

Molecular symmetry and translation-rotation coupling in orientationally disordered crystals

K. H. Michel

Department of Physics, University of Antwerp (Universitaire Instelling Antwerpen), B-2610 Wilrijk, Belgium

J. M. Rowe

Center of Materials Science, National Bureau of Standards, Gaithersburg, Maryland 20899

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The theory of coupling between rotational and translational degrees of freedom in orientationally disordered crystals is studied in detail, with careful attention to the requirements of symmetry. An essential feature of this coupling is the presence or absence of a center of symmetry in the molecule or molecular ion, which determines the nature of the coupling to optic- and acoustic-phonon modes. The present analysis is relevant for the understanding of ferroelastic phase transitions, of incommensurate transitions in insulators, and of structural transitions and related properties in synthetic organic conductors.

I. INTRODUCTION

Orientationally disordered crystals are characterized by large-amplitude orientational motions of molecules or molecular ions. In many cases the rotational motion of the molecules, taken as rigid bodies, is coupled to center-of-mass displacements of isolated atoms or neighboring molecules. This coupling is most apparent at phase transitions in which the formation of an orientationally ordered state is accompanied by a change of lattice structure. Often this change of lattice structure is preceded by anomalous properties in the high-temperature symmetric phase. As an example, we mention the softening of the shear elastic constants with decreasing temperature in the high-temperature cubic phase of the alkali cyanides¹ and the corresponding softening of transverse acoustic phonons as found by inelastic neutron scattering.² In cases in which the molecules have a dipole moment, orientational order may result in a ferroelectric or an antiferroelectric phase. As examples, we mention the antiferroelectric phase of KCN (Ref. 3) and the ferroelectric phases of NaNO_2 (Ref. 4) and $\text{SC}(\text{NH})_2$ (Ref. 5). The last two substances are of special interest, since they also exhibit incommensurate phases,^{6,7} and the question then arises as to whether translation-rotation (T-R) coupling is relevant at incommensurate phase transitions in insulators. This problem is of large experimental^{8,9} and theoretical¹⁰⁻¹² interest. The phenomenon of T-R coupling is also likely to be of relevance in electronic and structural phase transitions in quasi-one-dimensional synthetic organic conductors¹³ of type $(\text{TMTSF})_2X$, where X is either a ClO_4 (non-centrosymmetric) or a PF_6 (centrosymmetric) molecular ion.

In recent years, molecular dynamics calculations have been carried out for both three-¹⁴ and two-¹⁵ dimensional models of the alkali cyanides and for NaNO_2 .^{16,17} These calculations provide important information about the microscopic potentials and mechanisms which are responsible for the T-R coupling.

In the present paper, we perform a systematic study of translation-rotation coupling, paying special attention to whether or not the molecule is centrosymmetric. For that purpose, it is sufficient to consider linear molecules, the main technical simplification being that the orientation is described by two polar angles (Θ, φ) instead of three Euler angles. This simplification is not fundamental as far as the symmetry properties of the T-R coupling is concerned. It is, however, essential to assume that all molecules are located at centers of symmetry of the lattice in the disordered phase. Again, for technical transparency, we assume that the lattice structure is cubic, a nonessential restriction.

In Sec. II, we give a formulation of translation-rotation coupling, paying special attention to the molecular symmetry. A bilinear T-R coupling leads to an effective-lattice-mediated interaction between rotating molecules and to a modification of the single-particle potential (Sec. III). In Sec. IV, we study the nature of the coupling by separating the translations into acoustic and optic phonons. Finally, we give an extension of the theory to nonlinear molecules.

II. TRANSLATION-ROTATION COUPLING

As a model we consider a crystal which is composed of linear molecules located at centers of symmetry in the lattice. The linear molecules have orientational degrees of freedom determined by two polar angles $(\Theta, \varphi) \equiv \Omega$. The molecules are surrounded by nearest-neighbors individual atoms. (In crystals where the nearest neighbors themselves are molecules, we would take them in spherical approximation and that would bring us back to the situation where each molecule is a center of symmetry and surrounded by spherical objects.) To be specific, we consider the high-temperature crystalline structure³ of KCN (symmetry $Fm\bar{3}m$). The center-of-mass positions of the molecule (mass m_D) form a regular lattice with equilibrium position $\mathbf{X}(\mathbf{n})$. Here the triplet of integers $\mathbf{n} \equiv (n_1, n_2, n_3)$ labels the molecules, or equivalently, the unit cells. Each

molecule \mathbf{n} is surrounded by six alkali-metal atoms (mass m_a) in octahedral positions:

$$\mathbf{X}(\mathbf{n}, \tau) = \mathbf{X}(\mathbf{n}) + \tau(\kappa), \quad \kappa = 1, 2, \dots, 6. \quad (2.1)$$

Here, $\tau(1) = (a, 0, 0)$, $\tau(2) = (0, a, 0)$, $\tau(3) = (0, 0, a)$, $\tau(4) = (-a, 0, 0)$, $\tau(5) = (0, -a, 0)$, and $\tau(6) = (0, 0, -a)$, where a is half the cubic lattice constant. The translational degrees of freedom are center-of-mass displacements $\mathbf{u}(\mathbf{n})$ of the molecules and $\mathbf{u}(\mathbf{n}, \kappa)$ of the individual atoms. The actual positions of the n th molecule and of the n, κ th atom are then, respectively, given by

$$\mathbf{R}(\mathbf{n}) = \mathbf{X}(\mathbf{n}) + \mathbf{u}(\mathbf{n}), \quad (2.2a)$$

$$\mathbf{R}(\mathbf{n}, \kappa) = \mathbf{X}(\mathbf{n}, \kappa) + \mathbf{u}(\mathbf{n}, \kappa). \quad (2.2b)$$

The interaction potential of the n th molecule with the nearest-neighbor atom κ is of the general form

$$V(\mathbf{n}, \kappa) = V(\mathbf{R}(\mathbf{n}) - \mathbf{R}(\mathbf{n}, \kappa), \Omega). \quad (2.3)$$

We now follow and extend the method of Ref. 18. Expanding the right-hand side in terms of lattice displacements, we write

$$\begin{aligned} V(\mathbf{n}, \kappa) = & V^{(0)}(\mathbf{n}, \kappa) + \sum_i V_i^{(1)}(\mathbf{n}, \kappa) [u_i(\mathbf{n}) - u_i(\mathbf{n}, \kappa)] \\ & + \frac{1}{2} \sum_{i,j} V_{ij}^{(2)}(\mathbf{n}, \kappa) [u_i(\mathbf{n}) - u_i(\mathbf{n}, \kappa)] \\ & \times [u_j(\mathbf{n}) - u_j(\mathbf{n}, \kappa)] + \dots \end{aligned} \quad (2.4)$$

For the present, we shall restrict ourselves to first- and second-order terms in the lattice displacements. Higher-order terms can be classified into odd and even members and will have symmetry properties similar to $V_i^{(1)}$ and $V_{ij}^{(2)}$, respectively. The expansion coefficients $V_i^{(1)}$ and $V_{ij}^{(2)}$ are the first and second derivatives of the potential with respect to lattice displacements taken at $\mathbf{u} = \mathbf{0}$. $V^{(0)}$ is the rigid-lattice potential. These coefficients still depend on the molecular orientation. We therefore expand them in terms of symmetry-adapted functions,¹⁹ which are the most appropriate coordinates for the description of molecular orientations in disordered phases,^{20,21} since they take into account the symmetry of both the molecule and the lattice site. We therefore write

$$V^{(0)}(\mathbf{n}, \kappa) = \sum_{\lambda_0} v_{\lambda_0}^{(0)}(\kappa) Y_{\lambda_0}(\Omega(\mathbf{n})), \quad (2.5a)$$

$$V_i^{(1)}(\mathbf{n}, \kappa) = \sum_{\lambda} v_{\lambda i}^{(1)}(\kappa) Y_{\lambda}(\Omega(\mathbf{n})), \quad (2.5b)$$

$$V_{ij}^{(2)}(\mathbf{n}, \kappa) = \sum_{\lambda} v_{\lambda ij}^{(2)}(\kappa) Y_{\lambda}(\Omega(\mathbf{n})). \quad (2.5c)$$

Since the rotator functions Y_{λ} form a complete orthonormal set, we have

$$v_{\lambda_0}^{(0)}(\kappa) = \int d\Omega(\mathbf{n}) V^{(0)}(\mathbf{n}, \kappa) Y_{\lambda_0}(\Omega(\mathbf{n})), \quad (2.6a)$$

$$v_{\lambda i}^{(1)}(\kappa) = \int d\Omega(\mathbf{n}) V_i^{(1)}(\mathbf{n}, \kappa) Y_{\lambda}(\Omega(\mathbf{n})), \quad (2.6b)$$

$$v_{\lambda ij}^{(2)}(\kappa) = \int d\Omega(\mathbf{n}) V_{ij}^{(2)}(\mathbf{n}, \kappa) Y_{\lambda}(\Omega(\mathbf{n})). \quad (2.6c)$$

The index λ stands for $\{l, \Gamma, \alpha\}$, where l is the angular

momentum quantum number, Γ labels the irreducible representations of the molecular lattice site, and α labels the columns or rows of the irreducible representations.¹⁹ The lowest allowed value of l has to contain the unit representation of the molecular group M .^{20,21}

Summing over all molecules and atoms in the crystal, we write for the total potential

$$V = V^R + V^{TR} + V^{TTR} + \dots \quad (2.7)$$

Here,

$$V^R = \sum_{\mathbf{n}} \sum_{\lambda_0} \alpha_{\lambda_0} Y_{\lambda_0}(\Omega(\mathbf{n})) \quad (2.8a)$$

with

$$\alpha_{\lambda_0} \equiv \sum_{\kappa} v_{\lambda_0}^{(0)}(\kappa) \quad (2.8b)$$

a sum of single-particle potentials. Only those values λ of λ_0 occur which belong to the unit representation Γ_0 of the molecular site group, i.e., here the cubic group. Therefore, Y_{λ_0} corresponds to the cubic harmonics²² $K_{41}(\Omega)$, $K_{61}(\Omega)$, etc., of A_{1g} symmetry.

The T-R coupling terms in Eq. (2.7) are

$$V^{TR} = \sum_{\mathbf{n}} \sum_{\kappa} \sum_{\lambda, i} v_{\lambda i}^{(1)}(\kappa) Y_{\lambda}(\mathbf{n}) [u_i(\mathbf{n}) - u_i(\mathbf{n}, \kappa)], \quad (2.9)$$

$$\begin{aligned} V^{TTR} = & \frac{1}{2} \sum_{\mathbf{n}} \sum_{\kappa} \sum_{\lambda, i, j} v_{\lambda ij}^{(2)}(\kappa) Y_{\lambda}(\mathbf{n}) [u_i(\mathbf{n}) - u_i(\mathbf{n}, \kappa)] \\ & \times [u_j(\mathbf{n}) - u_j(\mathbf{n}, \kappa)]. \end{aligned} \quad (2.10)$$

Here, $Y_{\lambda}(\mathbf{n})$ stands for $Y_{\lambda}(\Omega(\mathbf{n}))$. The functions $Y_{\lambda}(\mathbf{n})$ need not belong to the unit representation of the site group.

If one approximates the molecule by a symmetric dumbbell,¹⁸ then only functions with l even are relevant, and the lowest order are those with $l=2$: a doublet of $\Gamma = E_g \equiv e$ symmetry (notation $Y_{l, \alpha}^e$)

$$Y_{2,1}^e = Y_2^0, \quad Y_{2,2}^e = Y_2^{2,c} \quad (2.11)$$

and a triplet of $T_{2g} \equiv f$ symmetry

$$Y_{2,1}^f = Y_2^{2,s}, \quad Y_{2,2}^f = Y_2^{1,c}, \quad Y_{2,3}^f = Y_2^{1,s}. \quad (2.12)$$

Here we use the notation of Ref. 19,

$$Y_l^{m,c} = (Y_l^m + Y_l^{-m})/\sqrt{2}, \quad (2.13a)$$

$$Y_l^{m,s} = -i(Y_l^m - Y_l^{-m})/\sqrt{2}. \quad (2.13b)$$

In the Appendix, the functions $Y_{2,\alpha}^e$, $\alpha=1,2$, and $Y_{2,\alpha}^f$, $\alpha=1-3$, are given in terms of Cartesian direction cosines.

If the molecule is not centrosymmetric, functions with l odd are also relevant, and the lowest-order terms are those with $l=1$: a triplet of $T_{1u} \equiv u$ symmetry¹⁹

$$Y_{1,1}^u = Y_1^{1,c}, \quad Y_{1,2}^u = Y_1^{1,s}, \quad Y_{1,3}^u = Y_1^0. \quad (2.14)$$

The expressions in Cartesian coordinates are again given in the Appendix. We will also need, for $l=3$, a triplet of $T_{1u} \equiv 1u$ symmetry¹⁹

$$Y_{3,1}^{1u} = \left(\frac{3}{8}\right)^{1/2} Y_3^{1,c} - \left(\frac{5}{8}\right)^{1/2} Y_3^{3,c}, \quad (2.15)$$

$$Y_{3,2}^{1u} = \left(\frac{3}{8}\right)^{1/2} Y_3^{1,s} + \left(\frac{5}{8}\right)^{1/2} Y_3^{3,s}, \quad Y_{3,3}^{1u} = -Y_3^0$$

and a second triplet of $T_{2u} \equiv 2u$ symmetry¹⁹

$$Y_{3,1}^{2u} = -\left(\frac{5}{8}\right)^{1/2} Y_3^{1,c} - \left(\frac{3}{8}\right)^{1/2} Y_3^{3,c}, \quad (2.16)$$

$$Y_{3,2}^{2u} = \left(\frac{5}{8}\right)^{1/2} Y_3^{1,s} - \left(\frac{3}{8}\right)^{1/2} Y_3^{3,s}, \quad Y_{3,3}^{2u} = Y_3^{2,c}.$$

Finally, there is a singlet of symmetry A_{2u}

$$Y_{3,1}^A = Y_3^{2,s}. \quad (2.17)$$

Since the functions $Y_{l,\alpha}^\Gamma$ are linear combinations of spherical harmonics, they transform under inversion of the molecule as

$$Y_{l,\alpha}^\Gamma(\Theta, \varphi) = (-1)^l Y_{l,\alpha}^\Gamma(\pi - \Theta, \varphi + \pi). \quad (2.18)$$

In case of a centrosymmetric molecule, the quantities $V^{(1)}$ and $V^{(2)}$, Eqs. (2.5b) and (2.5c), are invariant with respect to inversion of the molecule, and therefore only the coefficients $v^{(1)}$ and $v^{(2)}$ with l even will have nonzero matrix elements. If the molecule is located at a center of symmetry in the lattice, there corresponds to each neighbor atom at $\tau(\kappa)$ of the molecule, a neighbor atom at $\tau(\kappa')$, such that

$$\tau(\kappa) = -\tau(\kappa'). \quad (2.19)$$

Since $V_i^{(1)}(\mathbf{n}, \kappa)$ is a first-rank tensor, it changes sign under inversion. Correspondingly, for l even, the coefficients $v_{\lambda i}^{(1)}$ in Eq. (2.5b) have to satisfy¹⁸

$$v_{\lambda i}^{(1)}(\kappa) = -v_{\lambda i}^{(1)}(\kappa'), \quad l \text{ even}. \quad (2.20)$$

On the other hand, the second-rank tensor $V_{ij}^{(2)}(\mathbf{n}, \kappa)$ is invariant under inversion and therefore

$$v_{\lambda ij}^{(2)}(\kappa) = v_{\lambda ij}^{(2)}(\kappa'), \quad l \text{ even}. \quad (2.21)$$

If the molecule is noncentrosymmetric, functions $Y_{l,\alpha}^\Gamma$ with l odd are relevant, and one then has the properties

$$v_{\lambda i}^{(1)}(\kappa) = v_{\lambda i}^{(1)}(\kappa'), \quad l \text{ odd}, \quad (2.20')$$

$$v_{\lambda ij}^{(2)}(\kappa) = -v_{\lambda ij}^{(2)}(\kappa'), \quad l \text{ odd}, \quad (2.21')$$

where the positions κ and κ' are related by Eq. (2.19). The properties just obtained determine to a large extent the nature of the translation-rotation coupling. The explicit form of the matrices $v_{\lambda i}^{(1)}(\kappa)$ is given in the Appendix for various sets of symmetry-adapted functions.

It is useful to define Fourier transforms

$$u_i(\mathbf{n}, \kappa) = \frac{1}{(Nm_a)^{1/2}} \sum_{\mathbf{k}} u_i^a(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{X}(\mathbf{n}, \kappa)}, \quad (2.22a)$$

$$u_i(\mathbf{n}) = \frac{1}{(Nm_D)^{1/2}} \sum_{\mathbf{k}} u_i^D(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{X}(\mathbf{n})}, \quad (2.22b)$$

and

$$Y_\lambda(\Omega(\mathbf{n})) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} Y_\lambda(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{X}(\mathbf{n})}. \quad (2.23)$$

Here, N is the number of primitive cells in the lattice. Defining a total displacement vector as a six-component

column vector (τ denotes transposed), we write

$$(u_\rho(\mathbf{k}))^\tau = (u_1^D, u_2^D, u_3^D, u_1^a, u_2^a, u_3^a). \quad (2.24)$$

Similarly, for a given l and representation Γ , we define a row vector $Y_{l,\alpha}^\Gamma$ with α_s elements where α_s is the dimension of the representation Γ . Then we rewrite expression (2.9) in Fourier space as

$$V^{\text{TR}} = \sum_{\mathbf{k}} v_{\alpha\rho}^{(1)\Gamma, l}(\mathbf{k}) Y_{l,\alpha}^\Gamma(-\mathbf{k}) u_\rho(\mathbf{k}), \quad (2.25)$$

where the summation is understood over ρ, l and over Γ and α . For a fixed l, Γ and α , $v_{\alpha\rho}^{(1)\Gamma, l}$ has the six elements

$$(v_{\alpha\rho}^{(1)\Gamma, l}(\mathbf{k})) = \left[\begin{array}{c} \frac{v_{\lambda 1}^{(1)}(\mathbf{0})}{(m_D)^{1/2}}, \frac{v_{\lambda 2}^{(1)}(\mathbf{0})}{(m_D)^{1/2}}, \frac{v_{\lambda 3}^{(1)}(\mathbf{0})}{(m_D)^{1/2}}, \\ -\frac{v_{\lambda 1}^{(1)}(\mathbf{k})}{(m_a)^{1/2}}, -\frac{v_{\lambda 2}^{(1)}(\mathbf{k})}{(m_a)^{1/2}}, -\frac{v_{\lambda 3}^{(1)}(\mathbf{k})}{(m_a)^{1/2}} \end{array} \right]. \quad (2.26)$$

Here $(\mathbf{0})$ stands for $\mathbf{k} = \mathbf{0}$ and

$$v_{\lambda i}^{(1)}(\mathbf{k}) = \sum_{\kappa} v_{\lambda i}^{(1)}(\kappa) e^{i\mathbf{k} \cdot \tau(\kappa)}, \quad (2.27)$$

where the elements $v_{\lambda i}^{(1)}(\kappa)$ satisfy the symmetry property (2.20) and (2.20').

Therefore, we have

$$v_{\lambda i}^{(1)}(\mathbf{k}) = i \sum_{\kappa} v_{\lambda i}^{(1)}(\kappa) \sin[\mathbf{k} \cdot \tau(\kappa)], \quad l \text{ even} \quad (2.28)$$

and $v_{\lambda i}^{(1)}(\mathbf{k} = \mathbf{0}) = 0$. On the other hand, we obtain from property (2.20') that

$$v_{\lambda i}^{(1)}(\mathbf{k}) = \sum_{\kappa} v_{\lambda i}^{(1)}(\kappa) \cos[\mathbf{k} \cdot \tau(\kappa)], \quad l \text{ odd}. \quad (2.29)$$

The expressions (2.28) and (2.29) are the essential elements in the bilinear translation-rotation coupling.

The cubic interaction term V^{TTR} is treated in a very similar way. In Fourier space we obtain

$$V^{\text{TTR}} = \frac{1}{2} \sum_{\mathbf{k}} \sum_{\mathbf{p}} v_{\alpha\rho\sigma}^{(2)\Gamma, l}(\mathbf{k}, \mathbf{p}) Y_{l,\alpha}^\Gamma(-\mathbf{k} - \mathbf{p}) u_\rho(\mathbf{k}) u_\sigma(\mathbf{p}), \quad (2.30)$$

where for fixed (Γ, l, α) we have a 6×6 matrix

$$(v_{\alpha\rho\sigma}^{(2)\Gamma, l}(\mathbf{k}, \mathbf{p})) = \frac{1}{\sqrt{N}} \begin{bmatrix} (v^I) & (v^{\text{III}}) \\ (v^{\text{II}}) & (v^{\text{IV}}) \end{bmatrix}, \quad (2.31a)$$

where (v^I) , (v^{II}) , (v^{III}) , and (v^{IV}) are 3×3 submatrices:

$$(v^I) = \frac{1}{m_D} (v_{\lambda ij}^{(2)}(\mathbf{0}, \mathbf{0})), \quad (v^{\text{II}}) = \frac{-1}{(m_D m_A)^{1/2}} (v_{\lambda ij}^{(2)}(\mathbf{k}, \mathbf{0})),$$

$$(v^{\text{III}}) = -\frac{1}{(m_A, m_D)^{1/2}} (v_{\lambda ij}^{(2)}(\mathbf{p}, \mathbf{0})), \quad (2.31b)$$

$$(v^{\text{IV}}) = \frac{1}{m_a} (v_{\lambda ij}^{(2)}(\mathbf{k}, \mathbf{p})),$$

with

$$v_{\lambda ij}^{(2)}(\mathbf{k}, \mathbf{p}) = \sum_{\kappa} v_{\lambda ij}^{(2)}(\kappa) e^{i\tau(\kappa) \cdot (\mathbf{p} + \mathbf{k})}, \quad (2.32)$$

and $\lambda = (\Gamma, l, \alpha)$ fixed. The symmetry properties (2.21) and (2.21') imply

$$v_{\lambda ij}^{(2)}(\mathbf{k}, \mathbf{p}) = \begin{cases} \sum_{\kappa} v_{\lambda ij}^{(2)}(\kappa) \cos[(\mathbf{k} + \mathbf{p}) \cdot \boldsymbol{\tau}(\kappa)], & l \text{ even,} \\ i \sum_{\kappa} v_{\lambda ij}^{(2)}(\kappa) \sin[(\mathbf{k} + \mathbf{p}) \cdot \boldsymbol{\tau}(\kappa)], & l \text{ odd.} \end{cases} \quad (2.33a)$$

The coupling V^{TTR} is essential for the study of dissipative processes such as orientational relaxation and phonon viscosity.²³

III. LATTICE-MEDIATED INTERACTIONS

The bilinear interaction is essential for the study of static properties near the orientational phase transition. Assuming that the cubic terms V^{TTR} can be treated as a perturbation, we consider here only the bilinear terms. Adding to the potential (2.7) a translation-translation interaction V^{TT} and a direct rotation-rotation interaction V^{RR} , we obtain the potential

$$V = V^{\text{TT}} + V^{\text{TR}} + V^{\text{RR}} + V^{\text{R}}. \quad (3.1)$$

Here the harmonic lattice part reads

$$V^{\text{TT}} = \frac{1}{2} \sum_{\mathbf{k}} u_{\rho}(-\mathbf{k}) M_{\rho\sigma}(\mathbf{k}) u_{\sigma}(\mathbf{k}), \quad (3.2)$$

where $M(\mathbf{k})$ is the bare dynamical matrix.²⁴ The direct orientational interaction is of the form

$$V^{\text{RR}} = \frac{1}{2} \sum_{\mathbf{k}} J_{\lambda\lambda'}(\mathbf{k}) Y_{\lambda}(\mathbf{k}) Y_{\lambda'}(-\mathbf{k}). \quad (3.3)$$

The coefficients $J_{\lambda\lambda'}$ represent an electrostatic multipole interaction. In the alkali cyanides, the quadrupole-quadrupole coupling is relevant.^{14,25}

In Eq. (3.1), V^{TR} and V^{R} are given by Eqs. (2.25) and (2.8a), respectively. The total potential (3.1) is a functional of both orientations and displacements. Minimizing $V[u, Y]$ for a given configuration $\{Y(\mathbf{k})\}$ with respect to $u(\mathbf{k})$, we obtain

$$u_{\rho}(\mathbf{k}) = -(M^{-1}(\mathbf{k}))_{\rho\sigma} v_{\lambda\sigma}^{\tau}(-\mathbf{k}) Y_{\lambda}(\mathbf{k}). \quad (3.4)$$

Substitution into Eq. (3.1) yields

$$V = V^{\text{eff}} + V^{\text{RR}} + V^{\text{R}}, \quad (3.5)$$

with the effective rotational interaction

$$V^{\text{eff}} = -\frac{1}{2} \sum_{\mathbf{k}} C_{\lambda\lambda'}(\mathbf{k}) Y_{\lambda'}(\mathbf{k}) Y_{\lambda}(-\mathbf{k}). \quad (3.6a)$$

Here,

$$C_{\lambda\lambda'}(\mathbf{k}) = v_{\lambda\rho}(\mathbf{k}) (M^{-1}(\mathbf{k}))_{\rho\sigma} v_{\lambda'\sigma}^{\tau}(-\mathbf{k}) \quad (3.6b)$$

denotes the lattice-mediated orientational interaction. In Ref. 18 this result was obtained for the $l=2$, E_g , and T_{2g} rotational modes interacting with acoustic phonons. We rewrite V^{eff} in real space as

$$V^{\text{eff}} = -\frac{1}{2} \sum_{\mathbf{n}, \mathbf{n}'} Y_{\lambda}(\mathbf{n}) \tilde{C}_{\lambda\lambda'}(\mathbf{n} - \mathbf{n}') Y_{\lambda'}(\mathbf{n}'), \quad (3.7)$$

where

$$\tilde{C}_{\lambda\lambda'}(\mathbf{n} - \mathbf{n}') = \frac{1}{N} \sum_{\mathbf{k}} C_{\lambda\lambda'}(\mathbf{k}) e^{i\mathbf{k} \cdot [\mathbf{X}(\mathbf{n}) - \mathbf{X}(\mathbf{n}')]}. \quad (3.8)$$

Separating out from Eq. (3.7) the self-interaction $\mathbf{n} = \mathbf{n}'$, we obtain

$$V^{\text{eff}} = W^{\text{RR}} - \frac{1}{2} C_{\lambda\lambda}^s \sum_{\mathbf{k}} Y_{\lambda}(\mathbf{k}) Y_{\lambda}(-\mathbf{k}), \quad (3.9)$$

where the effective-lattice-mediated coupling reads

$$W^{\text{RR}} = -\frac{1}{2} \sum_{\mathbf{k}} [C_{\lambda\lambda'}(\mathbf{k}) - C_{\lambda\lambda}^s \delta_{\lambda\lambda'}] Y_{\lambda'}(\mathbf{k}) Y_{\lambda}(-\mathbf{k}), \quad (3.10a)$$

with

$$C_{\lambda\lambda}^s = \tilde{C}_{\lambda\lambda}(\mathbf{n} = \mathbf{n}') = \frac{1}{N} \sum_{\mathbf{k}} C_{\lambda\lambda}(\mathbf{k}). \quad (3.10b)$$

The separation of the self-interaction $C_{\lambda\lambda}^s$ from the intermolecular potential is necessary since the collective ordering is determined from the interaction at different sites $\mathbf{n} \neq \mathbf{n}'$. This procedure is characteristic for lattice-mediated interactions and was first proposed by Kanamori²⁶ in the theory of collective Jahn-Teller effects. (See also Ref. 27.) The separation of the self-energy part leads to a decrease of the transition temperature. The physical motivation of this procedure is analogous to the subtraction of self-energy effects due to the Onsager reaction field.²⁸ We should notice, however, that in the theory of Brout and Thomas,²⁹ the reaction field is obtained as a correction to primitive molecular-field theory if one takes into account the self-interaction due to fluctuations. The latter theory therefore applies already in the case where the original potential contains only interactions between different sites. The same remarks hold for the correlated effective-field theory of Lines and Glass.³⁰

Beside a modification of the effective interaction, the separation of the self-energy leads to a modification of the single-particle potential. Following Ref. 31, we add the last term on the right-hand side of Eq. (3.9) to the single-particle potential V^{R} and rewrite Eq. (3.5) in the form

$$V = W^{\text{RR}} + V^{\text{RR}} + \sum_{\mathbf{n}} W^{\text{R}}(\mathbf{n}), \quad (3.11)$$

where W^{R} is now the redefined single-particle potential [compare Eq. (2.8a)]:

$$W^{\text{R}}(\mathbf{n}) = \sum_{\lambda_0} \alpha_{\lambda_0} Y_{\lambda_0}(\mathbf{n}) - \frac{1}{2} \sum_{\lambda} C_{\lambda\lambda}^s [Y_{\lambda}(\mathbf{n})]^2. \quad (3.12)$$

The last term on the right-hand side of this expression can be rewritten as

$$V^s(\Omega) = -\frac{1}{2} \sum_{l, \Gamma} C_{l, \Gamma}^s \sum_{\alpha} [Y_{l, \alpha}^{\Gamma}(\Omega)]^2. \quad (3.13)$$

Here we use the fact that all members α of $C_{l, \Gamma, \alpha}^s$ (which for fixed l, α refers to the columns of a given representation) are equal. The sum over α in Eq. (3.13) is then carried out by using the generalized Unsöld theorem³²

$$\sum_{\alpha} [Y_{l, \alpha}^{\Gamma}(\Omega)]^2 = \sum_{\lambda_0} \beta_{\lambda_0}^{(\Gamma, l)} Y_{\lambda_0}, \quad (3.14)$$

where $\lambda_0 \equiv (\Gamma_0, l_0, 1)$ and Γ_0 is the unit representation of the molecular site group.

IV. ACOUSTIC AND OPTIC PHONONS

The symmetry properties determine the interaction of lattice displacements with molecular rotations. It is useful to perform a separation of lattice displacements into acoustic and optic phonons. We define three distinguished vectors ($i = 1, 2, 3$) of acoustic displacements in the six-dimensional space of lattice displacements [compare expression (2.24)]:

$$\mathbf{e}^{(i)} = [\delta_{ij}(m_D/m)^{1/2}, \delta_{ij}(m_a/m)], \quad j = 1, 2, 3. \quad (4.1)$$

Here, $m = m_D + m_a$ is the total mass per unit cell. Acoustic displacements are defined by

$$s_i(\mathbf{k}) = \sum_{\rho} e^{(i)}(\rho) u_{\rho}(\mathbf{k}). \quad (4.2)$$

In the new basis the bilinear coupling matrix becomes

$$\hat{v}_{\lambda i}^{(1)}(\mathbf{k}) = \sum_{\rho} e^{(i)}(\rho) v_{\lambda \rho}^{(1)}(\mathbf{k}), \quad (4.3)$$

where $v_{\lambda \rho}^{(1)}(k)$ is given by Eq. (2.26).

For the case l even, we find

$$\hat{v}_{\lambda i}^{(1)}(\mathbf{k}) = -v_{\lambda i}^{(1)}(\mathbf{k})/\sqrt{m}, \quad l \text{ even}. \quad (4.4)$$

Therefore, the coupling of even l rotations to acoustic phonons reads

$$V_{ac}^{TR} = \sum_{\mathbf{k}} \sum_{\lambda, i} \hat{v}_{\lambda i}^{(1)} Y_{\lambda}(-\mathbf{k}) s_i(\mathbf{k}), \quad (4.5)$$

with $\hat{v}_{\lambda i}^{(1)}(\mathbf{k}) \propto |\mathbf{k}|$ in the long wavelength limit. This result was previously obtained in Ref. 18 for $l = 2$ rotational modes. Transforming to real space, one finds that the interaction (4.5) corresponds to a coupling of orientational quadrupoles ($l = 2$) with lattice strain in agreement with phenomenological theory.³³

For the case of l odd, we obtain from Eq. (4.3)

$$\hat{v}_{\lambda i}^{(1)}(\mathbf{k}) = \frac{1}{\sqrt{m}} [v_{\lambda i}^{(1)}(\mathbf{k} = \mathbf{0}) - v_{\lambda i}^{(1)}(\mathbf{k})], \quad (4.6)$$

where $v_{\lambda i}^{(1)}(\mathbf{k})$ is now given by (2.29). Therefore, $\hat{v}_{\lambda i}^{(1)}(\mathbf{k} \rightarrow \mathbf{0})$ vanishes quadratically in \mathbf{k} for $l = \text{odd}$.

$$(v_{ai}^{(1)u,1}(\mathbf{k})) = 2(D \cos(k_x a) + E[\cos(k_y a) + \cos(k_z a)], D \cos(k_y a) + E[\cos(k_z a) + \cos(k_x a)], D \cos(k_z a) + E[\cos(k_x a) + \cos(k_y a)]). \quad (4.13)$$

Here we have quoted within the second set of bold parentheses only the three diagonal elements in the order $(\alpha, i) = (1, 1), (2, 2),$ and $(3, 3)$. The coefficients D and E are given by

$$D = \int d\Omega V_1^{(1)}(\Omega, \kappa = 1) Y_{1,1}^u(\Omega), \quad (4.14a)$$

$$E = \int d\Omega V_2^{(1)}(\Omega, \kappa = 1) Y_{1,2}^u(\Omega). \quad (4.14b)$$

For $l = 3, \Gamma = T_{1u}$, we obtain matrices $v_{\lambda i}^{(1)}(\kappa)$ of the same structure as (A7a)–(A7c). The values of the coefficients are different, D is replaced by F ,

We next examine the coupling to optical phonons. The corresponding three ($i = 1, 2, 3$) basic displacement vectors in six-dimensional space read

$$\mathbf{w}^{(i)} = [\delta_{ij}(\mu/m_D)^{1/2}, -\delta_{ij}(\mu/m_a)^{1/2}], \quad j = 1, 2, 3. \quad (4.7)$$

Here, $\mu = m_a m_D / m$ denotes the reduced mass. Optical displacements are defined by

$$\xi_i(\mathbf{k}) = \sum_{\rho} w^{(i)}(\rho) u_{\rho}(\mathbf{k}), \quad (4.8)$$

and the corresponding coupling matrix reads

$$\hat{v}_{\lambda i}^{(1)}(\mathbf{k}) = \sum_{\rho} w^{(i)}(\rho) v_{\lambda \rho}^{(1)}(\mathbf{k}), \quad (4.9)$$

where $v_{\lambda \rho}^{(1)}(\mathbf{k})$ is again given by Eq. (2.26).

Using Eqs. (2.26), we find in the case of l even

$$\hat{v}_{\lambda i}^{(1)}(\mathbf{k}) = \frac{\sqrt{\mu}}{m_a} v_{\lambda i}^{(1)}(\mathbf{k}), \quad l \text{ even}, \quad (4.10)$$

with $v_{\lambda i}^{(1)}(\mathbf{k})$ given by Eq. (2.28). Hence, we have no coupling to optical phonons at the Brillouin-zone center for l even. It follows that centrosymmetric molecules do not couple to optical phonons at the zone center. For finite \mathbf{k} , there is a coupling, linear in \mathbf{k} , to even l rotational modes:

$$V_0^{TR} = \sum_{\mathbf{k}} \sum_{\lambda, i} \hat{v}_{\lambda i}^{(1)}(\mathbf{k}) Y(-\mathbf{k}) \xi_i(\mathbf{k}). \quad (4.11)$$

On the other hand, in the case of l odd, we find by means of Eqs. (4.9), (4.7), and (2.29),

$$\hat{v}_{\lambda i}^{(1)}(\mathbf{k}) = \sqrt{\mu} \left[\frac{1}{m_D} v_{\lambda i}^{(1)}(\mathbf{k} = \mathbf{0}) + \frac{1}{m_a} v_{\lambda i}^{(1)}(\mathbf{k}) \right], \quad l \text{ odd}. \quad (4.12)$$

This coupling is maximum at the zone center. We recall that the molecule has to be noncentrosymmetric.

We now give the explicit expressions for the matrices $v_{\lambda i}^{(1)}(\mathbf{k})$. For $l = 1, \Gamma = T_{1u}$, we obtain from Eqs. (2.29) and (A7a)–(A7c) a diagonal matrix

$$F = \int d\Omega V_1^{(1)}(\Omega, \kappa = 1) Y_{3,1}^u(\Omega), \quad (4.15a)$$

and E is replaced by G ,

$$G = \int d\Omega V_2^{(1)}(\Omega, \kappa = 1) Y_{3,2}^u(\Omega). \quad (4.15b)$$

In analogy with Eq. (4.13), we then have again a diagonal matrix.

Similarly, for $l = 3$ and $\Gamma = T_{2u}$, we obtain expressions of the same structure as (4.13), with D and E replaced, respectively, by

$$H = \int d\Omega V_1^{(1)}(\Omega, \kappa=1) Y_{3,1}^{2u}(\Omega) \quad (4.16a)$$

and by

$$L = \int d\Omega V_2^{(1)}(\Omega, \kappa=1) Y_{3,2}^{2u}(\Omega). \quad (4.16b)$$

We recall that the coefficients $E, D; F, G;$ and H, L are

$$(v_{\lambda,i}^{(1)e,2}(\mathbf{k})) = i2A \begin{bmatrix} \sin(k_x a) & \sin(k_y a) & -2 \sin(k_z a) \\ -\sqrt{3} \sin(k_x a) & \sqrt{3} \sin(k_y a) & 0 \end{bmatrix}, \quad (4.17)$$

where the coefficient A is defined by

$$A = \int d\Omega V_1^{(1)}(\Omega, \kappa=1) Y_{2,1}^e(\Omega). \quad (4.18)$$

For $l=2$ and T_{2g} symmetry we obtain from Eqs. (2.27) and (A9a)–(A9c)

$$(v_{\alpha,i}^{(1)f,2}(\mathbf{k})) = i2B \begin{bmatrix} \sin(k_y a) & \sin(k_x a) & 0 \\ 0 & \sin(k_z a) & \sin(k_y a) \\ \sin(k_z a) & 0 & \sin(k_x a) \end{bmatrix}, \quad (4.19)$$

where

$$B = \int d\Omega V_2^{(1)}(\Omega, \kappa=1) Y_{2,1}^f(\Omega). \quad (4.20)$$

The coefficients A and B are the basic quantities which determine the coupling of $l=2$ rotational modes to acoustic phonons in the orientationally disordered phase of the alkali cyanides.¹⁸ Therefore, A and B govern the anomalous behavior of the elastic constants. Their precise numerical value depends on a competition between repulsive and electrostatic multipole forces.^{14,25} It is legitimate, in a first approximation, to consider the CN molecules as centrosymmetric dumbbells. Such an approximation is, however, not adequate if we want to study other properties, as for instance the coupling to optical phonons.

V. NONLINEAR MOLECULES

The basic results of the previous sections remain valid for nonlinear molecules. Here we briefly sketch the demonstration. The molecules are taken as rigid bodies with r arms which originate from the center of mass. The ν th arm has an orientation $\Omega_\nu = (\Theta_\nu, \varphi_\nu)$ with respect to a system of axes fixed in the crystal. We assume that the extremities of the arms determine the positions of atoms or charge centers on a spherical shell. The center-of-mass positions of the molecules (or molecular ions) are symmetry centers of the lattice, the molecules are surrounded by individual atoms. Such structures correspond to the classical examples of ionic disordered crystals, namely, those containing tetrahedral ions.³⁴

Denoting the center-of-mass position of the n th molecule by $\mathbf{R}(\mathbf{n})$ and the position of the κ th individual atom by $\mathbf{R}(\mathbf{n}, \kappa)$, we write for the interaction between all molecular atoms and one single individual atom

only different from zero for noncentrosymmetric molecules. Therefore, physical properties for which these coefficients play a dominant role are a measure of the noncentrosymmetry of the molecule.

We next turn to the coupling to l even rotational modes. For $l=2$ and E_g symmetry, we obtain from Eqs. (2.28) and (A8a)–(A8c) a coupling matrix

$$V(\mathbf{n}, \kappa) = \sum_{\nu=1}^r V(R(\mathbf{n}) - R(\mathbf{n}, \kappa), \Omega_\nu(\mathbf{n})). \quad (5.1)$$

We notice that Eq. (2.3), valid for a linear molecule, is a particular case of (5.1). We now proceed exactly as in Sec. II. First we expand Eq. (5.1) in terms of lattice displacements. Subsequently, we expand in terms of symmetry-adapted functions $Y_{l,\alpha}^\Gamma(\Omega)$. Again the lowest allowed value of l has to contain the unit representation of the molecular group, while Γ refers to a representation of the site group in the crystal. We then obtain a series of type (2.4). Here we quote only the first two coefficients

$$V^{(0)}(\mathbf{n}, \kappa) = \sum_{\lambda_0} v_{\lambda_0}^{(0)}(\kappa) \sum_{\nu} Y_{\lambda_0}(\Omega_\nu(\mathbf{n})), \quad (5.2a)$$

$$V_i^{(1)}(\mathbf{n}, \kappa) = \sum_{\lambda} v_{\lambda i}^{(1)}(\kappa) \sum_{\nu} Y_{\lambda}(\Omega_\nu(\mathbf{n})). \quad (5.2b)$$

The quantities $v_{\lambda_0}^{(0)}(\kappa)$ and $v_{\lambda i}^{(1)}(\kappa)$ are again given by Eqs. (2.6a)–(2.6b), for instance,

$$v_{\lambda i}^{(1)}(\kappa) = \int d\Omega_\nu(\mathbf{n}) Y_{\lambda}(\Omega_\nu(\mathbf{n})) V(\mathbf{X}(\mathbf{n}) - \mathbf{X}(\mathbf{n}, \kappa), \Omega_\nu(\mathbf{n})). \quad (5.3)$$

Notice that these expressions are independent of the arm index ν and the molecular index \mathbf{n} . Therefore, the summation over ν in Eqs. (5.2a) and (5.2b) can be carried out and we write

$$b_{\tau}(\omega(\mathbf{n})) = \sum_{\nu} Y_{\tau}(\Omega_\nu(\mathbf{n})), \quad (5.4)$$

where τ stands for λ_0 or λ . The quantity $b_{\tau}(\omega)$ is a rotator function.^{20,21,35} Here, $\omega \equiv (\alpha, \beta, \gamma)$ stands for the three Euler angles which specify the position of the molecule with respect to the crystal fixed system of axes. In Eqs. (5.2a) or (5.4), the index λ_0 refers to the unit representation of the site point group, while in Eqs. (5.2b), the index λ includes representations of higher dimensionality.

Since each molecular arm can be treated separately, we obtain again the symmetry relations (2.20) and (2.20'). If the molecule is centrosymmetric, only functions $Y_{l,\alpha}^\Gamma$ with l even are allowed. If the molecule is noncentrosymmetric, odd values of l are also relevant. All properties of the bilinear coupling which follow from Eqs. (2.28) and (2.29) remain valid for nonlinear molecules.

In particular, we have the important property (4.4), which indicates that the coupling $v_{\lambda i}^{(1)}(\mathbf{k})$ to acoustic phonons is linear in \mathbf{k} for centrosymmetric molecules. If the

shape of the molecule is only slightly asymmetric, then even though the lowest allowed value of l even is larger than the lowest value of l odd, the coupling of l even to acoustic phonons can still be dominant. On the other hand, if the shape of the molecule is largely noncentrosymmetric, odd values of l are dominant in the coupling to optic and acoustic phonons. These couplings are governed by relations (4.6) and (4.12), respectively. As an example we quote the high-temperature orientationally disordered phase I of the ammonium halides.³⁶ Here tetrahedral symmetry of the NH_4 group implies $l=3$. The coupling of orientational modes to optic phonons should be more pronounced than the coupling to acoustic phonons. This statement is in agreement with neutron scattering results in $\text{ND}_4\text{I}(\text{I})$, where it has been found that typical optic-neutron groups are much broader than the corresponding acoustic-neutron groups.³⁷

Particular experimental³⁸ and theoretical³⁹ attention has been given to phase II(β) of the ammonium halides. Here the structure in the disordered phase is cubic CsCl type and the NH_4 tetrahedra occupy one or the other of two sterically different positions. Since the tetrahedra are well localized in these positions, the orientational degree of freedom is described by a pseudospin variable $\sigma = \pm 1$. Such a description is also used for a treatment of T-R coupling.³⁹ The essential point is that the spin variable is odd under inversion. Therefore, all our statements made about the coupling of odd l orientational modes to lattice displacements apply. The theoretical results obtained in Ref. 39 for the T-R coupling of a pseudospin variable to lattice displacements can be regarded as a special case of the present theory and are in complete agreement with it. In particular, the coupling of acoustic phonons to the orientational order parameter is quadratic in \mathbf{k} for the small wave vector.

We finally mention the case of NaNO_2 . The NO_2 ion has C_{2v} symmetry; the lattice structure of the paraelectric phase is $I\text{mmm}$. The low symmetry of the molecular ion and the close packing of the structure are responsible for the fact that the T-R coupling matrix $v^{(1)}(\mathbf{k})$ has some large nonzero elements. Noncentrosymmetry implies that the coupling to optical phonons is large^{40,41} while the coupling to acoustical phonons increases quadratically with k away from the zone center. This coupling corresponds in real space to an interaction of an elastic shear wave with the gradient of the orientational order parameter and is considered as a driving mechanism for the incommensurate phase transition.¹⁰⁻¹² We notice that also in other molecular crystals with incommensurate phase transitions and T-R coupling, such as $\text{SC}(\text{NH}_2)_2$ (thiourea),⁹ the molecular units are noncentrosymmetric and, in addition, their symmetry is low.

As a general rule we can state that molecules of low symmetry (low value of l) favor a large value of the T-R matrix elements (5.3), while molecules with high symmetry have much weaker translation-rotation coupling. This general observation is confirmed by neutron scattering results on SF_6 and CBr_4 in the orientationally disordered crystalline phases.⁴² In addition to molecular symmetry, the strength of the interatomic potential (5.1) determines the value of the coupling coefficients.

VI. CONCLUDING REMARKS

We have made a study of translation-rotation coupling in orientationally disordered crystals by paying special attention to molecular symmetry. Most important is the distinction between centrosymmetric and noncentrosymmetric molecules. This distinctive property determines the nature of the translation-rotation coupling. We have first given an extensive treatment for linear molecules and then shown that our main results apply also for nonlinear molecules.

Our results concerning the nature of translation-rotation coupling as a consequence of molecular symmetry are general. We have been able to show that the overall theoretical picture is in agreement with experimental results in various crystals such as the alkali cyanides, the ammonium halides, NaNO_2 , and others. We expect that the present results should be useful beyond the usual domain of molecular crystals and have pointed out the relevance for incommensurate phase transitions in insulators and for the coupling of electronic and structural properties in synthetic organic conductors.

Finally, we should mention that the present theory can be applied to detailed calculations for specific substances. The starting point of such a calculation is the knowledge of the interaction potential of the molecule with its surroundings in the lattice. In a following paper we shall give an application of the present theory by studying the connection between local and collective properties at phase transitions in orientationally disordered crystals.

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APPENDIX

We give first the expressions for the symmetry-adapted functions in terms of Cartesian coordinates

$$x = \sin\Theta \cos\varphi, \quad y = \sin\Theta \sin\varphi, \quad z = \cos\Theta. \quad (\text{A1})$$

The three functions (2.14) for $l=1$ with T_{1u} symmetry are

$$Y_{1,1}^u = (3/4\pi)^{1/2} x, \quad (\text{A2a})$$

$$Y_{1,2}^u = (3/4\pi)^{1/2} y, \quad (\text{A2b})$$

$$Y_{1,3}^u = (3/4\pi)^{1/2} z. \quad (\text{A2c})$$

For $l=2$, the two functions (2.11) of E_g symmetry are

$$Y_{2,1}^e = (5/16\pi)^{1/2} (3z^2 - 1), \quad (\text{A3a})$$

$$Y_{2,2}^e = (5/16\pi)^{1/2} (x^2 - y^2), \quad (\text{A3b})$$

and the three functions (2.12) of T_{2g} symmetry are

$$Y_{2,1}^f = (15/4\pi)^{1/2} xy, \quad (\text{A4a})$$

$$Y_{2,2}^f = (15/4\pi)^{1/2} xz, \quad (\text{A4b})$$

$$Y_{2,3}^f = (15/4\pi)^{1/2} yz. \quad (\text{A4c})$$

The three functions (2.15) for $l=3$ and T_{1u} symmetry read

$$Y_{3,1}^{1u} = -(7/16\pi)^{1/2}(5x^3 - 3x), \quad (\text{A5a})$$

$$Y_{3,2}^{1u} = -(7/16\pi)^{1/2}(5y^3 - 3y), \quad (\text{A5b})$$

$$Y_{3,3}^{1u} = -(7/16\pi)^{1/2}(5z^3 - 3z), \quad (\text{A5c})$$

and those of T_{2u} symmetry are

$$Y_{3,1}^{2u} = -(105/16\pi)^{1/2}x(z^2 - y^2), \quad (\text{A6a})$$

$$Y_{3,2}^{2u} = -(105/16\pi)^{1/2}y(x^2 - z^2), \quad (\text{A6b})$$

$$Y_{3,3}^{2u} = -(105/16\pi)^{1/2}z(y^2 - x^2). \quad (\text{A6c})$$

These functions are used to calculate the matrix elements $v_{\lambda i}^{(1)}(\kappa)$. Here, κ corresponds to 1,2,3 [see definition of $\tau(\kappa)$ following Eq. (2.1)].

For $l=1$, $\Gamma=T_{1u}$, we find from Eq. (2.6b)

$$(v_{\alpha,i}^{(1)1u,1}(\kappa=1)) = \begin{pmatrix} D & 0 & 0 \\ 0 & E & 0 \\ 0 & 0 & E \end{pmatrix}, \quad (\text{A7a})$$

$$(v_{\alpha,i}^{(1)1u,1}(\kappa=2)) = \begin{pmatrix} E & 0 & 0 \\ 0 & D & 0 \\ 0 & 0 & E \end{pmatrix}, \quad (\text{A7b})$$

$$(v_{\alpha,i}^{(1)1u,1}(\kappa=3)) = \begin{pmatrix} E & 0 & 0 \\ 0 & E & 0 \\ 0 & 0 & D \end{pmatrix}. \quad (\text{A7c})$$

The matrices for $\kappa=4,5,6$ follow directly from the symmetry relation (2.19b). The coefficients D and E are given by Eqs. (4.14a) and (4.14b). For $l=3$, $\Gamma=T_{1u}$, we obtain matrices of the same structure as (A7a)–(A7c).

The values of the coefficients are different. The same is true for $l=3$, $\Gamma=T_{2u}$.

For the case $l=2$, $\Gamma=E_g$, we have matrices $v_{\lambda,i}^{(1)}(\kappa)$ of the form

$$(v_{\alpha,i}^{(1)e,2}(\kappa=1)) = A \begin{pmatrix} 1 & 0 & 0 \\ -\sqrt{3} & 0 & 0 \end{pmatrix}, \quad (\text{A8a})$$

$$(v_{\alpha,i}^{(1)e,2}(\kappa=2)) = A \begin{pmatrix} 0 & 1 & 0 \\ 0 & \sqrt{3} & 0 \end{pmatrix}, \quad (\text{A8b})$$

$$(v_{\alpha,i}^{(1)e,2}(\kappa=3)) = A \begin{pmatrix} 0 & 0 & -2 \\ 0 & 0 & 0 \end{pmatrix}. \quad (\text{A8c})$$

The matrices for $\kappa=4,5,6$ follow from relation (2.19a). The coefficient A is given by Eq. (4.20). Finally, for $l=2$ and $\Gamma=T_{2g}$, we obtain

$$(v_{\alpha,i}^{(1)f,2}(\kappa=1)) = B \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (\text{A9a})$$

$$(v_{\alpha,i}^{(1)f,2}(\kappa=2)) = B \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, \quad (\text{A9b})$$

$$(v_{\alpha,i}^{(1)f,2}(\kappa=3)) = B \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}. \quad (\text{A9c})$$

The coefficient B is given by Eq. (4.20).

- ¹S. Haussühl, *Solid State Commun.* **13**, 147 (1973).
²J. M. Rowe, J. J. Rush, N. Vagelatos, D. L. Price, D. G. Hinks, and S. Susman, *J. Chem. Phys.* **62**, 4551 (1975); A. Loidl, J. Knorr, J. Daubert, W. Dultz, and W. J. Fitzgerald, *Z. Phys.* **B 38**, 153 (1980).
³A review of structures and phases of the alkali cyanides is given by F. Lüty, in *Defects in Insulating Crystals*, edited by V. M. Turkevich and K. K. Shvarts (Springer, Berlin, 1981), p. 69.
⁴S. Sawada, S. Nomura, S. Fuji, and Y. Yoshida, *Phys. Rev. Lett.* **1**, 320 (1958).
⁵A. L. Solomon, *Phys. Rev.* **104**, 1191 (1956); M. Elcombe and J. C. Taylor, *Acta Crystallogr. Sect. A* **24**, 410 (1968).
⁶S. Tanisaki, *J. Phys. Soc. Jpn.* **16**, 579 (1961); Y. Yamada and T. Yamada, *J. Phys. Soc. Jpn.* **21**, 2167 (1966).
⁷H. Futuma, Y. Shiozaki, A. Chiba, E. Tanaka, T. Mitsui, and J. Furuichi, *Phys. Lett.* **25A**, 8 (1967); F. Denoyer, A. H. Moudén, A. Bellamy, R. Currat, C. Vettier, and M. Lambert, *Phys. Rev. B* **25**, 1697 (1982).
⁸D. Kucharczyk, A. Pietraszko, and K. Lukaszewicz, *Ferroelectrics* **21**, 445 (1978); H. Böhm, *Z. Kristallogr.* **148**, 207 (1978); M. Harada, N. Koyano, S. Mitani, Y. Iwata, and I. Shibuya, *Annu. Rep. Res. React. Inst. Kyoto Univ.* **12**, 1 (1979).
⁹A. H. Moudén, F. Denoyer, M. Lambert, and W. Fitzgerald, *Solid State Commun.* **32**, 933 (1979).
¹⁰A. P. Levanyuk, and D. G. Sannikov, *Fiz. Tverd. Tela* **18**, 1927 (1976) [*Sov. Phys.—Solid State* **18**, 1122 (1976)].
¹¹V. Heine and J. D. McConnell, *Phys. Rev. Lett.* **46**, 1092 (1981); *J. Phys. C* **17**, 1199 (1984).
¹²K. H. Michel, *Phys. Rev. B* **24**, 3998 (1981).
¹³R. Moret, J. P. Pouget, R. Comès, and K. Bechgaard, *Phys. Rev. Lett.* **49**, 1008 (1982). [TMTSF is an abbreviation for tetramethyltetraselenafulvalene, or $(\text{CH}_3)_4\text{C}_6\text{Se}_4$ with the structural formula 2,2'-bi(4,5-dimethyl-1,3-diselenole-2-ylidene).]
¹⁴M. L. Klein and I. R. McDonald, *Chem. Phys. Lett.* **78**, 383 (1981); R. M. Lynden-Bell, I. R. McDonald, and M. L. Klein, *Mol. Phys.* **48**, 1093 (1983).
¹⁵M. Yvinec, *Mol. Cryst. Liq. Cryst.* **89**, 359 (1982).
¹⁶R. M. Lynden-Bell, M. L. Klein, I. R. McDonald, *Z. Phys. B* **54**, 325 (1984).
¹⁷V. Heine, R. M. Lynden-Bell, J. D. C. McConnell, and I. R. McDonald, *Z. Phys. B* **56**, 229 (1984).
¹⁸K. H. Michel and J. Naudts, *Phys. Rev. Lett.* **39**, 212 (1977); *J. Chem. Phys.* **67**, 547 (1977).
¹⁹C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids* (Clarendon, Oxford, 1972).
²⁰W. Press and A. Hüller, *Acta Crystallogr. Sect. A* **29**, 252 (1973); *Phys. Rev. Lett.* **30**, 1207 (1973).
²¹R. M. Pick and M. Yvinec, *J. Phys. (Paris)* **41**, 1045 (1980).
²²F. C. von der Lage and H. A. Bethe, *Phys. Rev.* **71**, 612 (1947).
²³K. H. Michel, in *Proceedings of NATO Workshop on Condensed Matter Research Using Neutrons: Today and Tomorrow*

- row, edited by S. Lovesey and R. Scherm (Plenum, New York, 1984).
- ²⁴D. Strauch, U. Schröder, and W. Bauernfeind, *Solid State Commun.* **30**, 559 (1979).
- ²⁵D. Sahu and S. D. Mahanti, *Phys. Rev. B* **26**, 298 (1982).
- ²⁶J. Kanamori, *J. Appl. Phys.* **31**, 14 (1960).
- ²⁷G. A. Gehring and K. A. Gehring, *Rep. Progr. Phys.* **38**, 1 (1975).
- ²⁸L. Onsager, *J. Am. Chem. Soc.* **58**, 1486 (1936).
- ²⁹R. Brout and H. Thomas, *Physics (N.Y.)* **3**, 317 (1967).
- ³⁰See, M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1977), Chap. 2.
- ³¹B. De Raedt, K. Binder, and K. H. Michel, *J. Chem. Phys.* **75**, 2977 (1981).
- ³²See, e.g., M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill, New York, 1964), p. 81.
- ³³W. Rehwald, J. R. Sandercock, and M. Rossinelli, *Phys. Status Solidi A* **42**, 699 (1977).
- ³⁴M. L. Klein, I. R. McDonald, and Y. Ozaki, *J. Chem. Phys.* **79**, 5579 (1983).
- ³⁵H. M. James and T. A. Keenan, *J. Chem. Phys.* **31**, 12 (1959).
- ³⁶R. S. Seymour and A. W. Pryor, *Acta Crystallogr. Sect. B* **26**, 1487 (1970).
- ³⁷N. Vagelatos, J. M. Rowe, and J. J. Rush, *Phys. Rev. B* **12**, 4522 (1975).
- ³⁸H. Terauchi, Y. Noda, and Y. Yamada, *J. Phys. Soc. Jpn.* **32**, 1560 (1972); Y. Yamada, Y. Noda, J. D. Axe, and G. Shirane, *Phys. Rev. B* **9**, 4429 (1974).
- ³⁹Y. Yamada, M. Mori, and Y. Noda, *J. Phys. Soc. Jpn.* **32**, 1565 (1972).
- ⁴⁰K. D. Ehrhardt and K. H. Michel, *Phys. Rev. Lett.* **46**, 291 (1981); *Z. Phys. B* **41**, 329 (1981).
- ⁴¹M. L. Klein, I. R. McDonald, and Y. Ozaki, *Phys. Rev. Lett.* **48**, 1197 (1982).
- ⁴²G. Dolling, B. M. Powell, and V. F. Sears, *Mol. Phys.* **37**, 1859 (1979).