic harmonic[24] with $l = 4$ and A_{1g} symmetry. In Cartesian coordinates one has

$$K_{41}(\Omega) = \frac{5}{4} \left[\frac{21}{4\pi}\right]^{1/2} (x^4 + y^4 + z^4 - \tfrac{3}{5}) . \quad (3.7)$$

The contribution to (3.3b) due to $l = 2$ modes of E_g and T_{2g} are $\alpha^{s(e,2)}_4 = 0.185 C^s_{(e,2)}$ and $\alpha^{s(f,2)}_4 = -0.185 C^s_{(f,2)}$, respectively.

The quantities $C^2_{(e,2)}$ and $C^s_{(f,2)}$ are calculated by means of Eq. (3.5). For the evaluation of $C^s_{(e,2)}$, $e \equiv E_g$, $l = 2$, we use the bilinear coupling matrix

$$\bar{v}^{(e,2)}(\mathbf{k}) = \left[\bar{0} , \; \frac{-\bar{v}^{(e,2)}(\mathbf{k})}{(m_a)^{1/2}}\right] , \quad (3.8a)$$

where $\bar{0}$ is a 2×3 null matrix and $\bar{v}^{(e,2)}(\mathbf{k})$ is given by Eq. (4.17) of I:

$$\bar{v}^{(e,2)}(\mathbf{k}) = i 2A \begin{bmatrix} \sin(k_x a) & \sin(k_y a) & -2\sin(k_z a) \\ -\sqrt{3}\sin(k_x a) & \sqrt{3}\sin(k_y a) & 0 \end{bmatrix} . \quad (3.8b)$$

Here, m_a is the mass of the alkali atom; the coupling coefficient A is given by Eq. (4.18) of I. Similarly, for the calculation of $C^s_{(f,2)}$, $f \equiv T_{2g}$, $l = 2$, we use the coupling matrix

$$\bar{v}^{(f,2)}(\mathbf{k}) = \left[\bar{0} , \; \frac{-\bar{v}^{(f,2)}(\mathbf{k})}{(m_a)^{1/2}}\right] , \quad (3.9a)$$

where $\bar{0}$ is the 3×3 null matrix, while $\bar{v}^{(f,2)}(\mathbf{k})$ is given by Eq. (4.19) of I:

$$\bar{v}^{(f,2)}(\mathbf{k}) = i 2B \begin{bmatrix} \sin(k_y a) & \sin(k_x a) & 0 \\ 0 & \sin(k_z a) & \sin(k_y a) \\ \sin(k_z a) & 0 & \sin k_x a \end{bmatrix} . \quad (3.9b)$$

The coupling coefficient B is given by Eq. (4.20) of I.

So far we have considered only the contribution of $l=2$ of the T-R coupling to the self-interaction. Since the CN^- ion is not a symmetric dumbbell, we also have to investigate the contributions to the self-interaction which are due to odd values of l. We start with the three functions $l=1$ of T_{1u} symmetry, which have been defined in Eqs. (A2a)–(A2c) of I. We obtain immediately $\sum_{\alpha}(Y_{1,\alpha}^u)^2=3/4\pi$ and the corresponding contribution to W^R is an irrelevant constant. More interesting are the contributions from $l=3$ functions. First we have a triplet of T_{1u} symmetry, given by expressions (A5a)–(A5c) of I. The corresponding sum (3.2) is obtained as

$$\sum_{\alpha}[Y_{3,\alpha}^{1u}(\Omega)]^2=0.35K_{41}(\Omega)+0.25K_{61}(\Omega) , \qquad (3.10)$$

where K_{61} is the cubic harmonic with $l=6$ of A_{1g} sym-

metry. It reads in Cartesian coordinates

$$K_{61}(\Omega=\tfrac{231}{8}(26/4\pi)^{1/2}\{x^2y^2z^2+\tfrac{1}{22}[K_{41}]-\tfrac{1}{105}\} . \qquad (3.11)$$

Here the square brackets indicate that the function K_{41} is taken without its normalization factor. The contributions to (3.3b) due to $l=3$ modes of T_{1u} symmetry then are $\alpha_4^{s(1u,3)}=0.175C_{(1u,3)}^s$ for the coefficient of K_{41} and $\alpha_6^{s(1u,3)}=0.125C_{(1u,3)}^s$ for the coefficient of K_{61}. The matrix element $C_{(1u,3)}^s$ is obtained from Eq. (3.5) with the coupling matrix

$$\bar{v}^{(1u,3)}(\mathbf{k})=\left[\frac{\bar{v}^{(1u,3)}(0)}{(m_D)^{1/2}} , \frac{-\bar{v}^{(1u,3)}(\mathbf{k})}{(m_a)^{1/2}}\right] . \qquad (3.12a)$$

Here, m_D stands for the mass of the molecular ion; $\bar{v}^{(1u,3)}$ is a 3×3 diagonal matrix, similar to Eq. (4.13) of I:

$$\bar{v}^{(1u,3)}(\mathbf{k})=2(F\cos(k_xa)+G[\cos(k_ya)+\cos(k_za)] ,F\cos(k_ya)$$

$$+G[\cos(k_za)+\cos(k_xa)] , F\cos(k_za)+G[\cos(k_xa)+\cos(k_ya)]) . \qquad (3.12b)$$

Here we have quoted within the heavy parentheses only the diagonal elements. The coefficients F and G are defined by Eqs. (4.15a) and (4.15b) of I.

A second contribution from $l=3$ modes to the self-interaction is obtained from the triplet of T_{2u} symmetry. The functions $Y_{3,\alpha}^{2u}$ are given by Eqs. (A6)–(A6c) of I. The sum (3.2) now reads

$$\sum_{\alpha}[Y_{3,\alpha}^{2u}(\Omega)]=-0.12K_{41}(\Omega)-0.45K_{61}(\Omega) . \qquad (3.13)$$

The contributions to (3.3b) are $\alpha_4^{s(2u,3)}=-0.06C_{(2u,3)}^s$ for the coefficient of K_{41} and $\alpha_6^{s(2u,3)}=-0.225C_{(2u,3)}^s$ for the coefficient of K_{61}. The matrix element $C_{(2u,3)}^s$ is obtained form a 3×6 coupling matrix of the same structure as Eqs. (3.12a) and (3.12b) with

$$\bar{v}^{(2u,3)}(\mathbf{k})=2(H\cos(k_xa)+L[\cos k_ya)+\cos(k_za)] ,H\cos(k_ya)$$

$$+L[\cos(k_za)+\cos(k_xa)] , H\cos(k_za)+L[\cos(k_xa)+\cos(k_ya)]) . \qquad (3.14)$$

The coefficients H and L are given by Eqs. (4.16a) and (4.16b) of I. The total single-particle potential (3.4) for the high-temperature $Fm\,3m$ phase of the alkali cyanides is then obtained in the form

$$W^R(\Omega)=\alpha_{41}K_{41}(\Omega)+\alpha_{61}K_{61}(\Omega) , \qquad (3.15)$$

where

$$\alpha_{n1}\equiv\alpha_n-\alpha_n^s , \qquad (3.16)$$

with $n=4$ or 6. Here, α_4 and α_6 are the expansion coefficients of the rigid-lattice potential (2.2d). The coefficients α_4^s and α_6^s are obtained by addition of the respective contributions from the self-interactions

$$\alpha_4^s=\alpha_4^{s(e,2)}+\alpha_4^{s(f,2)}+\alpha_4^{s(1u,3)}+\alpha_4^{s(2u,3)} \qquad (3.17a)$$

and

$$\alpha_6^s=\alpha_6^{s(1u,3)}+\alpha_6^{s(2u,3)} . \qquad (3.17b)$$

Knowledge of the single-particle potential (3.15) enables us to calculate the single-particle orientational probability distribution

$$P(\Omega)=Z_0^{-1}\exp[-\beta W^R(\Omega)] , \qquad (3.18)$$

where Z_0 is defined by Eq. (2.9b). The orientational probability distribution is expanded in terms of cubic harmonics

$$P(\Omega)=\frac{1}{4\pi}+\bar{\alpha}_{41}K_{41}(\Omega)+\bar{\alpha}_{61}K_{61}(\Omega)+\cdots , \qquad (3.19a)$$

where the coefficients

$$\bar{\alpha}_{n1}=\int d\Omega P(\Omega)K_{n1}(\Omega) , \quad n=4,6 \qquad (3.19b)$$

depend on temperature. These coefficients are usually determined from neutron-diffraction data;[7,10,11] $\bar{\alpha}_{41}$ has also been obtained from the integrated intensities of the E_g and T_{2g} Raman spectra.[25]

IV. LOCAL DISPLACEMENTS

The softening of the elastic constants or of the corresponding acoustic phonons is the most obvious manifestation of the ferroelastic phase transition.[2,3] On the other hand, various experiments such as neutron scattering,[4] Mössbauer techniques,[5] and synchroton radiation[6] reveal anomalies in the local displacive correlation function.

We recall that the displacement vector $(u_\rho(\mathbf{k}))$ has the components [see Eq. (2.24) of I]

$$(u_\rho(\mathbf{k}))^\tau = (u_1^D(\mathbf{k}), u_2^D(\mathbf{k}), u_3^D(\mathbf{k}), u_1^a(\mathbf{k}), u_2^a(\mathbf{k}), u_3^a(\mathbf{k})) ,$$

(4.1)

where the index D refers to the CN ion and the index a to the alkali atom. Combining Eqs. (2.11a) and (2.11b), we find that the various matrix elements of the collective displacement-displacement correlation function are given by

$$\langle u_\rho(\mathbf{k}) u_\sigma(-\mathbf{k}) \rangle$$

$$= \beta^{-1} M_{\rho\nu}^{-1}(\mathbf{k})[\overline{1} + \overline{v}^\tau(-\mathbf{k})\overline{\chi}(\mathbf{k})\overline{v}(\mathbf{k})\overline{M}^{-1}(\mathbf{k})]_{\nu\sigma} .$$ (4.2)

From the definition of the Fourier transforms, Eqs. (2.22a) and (2.22b) from I, it follows that the displacement-displacement correlation functions in real space are given by

$$\langle u_i^a(\mathbf{n},\kappa) u_j^a(\mathbf{n},\kappa) \rangle = \frac{1}{Nm_a} \sum_{\mathbf{k}} \langle u_i^a(\mathbf{k}) u_j^a(-\mathbf{k}) \rangle ,$$ (4.3a)

$$\langle u_i^D(\mathbf{n}) u_j^D(\mathbf{n}) \rangle = \frac{1}{Nm_D} \sum_{\mathbf{k}} \langle u_i^D(\mathbf{k}) u_j^D(-\mathbf{k}) \rangle ,$$ (4.3b)

$$\langle u_i^a(\mathbf{n},\kappa) u_j^D(\mathbf{n}) \rangle = \frac{1}{N(m_a m_D)^{1/2}} \sum_{\mathbf{k}} \langle u_i^a(\mathbf{k}) u_j^D(-\mathbf{k}) \rangle$$

$$\times \cos[\mathbf{k}\cdot\tau(\kappa)] .$$ (4.3c)

Here we have used the inversion symmetry of the disordered crystal. Knowing the matrix elements (4.2), we carry out the sums on the right-hand side in Eqs. (4.3a)—(4.3c) and obtain the displacement correlation function in real space. Although the $\mathbf{k}$ sums have to be carried out numerically, the qualitative behavior of these correlation functions can be discussed as follows. At large $T \gg T_c$, $\overline{\chi}(k) \propto \chi^0 \propto T^{-1}$ and $\langle uu \rangle \propto \beta^{-1}M^{-1} \propto T$, as follows from Eq. (4.2). Consequently, the correlation functions (4.3a)—(4.3c) decrease with decreasing temperature. This normal behavior disappears at lower T, where the full structure of $\overline{\chi}(k)$, Eq. (2.8), has to be taken into account. An increase of the orientational susceptibility $\overline{\chi}(\mathbf{k})$ leads also to an increase of the displacement correlation function. By approaching T_c, the increase of $\overline{\chi}(\mathbf{k})$ dominates the influence of the factor β^{-1} in Eq. (4.2). The drastic change of $\overline{\chi}(\mathbf{k})$ by approaching T_c is smoothed out in Eqs. (4.3a)—(4.3c) by the $\mathbf{k}$ integral over the Brillouin zone. The temperature behavior depends on the anisotropy of $\overline{\chi}(\mathbf{k})$ in $\mathbf{k}$ space.[20] In the disordered phase of the alkali cyanides, the divergence of $\overline{\chi}(\mathbf{k})$ occurs for $\mathbf{k}$ approaching zero in a plane perpendicular to one of the cubic axes. This is explicitly the case[9] for the present microscopic model. On the other hand, it can be inferred[19,20] from the softening of the elastic constants c_{44}. One then expects a logarithmic increase of $\langle (u(\mathbf{n}))^2 \rangle$ for T approaching T_c.[20] On the basis of Eq. (4.2), we have calculated the integrals in expressions (4.3a)—(4.3c), by computer. The results have been considered as a function of temperature down to values of T corresponding to the experimental (first-order) phase transition. The results are shown in Fig. 1. Beside the anomalous temperature behavior, one should also notice the anomalously large numerical value of the mean-square displacements. Both
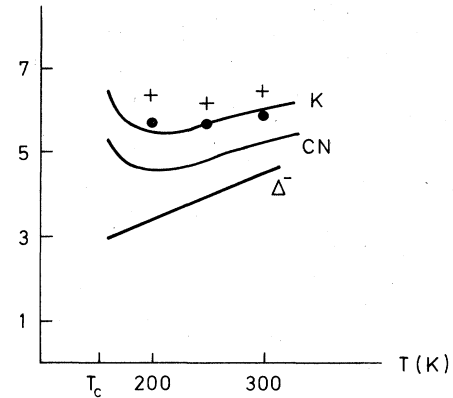

FIG. 1. Temperature dependence of mean-square displacements $\langle u_x^2 \rangle$ for K^+ and CN^-, and of $\Delta_{xx}^-(\kappa)$ with κ corresponding to position $(a,0,0)$ of K^+. All in units 10^{-2} Å^2. $+$'s are experimental results for K^+, $\bullet$'s for CN^-, experimental errors $\pm 0.2 \times 10^{-2}$ Å^2.

features have been found previously by neutron-diffraction experiments.[4,7]

Finally, we have also calculated the displacement-displacement correlation function

$$\Delta_{ij}^-(\kappa) = \langle [u_i^D(\mathbf{n}) - u_i^a(\mathbf{n},\kappa)][u_j^D(\mathbf{n}) - u_j^a(\mathbf{n},\kappa)] \rangle ,$$ (4.4a)

which can be rewritten as

$$\Delta_{ij}^-(\kappa) = \frac{1}{N} \sum_{\mathbf{k}} \left[\frac{\langle u_i^D(\mathbf{k}) u_j^D(-\mathbf{k}) \rangle}{m_D} + \frac{\langle u_i^a(\mathbf{k}) u_j^a(-\mathbf{k}) \rangle}{m_a} \right.$$

$$\left. -2 \frac{\langle u_i^D(\mathbf{k}) u_j^a(-\mathbf{k}) \rangle}{(m_a m_D)^{1/2}} \cos\mathbf{k}\cdot\tau(\kappa) \right] .$$ (4.4b)

The temperature variation of Δ^- is also shown in Fig. 1. We should notice that the function Δ, which has been plotted in Ref. 26, corresponds to

$$\Delta_{ij}^+(\kappa) = \langle [u_i^D(\mathbf{n}) + u_i^a(\mathbf{n},\kappa)][u_j^D(\mathbf{n}) + u_j^a(\mathbf{n},\kappa)] \rangle$$ (4.5)

and not to Δ_{ij}^+, as has been erroneously stated. Both quantities differ by the sign of the mixed term $\langle u_i^D u_j^a \rangle$.

Concluding this section we may state that the mean-square displacements in the $Fm\,3m$ phase of the alkali cyanides are much larger than the corresponding quantities in the alkali halides[27] and show anomalous temperature behavior. Both features are due to the important T-R coupling.

V. NUMERICAL STUDY OF A MODEL

Here we want to illustrate the main theoretical results of the previous sections by carrying out a numerical study of KCN as a model system with T-R coupling. The procedure of such a study, irrespective of the particular system, contains several steps. First, one has to make an appropriate choice of the interaction potential [Eq. (2.3) of I] which determines the T-R coupling. Depending on the nature of the interactions, this potential can be the sum of several contributions: repulsive sterical hindrance, electrostatic multipole, van der Waals, etc. Secondly, one makes a choice of symmetry-adapted functions, taking

into account the symmetry of the molecule (or ion) and of the site. Thirdly, the elements of the bilinear interaction matrix $\bar{v}^{(1)}(\kappa)$ and the expansion coefficients of the rigid-lattice potential $v_{\lambda_0}^{(0)}$ have to be calculated for the various contributions to the potential. The terms which refer to a same representation Γ and angular momentum number l have to be added. As a result, one obtains the value of the coefficients α_4, α_6, A, B, D, etc. As a fourth step, one calculates the bilinear coupling matrices $\bar{v}^{(\Gamma,l)}$ in **k** space. Finally, one evaluates the various physical quantities using the general expressions of $\bar{X}(\mathbf{k})$, T_c, W^R, etc.

The potential of a CN^- ion in KCN interacting with one of the six nearest-neighbor K atoms in position $\tau(\kappa)$ is taken as a sum of three terms

$$V(\mathbf{n},\kappa) = V^{BM}(\mathbf{n},\kappa) + V^W(\mathbf{n},\kappa) + V^C(\mathbf{n},\kappa) . \tag{5.1}$$

Here, V^{BM} denotes the repulsive sterical hindrance potential of the form[8]

$$V^{BM}(\mathbf{n},\kappa) = \sum_\nu C_1^{(\nu)} e^{-C_2^{(\nu)} R(\mathbf{n},\nu,\kappa)} . \tag{5.2}$$

This is a sum of Born-Mayer potentials, where $R(\mathbf{n},\nu,\kappa)$ is the distance between the position of the νth nucleus in the molecule **n** and the position of the surrounding single atom κ:

$$R(\mathbf{n},\nu,\kappa) = |\mathbf{R}(\mathbf{n},\kappa) - \mathbf{R}(\mathbf{n},\mathbf{d}^\nu)| . \tag{5.3}$$

Here the nucleus of the single atom is located at

$$\mathbf{R}(\mathbf{n},\kappa) = \mathbf{X}(\mathbf{n}) + \tau(\kappa) + \mathbf{u}(\mathbf{n},\kappa) , \tag{5.4}$$

where $\mathbf{X}(\mathbf{n})$ is the equilibrium position of the center of mass of the nth molecule, $\tau(\kappa)$ the equilibrium position of the κth surrounding atom with respect to $\mathbf{X}(\mathbf{n})$, and $\mathbf{u}(\mathbf{n},\kappa)$ denotes the atomic displacement. For further details on the lattice structure of KCN, we refer to Sec. II of I. The position of the νth nucleus of the nth molecule is given by

$$R(\mathbf{n},\mathbf{d}^\nu) = \mathbf{X}(\mathbf{n}) + \mathbf{d}^\nu(\Omega(\mathbf{n})) + \mathbf{u}(\mathbf{n}) . \tag{5.5}$$

Here, $\mathbf{d}^\nu(\Omega)$ denotes the position of the νth nucleus in the molecule (ion) with respect to the molecular center of mass. The polar angles $(\Theta,\varphi) \equiv \Omega$ are defined in the crystal fixed system of axes. The length of the vector $\mathbf{d}^\nu$ is denoted by $d^{(\nu)}$. For the CN ion interacting with the six surrounding K atoms in KCN, we have taken the following values of the parameters:[28] position of C ($\nu=1$) nucleus with respect to the center of mass $d^{(1)} = -0.63$ Å; position of the N ($\nu=2$) nucleus, $d^{(2)} = +0.54$ Å; constants of the Born-Mayer interaction of the C atom with K, $C_1^{(1)} = 1.952 \times 10^7$ K, $C_2^{(1)} = 3.18$ Å^{-1}; interaction of N with K, $C_1^{(2)} = 2.05 \times 10^7$ K, $C_2^{(2)} = 3.28$ Å^{-1}.

The second term on the right-hand side of Eq. (5.1) stands for a van der Waals potential[29] of the form

$$V^W(\mathbf{n},\kappa) = -\sum_\nu B^{(\nu)}/R^6(\mathbf{n},\nu,\kappa) . \tag{5.6}$$

The constants have the value $B^{(1)} = 2.33 \times 10^5$ K/Å^6, $B^{(2)} = 1.91 \times 10^5$ K/Å^6.

The last term in Eq. (5.1) stands for the Coulomb interaction[14,15] of the electric charge distribution of the CN

ion, with the positive charge of the K atom,

$$V^C(\mathbf{n},\kappa) = \sum_\gamma q_\gamma q_\kappa / R(\mathbf{n},\gamma,\kappa) . \tag{5.7}$$

Here, $R(\mathbf{n},\gamma,\kappa)$ is of the form (5.3), where $\mathbf{d}^\nu(\Omega)$ has to be replaced by $\mathbf{r}^\gamma(\Omega)$, the position vector of the γth charge in the molecule. The charge distribution of the CN ion in the crystal is different from the charge distribution of the isolated ion in the gas phase.[30] The real charge distribution in the crystal is not very well known. Here we shall use a three-charge model,[31] with the following coordinates for the CN ion: $q^{(1)} = -1.0$ (in electronic charge units $|e|$), located at $r^{(1)} = -0.800$ Å (with respect to the center of mass of the CN ion); $q^{(2)} = +0.8$, $r^{(2)} = -0.363$ Å; $q^{(3)} = -0.8$, $r^{(3)} = +0.540$ Å.

Taking half the cubic lattice constant $a = 3.26$ Å, we have first calculated by numerical integration the rigid-lattice coefficients α_4 and α_6 in Eq. (2.2d). According to Eqs. (2.6a) and (2.8b) of I, we obtain

$$\alpha_{\lambda_0}^P = \sum_\kappa v_{\lambda_0}^{(0)P}(\kappa) , \quad \kappa = 1-6 , \tag{5.8a}$$

where

$$v_{\lambda_0}^{(0)}(\kappa) = \int d\Omega \, V^{(0)P}(\Omega,\kappa) Y_{\lambda_0}(\Omega) . \tag{5.8b}$$

Here, Y_{λ_0} stands for K_{41} or K_{61} of A_{1g} symmetry, corresponding to α_4^P and α_6^P, respectively. The index P indicates the nature of the potential: BM, W, or C. $V^{(0)P}$ stands for the corresponding rigid-lattice potential. The total values of α_{λ_0} are then obtained as

$$\alpha_{\lambda_0} = \sum_P \alpha_{\lambda_0}^P , \quad P \equiv \{BM, W, C\} . \tag{5.8c}$$

The total values α_4 and α_6 are given in Table I, last column.

The other coefficients which determine the translation-rotation coupling are obtained from Eq. (4.18) of I,

$$A^P = \int d\Omega \, V_1^{(1)P}(\Omega,\kappa=1) Y_{2,1}^e(\Omega) , \tag{5.9}$$

for the coupling of E_g symmetry, and from Eq. (4.20) of I, for the coupling of T_{2g} symmetry

$$B^P = \int d\Omega \, V_2^{(1)}(\Omega,\kappa=1) Y_{2,1}^f(\Omega) . \tag{5.10}$$

TABLE I. Values of coefficients calculated for three contributions to the potential. ($\sum_P$ stands for the sum of the potentials.)

P	BM	C	W	$\sum_P$
α_4	1452.0	-1138.1	-129.7	184.2
α_6	45.6	-25.1	-3.9	16.5
A	4457.1	-2699.8	-421.4	1335.9
B	1470.4	-3117.5	-176.9	-1824.0
D	-3738.2	-1531.1	401.0	-4868.3
E	385.3	765.5	-53.6	1097.2
F	1065.9	845.4	-97.8	1813.4
G	156.43	317.1	-15.7	457.8
H	0	0	0	0
L	-201.7	-409.2	20.3	-590.6

TABLE II. Values calculated by numerical integration for self-energies $C^s_{(\Gamma,l)}$ [units (K)].

Γ, l	$e,2$	$f,2$	$1u,1$	$1u,3$	$2u,3$
$C^s_{(\Gamma,l)}$	1536.2	928.1	2820	2228.6	429.0

Here, $V_i^{(1)P}$ denotes the first derivative with respect to X_i of the potential V^P. The total values of A and B enter the coupling matrix (3.8b) and (3.9b), respectively:

$$A = \sum_P A^P, \quad B = \sum_P B^P. \tag{5.11}$$

The values are given in Table I, last column.

In a similar way we calculate the values of D and E, making use, respectively, of Eqs. (4.14a) and (4.14b) of I. These coefficients couple the $l=1$ orientational fluctuations of T_{1u} symmetry to translations. We find with the present set of parameters the values quoted in Table I. We recall from I that the odd values of l account for the fact that the molecule is noncentrosymmetric. For the case of $l=3$, we have a first triplet of basis functions with T_{1u} symmetry. The corresponding coefficients F and G are obtained, respectively, from Eqs. (4.15a) and (4.15b) of I. Finally, we have a second triplet for the case $l=3$, of T_{2u} symmetry. The coefficients H and L are obtained from Eqs. (4.16a) and (4.16b), respectively, of I.

All coefficients for the potentials BM, C, and W are quoted in Table I, $\sum_P$ stands for the sum of the contributions from the three potentials. These values from the last column of Table I are used to calculate the coupling matrices $\overline{v}_\lambda(\mathbf{k})$, given by Eqs. (3.8b), (3.9b), (3.12b), and (3.14). The effective-lattice-mediated interaction follows then from Eq. (2.5). The dynamical matrix $M(\mathbf{k})$ is the one derived in Ref. 32 by using the shell model, without the translation-rotation terms which are not included in the bare dynamical matrix. The self-energies $\overline{C}^s_{(\Gamma,l)}$ are calculated by numerical integrations. The k-space summations were performed by a sampling technique in the irreducible $\frac{1}{48}$ portion of the Brillouin zone, in which the sampling mesh is increased near $\mathbf{k}=0$ in order to minimize the errors arising from the strong elastic anisotropy in the KCN crystal dynamics. Since the summand in this and other summations does *not* have the full cubic symmetry, transformation matrices are used to reduce the sum back to the irreducible zone. The method of setting up a mesh in $\mathbf{k}$ space is that of Gilat and Raubenheimer.[33] The mesh is shifted, as in Ref. 33, so that the term $\mathbf{k}=0$ is excluded. The exclusion of this term is justified in this case since it involves the shape of the sample[9] and cannot affect the results of the present calculation. Several tests of this program (e.g., summing over the entire Brillouin

zone rather than $\frac{1}{48}$, calculating separately for quantities that are related by symmetry, and changing mesh sizes) have been performed in order to ensure that the results are reliable. The values of $C^s_{(\Gamma,l)}$ are quoted in Table II [units (K)].

Next we calculate the self-energy contributions to the single-particle potential. The coefficients $\alpha^{s(\Gamma,l)}_{\lambda_0}$ are obtained from Sec. III. They are quoted in Table III. In the last column we have quoted again the sum, i.e., α_4^s and α_6^s. These values have to be combined, according to Eq. (3.16), with the corresponding quantities α_4 and α_6 from the rigid-lattice potential, which are quoted in the last column of Table I. We then obtain $\alpha_{41}=-295$ K; $\alpha_{61}=-165$ K as coefficients of the single-particle potential W^R, Eq. (3.15). The single-particle potential has been used for the evaluation of $P(\Omega)$ according to Eqs. (3.19a) and (3.19b). The projection of $P(\Omega)$ in the [110] plane of the crystal is shown in Fig. 2. Comparing this result with the corresponding Fig. 1 in Ref. 7, obtained from neutron-diffraction data, we see that our theoretical result is in more close agreement with the shape of $P(\Omega)$ for NaCN than for KCN. The present theory reproduces several important features which are common to the diffraction data[34] for both substances: the direction [110] corresponds to an absolute minimum in $P(\Omega)$ and its intensity decreases with decreasing temperature; on the other hand, the importance of the orientation in the [001] direction increases with decreasing T. The coefficient $\overline{\alpha}_{41}$, defined by Eq. (3.19), is found to increase slightly with decreasing T. This theoretical result is also in agreement with conclusions drawn from Raman scattering measurements[25] in NaCN and in KCN.

The transition temperature is obtained from Eqs. (2.12) and (2.13). We use the values of parameters: $B=-1824$ K/Å, $C^s_f=928.12$ K, α_{41} and α_{61} given by Eq. (5.11), $a=3.26$ Å, and $c^0_{44}=0.5\times10^{11}$ dyn/cm. Our present charge distribution gives a quadrupole moment $Q=0.8Q_0$, where $Q_0=-4.64(10^{-10}$ esu Å$^2)$ is the free-ion value. From the expressions of the direct interaction given in Ref. 15, we then deduce that J_f has the value 828.37 K. The single-particle expectation value y_f entering Eq. (2.12) is calculated by means of Eq. (2.13) as a function of temperature. We obtain a solution $T_c=255$ K, $y_f=0.066$. This value of T_c is too large in comparison with the experimental value ≈168 K in KCN.

TABLE III. Self-energy contributions to the single-particle potential [units (K)].

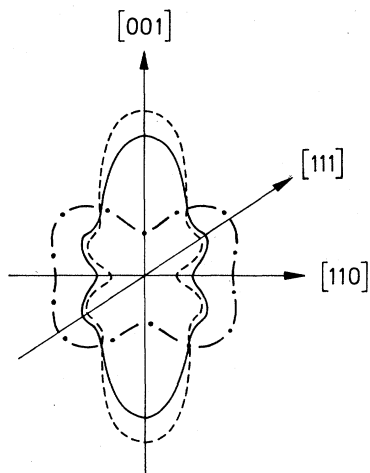|	Γ, l	$e,2$	$f,2$	$1u,3$	$2u,3$	Sum
$Q=0.8Q_0$	$\alpha_4^{s(\Gamma,l)}$	283.7	-171.7	392.8	-25.7	479.1
	$\alpha_6^{s(\Gamma,l)}$			278.0	-96.5	181.5
$Q=0.7Q_0$	$\alpha_4^{s(\Gamma,l)}$	433.3	-110.0	238.3	-12.9	548.7
	$\alpha_6^{s(\Gamma,l)}$			168.0	-50.31	117.69

FIG. 2. Single-particle orientational probability distribution function of CN^- in the [110] plane of the crystal. Full single-particle potential values $\alpha_{41} = -295.7$ K and $\alpha_{61} = -164.8$ K, temperature $T = 350$ K (solid line) and $T = 250$ K (dashed line). Dashed-dotted line corresponds to rigid-lattice part of single-particle potential, $\alpha_4 = 184.2$, $\alpha_6 = 16.5$, with $T = 250$ K. Potential parameters of KCN, $Q = 0.8Q_0$.

FIG. 3. Single-particle orientational distribution function in the [110] plane. Full single-particle potential values $\alpha_{41} = 23.8$ K, $\alpha_{61} = -88.5$ K, with $T = 200$ K. Potential parameters of KCN, $Q = 0.7Q_0$.

It is not a trivial matter to change the values of the potential parameters in order to obtain a better agreement for both the shape of $P(\Omega)$ and the value of T_c. Our knowledge about the parameters of the Born-Mayer potential has uncertainties of the order of 10%. More serious is the imprecise information about the electric charge distribution of the CN^- ion. It is generally accepted that the quadrupole moment of the CN ion in the solid is smaller than the free-ion value.[31] This question has been investigated for a fixed orientation of the CN ion in the crystal.[30] It is, however, certain that the charge distribution and therefore also the multipole moments of the molecular ion depend on the instantaneous orientation in an anisotropic crystalline environment. Since we are not able for the moment to describe this effect in a satisfactory way, we just show, as a matter of illustration, the effect of an orientation-independent change of the charge distribution. We take the previous three-charge-center model with the location of $q^{(1)} = -1.0$ at $r^{(1)} = 0.700$ Å and of $q^{(2)} = +0.8$ at $r^{(2)} = -0.237$ Å but leave $q^{(3)}$ and $r^{(3)}$ unchanged. All parameters of the Born-Mayer and van der Waals potential are the same as in the previous case. The new charge distribution has been chosen such that the dipole moment is unchanged but the quadrupole moment is reduced: $Q = 0.70Q_0$. The change of the hexadecapole moment which determines the strength of the Coulomb contribution to the single-particle potential leads to new values $\alpha_4^C = -749.7$ and $\alpha_6^C = -12.508$; the values of the other coupling parameters due to Coulomb interaction are $J_f = 644.5$, $A^c = -2385.1$, $B^C = -2754.0$, $F^C = 501.7$, $G^C = 188.15$, $H^C = 0$, and $L^C = -242.9$; (compare with column C of Table I). The values of $\alpha_{4,6}^{s(\Gamma, l)}$ are given in Table III. Using the other values BM and W from Table I, we obtain as a final result $\alpha_{41} = 23.8$ and $\alpha_{61} = -88.5$, and $T_c = 191$ K, with $y_f = 0.08$. The corresponding orientational probability distribution is shown in Fig. 3. It
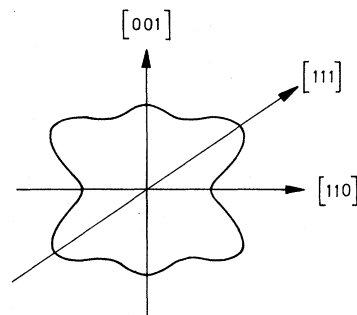
seems in better qualitative agreement with the neutron-diffraction results of Ref. 7 for KCN.

VI. CONCLUDING REMARKS

We have studied the collective and local static susceptibilities of an orientationally disordered crystal by paying special attention to molecular symmetry. In the alkali cyanides, this amounts to an extension of the previous analytical theory[8] by taking into account the noncentrosymmetric shape of the CN ion. The noncentrosymmetric shape affects in an important quantitative and qualitative way the single-particle properties. The self-interaction of the $l = 3$ orientational modes due to the reaction field of the lattice leads to a modification of both the K_4 and the K_6 contributions to the single-particle potential. We have calculated the single-particle, orientational distribution function $P(\Omega)$ in a deformable lattice. We obtain qualitative agreement with the overall shape of $P(\Omega)$ determined from neutron diffraction. In addition, the theoretical result shows the correct temperature dependence, namely, an increase in the orientational order in $\langle 100 \rangle$ directions with decreasing temperature.

The theory still has shortcomings. Recently we have shown that lattice anharmonicities have a quantitative influence on the transition temperature and on the single-particle potential.[35] In fact, an extension of the theory of T-R coupling in orientationally disordered crystals, using concepts from the theory of quantum crystals, has been proposed.[36] However, a complete quantitative calculation along those lines is not meaningful as long as we have such large uncertainties about the electronic charge distribution of the molecule.[31]

It is expected that the present theory for the calculation of the orientational probability density function in a deformable lattice is of general use and has a wide range of applications in the orientationally disordered phases of molecular crystals.

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APPENDIX

The relation between the results (2.8) and (2.11b) for the orientational and displacive susceptibility becomes most transparent by considering the free energy of the translation-rotation-coupled system. Starting from the potential (2.1) we obtain the following expression for the free energy:[37]

$$F = \sum_{\mathbf{k}} \{ \tfrac{1}{2} u_\rho^{e*}(\mathbf{k}) M_{\rho\sigma}(\mathbf{k}) u_\sigma^e(\mathbf{k}) + v_{\lambda\rho}(\mathbf{k}) Y_\lambda^{e*}(\mathbf{k}) u_\rho^e(\mathbf{k})$$

$$+ [(\chi_{\lambda\lambda}^0)^{-1} \delta_{\mu\lambda} + C_{\lambda\lambda}^s \delta_{\mu\lambda}$$

$$+ J_{\lambda\mu}(\mathbf{k})] Y_\lambda^{e*}(\mathbf{k}) Y_\mu^e(\mathbf{k}) \} . \qquad (A1)$$

Here we have only retained terms up to second order in the nonequilibrium expectation values $u_\rho^e(\mathbf{k})$ and $Y_\lambda^e(\mathbf{k})$. For a given configuration of orientations $\{ Y_\lambda^e(\mathbf{k}) \}$, we minimize F with respect to the displacements $u^e(\mathbf{k})$ and obtain

$$u_\rho^e(\mathbf{k}) = -(M^{-1}(\mathbf{k}))_{\rho\sigma} v_{\sigma\lambda}^\tau(-\mathbf{k}) Y_\lambda^e(\mathbf{k}) . \qquad (A2)$$

The corresponding expression for F then reads

$$F[Y^e(\mathbf{k})] = \tfrac{1}{2} [(\chi_{\lambda\lambda}^0)^{-1} \delta_{\lambda\mu} + C^s \delta_{\lambda\mu} + J_{\lambda\mu}(\mathbf{k})$$

$$- C_{\lambda\mu}(\mathbf{k})] Y_\lambda^{e*}(\mathbf{k}) Y_\mu^e(\mathbf{k}) , \qquad (A3)$$

where $C(\mathbf{k})$ is given by Eq. (2.5). We see that the sum of terms within square brackets is equal to the inverse of the right-hand-side (rhs) terms in Eq. (2.8). On the other hand, using a well-known procedure in thermodynamics,[38] we start from expression (A3) to calculate the orientation-orientation susceptibility and obtain Eq. (2.8).

The displacement-displacement susceptibility (2.11a) is obtained in a similar way. For a given configuration of displacements $\{ u_\rho^e(\mathbf{k}) \}$, we minimize F, Eq. (A1), with respect to the orientations $Y_\lambda^e(\mathbf{k})$ and obtain

$$Y_\lambda^e(\mathbf{k}) = -((\overline{\chi}^0)^{-1} + \overline{C}^s + \overline{J}(\mathbf{k}))^{-1}_{\lambda\mu} v_{\mu\rho}(\mathbf{k}) u_\rho^e(\mathbf{k}) . \qquad (A4)$$

The corresponding expression for F now reads

$$F[u^e(k)] = \tfrac{1}{2} [M_{\rho\sigma}(\mathbf{k}) - v_{\rho\lambda}^\tau(-\mathbf{k})((\overline{\chi}^0)^{-1} + \overline{C}^s + \overline{J}(\mathbf{k}))^{-1}_{\lambda\mu}$$

$$\times v_{\mu\sigma}(\mathbf{k})] u_\rho^{e*}(\mathbf{k}) u_\sigma^e(\mathbf{k}) . \qquad (A5)$$

Calculating the displacement-displacement susceptibility, we obtain expression (2.11b). In fact, the sum of terms within square brackets on the rhs of Eq. (A5) corresponds to the inverse of the rhs of of Eq. (2.11b). The present derivation leads to the conclusion that the orientational susceptibility $\overline{X}$ and the displacement susceptibility $\overline{D}^{-1}$ can be obtained from each other by making the substitutions

$$\overline{M}(\mathbf{k}) \leftrightarrow ((\overline{\chi}^0)^{-1} + \overline{C}^s + \overline{J}(k)) , \qquad (A6a)$$

$$\overline{v}(\mathbf{k}) \leftrightarrow \overline{v}^\tau(-\mathbf{k}) . \qquad (A6b)$$

We have this same formal symmetry between Eqs. (A3) and (A5).

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