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Theory of elastic and phonon softening in ionic molecular solids. Application to alkali cyanides

D. Sahu and S. D. Mahanti
Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824
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We have carried out a theoretical study of the effect of coupling between rotational and translational degrees of freedom first proposed by Michel and Naudts on the elastic constants and phonon frequencies of ionic molecular solids. We have applied our theory to the high-temperature plastic phase of alkali cyanides NaCN, KCN, and RbCN. We find that the competition between short-range repulsion and the interaction of the electric quadrupole moment of the CN^- ion with the fluctuating electric field gradient strongly influences the elastic softening and ferroelastic instabilities in these systems. The effect of direct intermolecular interaction and anharmonicity is found to be significant in some cases. The ferroelastic transition temperatures for the above three compounds are found to be 337.5, 190, and 179 K which compare favorably with the experimental values 255.4, 156, and 130 K if we note the mean-field nature of our theory. Within our model we can understand the qualitative differences between the cyanides and the superoxides, a similar class of compounds showing drastically different ferroelastic behavior. Our calculations provide a microscopic justification for the use of certain phenomenological parameters by Strauch *et al.* in their calculation of phonon frequencies in NaCN and KCN at 300 K.

I. INTRODUCTION

Ionic molecular solids undergo a series of structural phase transitions and show anomalous thermoelastic properties which are intimately connected with the orientational, spin, and orbital degrees of freedom of the ionic molecular species. Typical examples are alkali cyanides[1-7] (MCN), superoxides[8-10] (MO_2), azides[11] (MN_3), hydroxides[12] (MOH), and nitrites[13] (MNO_2) where M is an alkali ion. In this class cyanides are the simplest, the $(CN)^-$ molecular ion possessing only orientational degrees of freedom whereas the superoxides are perhaps the most complex, the O_2^- ion possessing all three, i.e., orientational, orbital, and spin degrees of freedom.

The structure of the highest-temperature solid phase in almost all these systems is face-centered pseudocubic, the molecules undergoing hindered rotations between several equivalent directions of minimum energy. This high-temperature solid phase (referred to as phase I in the literature) shows anomalous thermoelastic properties and the systems behave like plastic crystals. In the case of cyanides careful measurements[1-3,6] of elastic constants have been made and it is found that C_{11} and C_{44} decrease with temperature and C_{44} approaches zero at a temperature T^* where one expects a ferroelastic instability of the pseudocubic phase. However, the transition to the ferroelastic phase is usually[1-3,8,14] first order, the transition temperature T_c being higher than T^* (see Table I for values of T_c and T^* in cyanides).

The symmetry of the low-temperature phase (phase II) is different for different classes of these systems. For example, in cyanides, the orientation of the $(CN)^-$ molecular axis is along the original [110] direction[15] of the phase I; the structure of phase II is body-centered orthorhombic. In contrast, the average orientation of the superoxide molecule is parallel to the z axis, and the structure of phase II is body-centered tetragonal (CaC_2 structure). There are, however, significant fluctuations in the molecular orientations about the c axis due to the Jahn-Teller (JT) splitting of the O_2^- orbital degeneracy.[8] In this work we are primarily concerned with the cyanides and superoxides al-

TABLE I. First-order ferroelastic transition temperature T_c (experimental), extrapolated and theoretical C_{44} softening temperatures T^*, and T_{44}.

System	T_c (K)	T^* (K)	T_{44} (K)
NaCN	283.5	255.4	337.5
KCN	168	156	190
RbCN	133	130	179

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though our results should be applicable to other ionic molecular solids as well.

In this paper we develop a microscopic theory of elastic softening and phonon renormalization in these systems. We analyze the effect of the orientational degrees of freedom on the elastic properties and phonons by extending the earlier work of Michel and Naudts[16] (MN). In the evaluation of the coupling between the translational and rotational degrees of freedom, we include[17] the effects of (i) short-range steric (repulsion) forces, (ii) anisotropic electrostatic forces,[18] and (iii) the effects associated with the splitting of the orbital degeneracy of the molecular ions. In addition we include the direct interaction between the molecules. We do not consider here the coupling between the spin and either the translational or the rotational degrees of freedom. Alkali superoxides show low-T structural phase transitions involving large-scale molecular reorientations (referred to as magnetogyric phase transitions) which can be understood in terms of spin-rotational coupling (see Ref. 19). This interaction does not appreciably affect the high-T ferroelastic phase transitions. One possible exception is the ordered pyrite to marcasite transition in NaO_2 (see Ref. 20) which occurs at about 200 K.

For cyanides, (iii) is not present and only (i) was considered in the earlier work[16] on elastic softening. The importance of (ii) for the cubic phase of cyanides was recently discussed by Bound *et al.*,[21] although for the noncubic phase of superoxides it has been pointed out by Mahanti and Kemeny.[20] Bound *et al.*, in their molecular dynamics calculation of the rotational-translational dynamics of KCN, NaCN, and RbCN, have found that the inclusion of the electric quadrupole moment Q of the $(CN)^-$ ion was essential to understand the experimental orientational probability distribution functions (OPDF) and other low-frequency local dynamic properties. A careful study of the interplay of (i) and (ii) in the observed[1-3] anomalous elastic softening, ferroelastic phase transitions, and phonon softening in cyanides is the main subject of this paper. In a separate paper we will report the combined effects of (i), (ii), and (iii) on the ferroelastic instabilities and apply our theory to the case of superoxides.

Our main results can be summarized as follows. Because of the large electric quadrupole moment (Q) of the $(CN)^-$ molecular ion, there is an appreciable contribution to the rotational-translational coupling (Γ_Q) arising from the interaction between Q and the fluctuating electric field gradient (EFG) present in the high-T orientationally disordered pseudocubic phase. Because of the negative sign of Q, this coupling has opposite sign to that obtained from considering short-range repulsive forces alone (to be denoted as Γ_R). We find that when $\Gamma_R \neq 0$ and $\Gamma_Q = 0$, $C_{11} \to 0$ at a temperature T_{11} which is higher than T_{44} where $C_{44} \to 0$. On the other hand, when $\Gamma_R = 0$ and $\Gamma_Q \neq 0$, $T_{44} > T_{11}$, i.e., C_{44} softens at a higher temperature than C_{11} which is observed experimentally in NaCN, KCN, and RbCN. Actually Γ_Q and Γ_R are nonzero and appreciable, with Γ_Q dominating the ferroelastic instabilities in cyanides. In contrast, Γ_R is more important in superoxides because of smaller value of Q of the O_2^- ions. As a result $C_{11} \to 0$ at higher temperature than C_{44} and since C_{11} couples to the order parameter $\langle Y_{20} \rangle$, one expects the molecules to orient parallel to the c axis, giving rise to a CaC_2 structure. This structure is seen experimentally.[8] However, for a quantitative understanding of the ferroelastic transition temperature in the superoxides one must incorporate the orbital degeneracy of the superoxide ion and go beyond simple molecular field theory.[22] Within a molecular field treatment of translational-rotational coupling and the intermolecular interaction, our theoretical transition temperature T_{44} compares favorably with the experimental values for the three cyanides (see Table I).

For a better agreement between theoretical and experimental C_{11} and C_{44} values, we find that anharmonicity effects,[23] particularly for C_{11} are very important. As a measure of the anharmonicity we take the values of dC_{11}/dT (for $T \approx 300$ K) appropriate for alkali-halide crystals and find that the observed peak in $C_{11}(T)$ for the cyanides can be understood in terms of two canceling contributions to dC_{11}/dT; one coming from anharmonicity effects and the other from the rotational-translational coupling. The results for NaCN and KCN are extremely good but for RbCN there are discrepancies.

The outline of the paper is as follows. In Sec. II we discuss the model and the Hamiltonian that we have used to study the elastic properties and phonons of ionic molecular solids. In Sec. III, a Green's-function method is used to calculate phonon frequencies and elastic constants which are renormalized by the coupling between the translational and rotational degrees of freedom. Section IV contains a brief discussion on the isothermal rotational susceptibility which plays an important role in the T dependence of elastic softening. In Sec. V, we discuss the different contributions to the translational-rotational coupling. Finally in Sec. VI we discuss our results and make comparison with earlier theories and available experiments.

II. HAMILTONIAN

A. Model

We treat the CN^- ion as a rigid dumbbell consisting of two identical centers separated by a distance $2d$. Each molecule sits in an octahedral cage (in the high-T phase) of six nearest-neighbor (NN) M^+ ions, the NN distance being a. The M^+ ions are represented by spherically symmetric charge distributions.

In addition to the electrostatic forces, there are short-range (SR) repulsive forces between the ions. This repulsion can be expressed in a Born-Mayer form,

$$V^{\mathrm{SR}}_{\alpha\beta}(\vec{r})=(C_1)_{\alpha\beta}\,e^{-(C_2)_{\alpha\beta}|\vec{r}|}\;, \qquad (2.1)$$

where α (or β) stands for any one of the two atoms of the anion or cation. The constants $(C_1)_{\alpha\beta}$ and $(C_2)_{\alpha\beta}$ represent the strength and the inverse of the range of the repulsion potential, respectively. The quantities $(C_1)_{\alpha\alpha}$ and $(C_2)_{\alpha\alpha}$ are available in the literature,[24,25] and one can use the equations

$$(C_1)_{\alpha\beta}=\sqrt{(C_1)_{\alpha\alpha}(C_1)_{\beta\beta}}$$

$$\text{and} \qquad (2.2)$$

$$(C_2)_{\alpha\beta}=\tfrac{1}{2}[(C_2)_{\alpha\alpha}+(C_2)_{\beta\beta}]$$

to obtain the values of C_1 and C_2 for appropriate systems.

The short-range repulsive interaction between a $(CN)^-$ ion whose center of mass (c.m.) is at $\vec{R}_i$ and a M^+ ion at $\vec{R}_j$ is given by a sum of atom-atom potential,

$$V^{\mathrm{SR}}_{M^+(\mathrm{CN})^-}(ij)=C_1\sum_{s=\pm 1} e^{-C_2|\vec{R}_{ij}+sd\hat{n}_i|}\;, \qquad (2.3)$$

where $\hat{n}_i$ is a unit vector specifying the orientation of the $(CN)^-$ ion with respect to the crystal axes. We have also assumed that both C and N atoms can be replaced by an average atom whose repulsion with M^+ is characterized by the parameters C_1 and C_2. Following MN we discuss the elastic properties of these systems using a Hamiltonian H that consists of three parts, i.e.,

$$H=H_{\mathrm{tr}}+H_{\mathrm{rot}}+H_{\mathrm{tr\text{-}rot}}\;, \qquad (2.4)$$

where

$$H_{\mathrm{tr}}=\sum_{\vec{k},\kappa,\mu}\frac{1}{2m_\kappa}p^{\dagger}_{\mu}(\kappa\,|\,\vec{k})p_{\mu}(\kappa\,|\,\vec{k}) +\tfrac{1}{2}\sum_{\vec{k},\kappa\kappa',\mu\mu'}C_{\mu\mu'}(\kappa\kappa'\,|\,\vec{k})u^{\dagger}_{\mu}(\kappa\,|\,\vec{k})u_{\mu'}(\kappa'\,|\,\vec{k}) \qquad (2.5)$$

represents the translational part of the Hamiltonian in the harmonic approximation and is obtained by treating the ions as spherical charge distributions. For example, this part would be analogous to that of a KBr crystal.[26] Here m_κ is the mass of the κth ion (+ or −) in a unit cell, $\vec{k}$ is the wave vector, μ is the Cartesian component x,y,z; $C_{\mu\mu'}(\kappa\kappa'\,|\,\vec{k})$ is the dynamical matrix and $\vec{u},\vec{p}$ are the Fourier transforms of the displacements (from the fcc structure) and momentum, respectively. Here and in the following we define Fourier transforms by the equation

$$f(\vec{r})=\frac{1}{\sqrt{N}}\sum_{\vec{k}}f(\vec{k})e^{i\vec{k}\cdot\vec{r}}\;, \qquad (2.6)$$

where N is the total number of unit cells. We will use $1/\sqrt{N}$ in the definition unless otherwise specified. The rotational part of H is obtained by fixing the c.m. of all the ions at fcc sites $(\vec{R}^0_i)$ and is given by

$$H_{\mathrm{rot}}=\sum_{\vec{k}}\sum_{\lambda=1}^{2}\frac{1}{2I}L^{\dagger}_{\lambda}(\vec{k})L_{\lambda}(\vec{k})+\sum_{i=1}^{N}V_0(\hat{n}_i) +\sum_{\langle ij\rangle}V_d(ij)\;. \qquad (2.7)$$

Here I is the moment of inertia of the dumbell about each of the two principal axes and $\vec{L}$ is the angular momentum. $V_0(\hat{n}_i)$ is the orientation-dependent single-site potential which is given by

$$V_0(\hat{n}_i)=C_1\sum_{j=1}^{6}\sum_{s=\pm 1}e^{-C_2|\vec{R}^0_{ij}+sd\hat{n}_i|}\;. \qquad (2.8)$$

Only the repulsion contributes to $V_0(\hat{n}_i)$ because the electric field and electric field gradient at the lattice sites vanish because of cubic symmetry. In Eq. (2.8) only NN contributions are retained because of the short-range nature of the repulsive potential. The other contribution to the cubic single-site potential will come from the anisotropic dispersion interaction between $(CN)^-$ molecules. This contribution was evaluated[20] for sodium superoxide (NaO_2) and was found to be about 6% of the short-range repulsion contribution. We expect a similar behavior for the cyanides.

We have included the term $V_d(ij)$ in Eq. (2.7) which represents the direct interaction between two $(CN)^-$ ions at sites $\vec{R}^0_i$ and $\vec{R}^0_j$. We write

$$V_d(ij)=\sum_{m=-2}^{2} A_m Y_2^m(\hat{\omega}_i)Y_2^{-m}(\hat{\omega}_j)\ , \tag{2.9}$$

$$A_m=A_m^{QQ}+A_m^{\text{rep}}+A_m^{\text{AD}}\ . \tag{2.10}$$

Here A_m is a measure of the strength of the direct interaction which has three main sources[27]: quadrupole-quadrupole interaction, short-range repulsion, and anisotropic dispersion, the last one arising from the fluctuating dipole moments of the $(\text{CN})^-$ ion. In addition, for cyanides there is a direct electric dipole-dipole contribution to $V_d(ij)$ and its effect will be discussed later. The unit vectors $\hat{\omega}_i$ and $\hat{\omega}_j$ are the orientations of the molecules i and j with respect to the intermolecular axis taken as polar axis. The coefficients A_m^{QQ} are explicitly given as follows:

$$\begin{aligned} A_0^{QQ}&=(24\pi/5)Q^2/(\sqrt{2}a)^5\ ,\\ A_1^{QQ}&=A_{-1}^{QQ}=\tfrac{2}{3}A_0^{QQ}\ ,\\ A_2^{QQ}&=A_{-2}^{QQ}=\tfrac{1}{6}A_0^{QQ}\ , \end{aligned} \tag{2.11}$$

where Q is the quadrupole moment of the molecule. For the rest of the coefficients we refer the reader to the literature.[28]

In order to go from a system of reference where the intermolecular axis is the z axis to the crystal axis system one makes a transformation involving the Euler angles[29] $(\alpha_{ij},\beta_{ij},\gamma_{ij})$ associated with the vector $\vec{\text{R}}_{ij}^0$ to obtain

$$V_d(ij)=\sum_{l=0}^{4}\sqrt{4\pi(2l+1)}\sum_{m=-2}^{2}A_m\begin{bmatrix}2 & 2 & l\\ m & \overline{m} & 0\end{bmatrix}\sum_{m_1,m_2}\begin{bmatrix}2 & 2 & l\\ m_1 & m_2 & -(m_1+m_2)\end{bmatrix} \times Y_{l,m_1+m_2}(\beta_{ij},\gamma_{ij})Y_{2m_1}(\hat{n}_i)Y_{2m_2}(\hat{n}_j)\ , \tag{2.12}$$

where the quantities in the square brackets are the Clebsch-Gordan (CG) coefficients. Using the properties of CG coefficients one finds that only even l terms contribute in Eq. (2.12). Further if one considers only the quadrupole contribution to A_m then only the $l=4$ term survives.

Next we introduce the five symmetry-adapted spherical harmonics Y_α (see Ref. 16) through

$$Y_{2m}(\hat{n}_i)=\sum_{\alpha=1}^{5}c_{m\alpha}Y_\alpha(\hat{n}_i)\ , \tag{2.13}$$

where the 5×5 matrix $\{c_{m\alpha}\}$ is given in Table II, and obtain

$$\sum_{\langle ij\rangle}V_d(ij)=\tfrac{1}{2}\sum_{\vec{\text{k}}}\sum_{\alpha,\beta=1}^{5}D_{\alpha\beta}(\vec{\text{k}})Y_\alpha^\dagger(\vec{\text{k}})Y_\beta(\vec{\text{k}})\ , \tag{2.14}$$

where

$$D_{\alpha\beta}(\vec{\text{k}})=\sum_{\vec{\text{R}}\neq0}e^{i\vec{\text{k}}\cdot\vec{\text{R}}}\sum_{m_1,m_2}\sqrt{36\pi}\begin{bmatrix}2 & 2 & 4\\ m_1 & m_2 & -(m_1+m_2)\end{bmatrix}\sum_m A_m\begin{bmatrix}2 & 2 & 4\\ m & -m & 0\end{bmatrix} \times Y_{4m_1+m_2}(\beta_{\vec{\text{R}}},\gamma_{\vec{\text{R}}})c_{m_1\alpha}c_{m_2\beta}\ . \tag{2.15}$$

Here the sum $\vec{\text{R}}$ is over $(\text{CN})^-$ ions surrounding the central $(\text{CN})^-$ ion at $\vec{\text{R}}=0$.

Finally the last term in Eq. (2.4) represents a coupling between the orientational degrees of freedom Y_α of the molecular ion and the translational degrees of freedom of the anions and cations. We write

$$H_{\text{tr-rot}}=i\sum_{\vec{\text{k}},\alpha,\mu}\sum_{\kappa=\pm}Y_\alpha^\dagger(\vec{\text{k}})v_{\alpha\mu}(\kappa\mid\vec{\text{k}})u_\mu(\kappa\mid\vec{\text{k}})\ . \tag{2.16}$$

This is obtained by displacing the center of mass from the equilibrium position, i.e., $\vec{\text{R}}_i=\vec{\text{R}}_i^0+\vec{\text{u}}_i$ and calculating terms in the Hamiltonian which are linear in the displacements $\vec{\text{u}}_i$. The elements of the coupling constant matrix $v_{\alpha\mu}$ form a 3×5 matrix. An explicit form of $v_{\alpha\mu}$ including different contributions will be given in Sec. V.

B. Phonon description

If we describe the translational degrees of freedom in terms of phonons, then H_{tr} and $H_{\text{tr-rot}}$ can be rewritten in terms of creation $(b_{j\vec{\text{k}}}^\dagger)$ and destruc-

TABLE II. Coefficients of expansion of unnormalized real order parameters Y_α in terms of Y_{2m}'s.

$m \diagdown \alpha$	1	2	3	4	5
-2	0	$\sqrt{1/6}$	$i/2$	0	0
-1	0	0	0	$-\frac{1}{2}$	$i/2$
0	1	0	0	0	0
1	0	0	0	$\frac{1}{2}$	$i/2$
2	0	$\sqrt{1/6}$	$-i/2$	0	0

tion ($b_{j\vec{k}}$) operators of phonons of wave vector $\vec{k}$ and polarization index j. We have

$$H_{\text{tr}} = \sum_{j,\vec{k}} \hbar\omega^0_{j\vec{k}} (b^\dagger_{j\vec{k}} b_{j\vec{k}} + \tfrac{1}{2}) \,. \tag{2.17}$$

The bare phonon frequencies $\omega^0_{j\vec{k}}$ are obtained by solving the secular equation

$$| C_{\mu\mu'}(\kappa\kappa' \,|\, \vec{k}) - \omega^{0^2}_{\vec{k}} \delta_{\mu\mu'} \delta_{\kappa\kappa'} | = 0 \,. \tag{2.18}$$

In terms of phonon creation and destruction operators, we have

$$H_{\text{tr-rot}} = i \sum_{\vec{k},j,\alpha} Y^\dagger_\alpha(\vec{k}) V_{\alpha j}(\vec{k}) (b_{j\vec{k}} + b^\dagger_{j-\vec{k}}) \,, \tag{2.19}$$

$$V_{\alpha j}(\vec{k}) = (1/2\omega^0_{j\vec{k}})^{1/2} \sum_{\mu,\kappa} \frac{1}{\sqrt{m_\kappa}} e_\mu(\kappa \,|\, \vec{k} j) v_{\alpha\mu}(\kappa \,|\, \vec{k}) \,. \tag{2.20}$$

In Eq. (2.20), $e_\mu(\kappa \,|\, \vec{k} j)$ gives the μth component of polarization vector for κ-type ion for the mode $j\vec{k}$. $V_{\alpha j}(\vec{k})$ is determined from a knowledge of bare phonon frequencies, the masses, polarization vectors, and the coefficients $v_{\alpha\mu}$.

III. RENORMALIZATION OF PHONON FREQUENCIES AND ELASTIC CONSTANTS

The rotation-phonon coupling [Eq. (2.19)] renormalizes the phonon frequencies from their bare value $\omega^0_{j\vec{k}}$. We use the Zubarev's Green's-function method[30] to obtain the renormalized phonon frequencies $\omega_{j\vec{k}}$. We define the time- and temperature-dependent retarded Green's function G by

$$G_{j\vec{k}}(t-t') = \frac{1}{i} \langle [\phi_{j\vec{k}}(t), \phi^\dagger_{j\vec{k}}(t')] \rangle \Theta(t-t') \,, \tag{3.1}$$

where $\phi_{j\vec{k}}(t) = b_{j\vec{k}}(t) + b^\dagger_{j-\vec{k}}(t)$ is the phonon field operator in the Heisenberg representation. The square bracket is the commutator, $\langle \;\rangle$ stands for the average over a grand canonical ensemble, and $\Theta(t-t')$ is the step function. The equation of motion for G is

$$\begin{aligned} i\frac{d}{dt} G_{j\vec{k}}(t-t') &= \delta(t-t') \langle [\phi_{j\vec{k}}(t), \phi^\dagger_{j\vec{k}}(t')] \rangle \\ &\quad + \frac{1}{i} \Theta(t-t') \langle [[\phi_{j\vec{k}}(t), H], \phi^\dagger_{j\vec{k}}(t')] \rangle \,. \end{aligned} \tag{3.2}$$

For simplicity of notation let $\omega_0 = \omega^0_{j\vec{k}}$ and $\phi_{j\vec{k}} = \phi_{j\vec{k}}$ ($t = 0$). The Fourier transform of $G_{j\vec{k}}(t-t')$ is given by the equation

$$\begin{aligned} \omega \langle\langle \phi_{j\vec{k}}; \phi^\dagger_{j\vec{k}} \rangle\rangle_\omega &= \langle [\phi_{j\vec{k}}, \phi^\dagger_{j\vec{k}}] \rangle \\ &\quad + \langle\langle [\phi_{j\vec{k}}, H]; \phi^\dagger_{j\vec{k}} \rangle\rangle_\omega \,, \end{aligned} \tag{3.3}$$

where

$$\langle\langle \phi_{j\vec{k}}; \phi^\dagger_{j\vec{k}} \rangle\rangle_\omega \equiv G_{j\vec{k}}(\omega) = \int_{-\infty}^{\infty} G_{j\vec{k}}(t) e^{i\omega t} dt \,. \tag{3.4}$$

Since $b_{j\vec{k}}$ and $b^\dagger_{j\vec{k}}$ satisfy the usual boson commutation relations, we obtain

$$\begin{aligned} &[\phi_{j\vec{k}}, H_{\text{tr}}] = \omega_0 \psi_{j\vec{k}} \,, \\ &[\phi_{j\vec{k}}, H_{\text{rot}}] = [\phi_{j\vec{k}}, H_{\text{tr-rot}}] = 0 \,, \\ &[\psi_{j\vec{k}}, H_{\text{tr}}] = \omega_0 \phi_{j\vec{k}} \,, \end{aligned} \tag{3.5}$$

where

$$\psi_{j\vec{k}} = b_{j\vec{k}} - b^\dagger_{j\vec{k}} \,. \tag{3.6}$$

Using the above equalities it follows that

$$(\omega^2 - \omega_0^2) \langle\langle \phi_{j\vec{k}}; \phi^\dagger_{j\vec{k}} \rangle\rangle_\omega = 2\omega_0 \left[1 + \sum_\alpha V^*_{\alpha j} \langle\langle Y_\alpha; \phi^\dagger_{j\vec{k}} \rangle\rangle_\omega \right] , \tag{3.7}$$

and

$$\omega \langle\langle Y_\alpha; \phi^\dagger_{j\vec{k}} \rangle\rangle_\omega = \langle\langle Y_{1,\alpha}; \phi^\dagger_{j\vec{k}} \rangle\rangle_\omega \,, \tag{3.8}$$

where

$$Y_{1,\alpha}(\vec{k}) \equiv [Y_\alpha(\vec{k}), H_{\text{rot}}] \,. \tag{3.9}$$

It is clear that to obtain the Green's functions on the right-hand side (RHS) of Eq. (3.7) one needs the Green's function on the RHS of Eq. (3.8) and the hierarchy of equations extends to infinity. We further write

$$Y_{r,\alpha}(\vec{k}) = [Y_{r-1,\alpha}(\vec{k}), H_{\text{rot}}] \quad (r = 2, 3, \ldots, \infty) \,. \tag{3.10}$$

Note that the operators $Y_{1,\alpha}, Y_{2,\alpha}, \ldots$ do not contain the operators b and $b^\dagger$ and hence commute with ϕ and H_{tr}. Hence one can write, using Eq. (2.19),

$$\omega\langle\langle Y_{1,\alpha};\phi^\dagger_{j\vec{k}}\rangle\rangle_\omega \approx \langle\langle Y_{2,\alpha};\phi^\dagger_{j\vec{k}}\rangle\rangle_\omega + \sum_{\beta\vec{k}} V_{\beta j}(\vec{k})\langle[Y_{1,\alpha}(\vec{k}),Y_\beta(\vec{k})]\rangle\langle\langle\phi_{j\vec{k}};\phi^\dagger_{j\vec{k}}\rangle\rangle_\omega . \tag{3.11}$$

In obtaining Eq. (3.11) we have replaced the commutator $[Y_{1,\alpha}, Y^\dagger_\beta]$ by its average value. This is equivalent to a random-phase approximation. We can now generalize Eq. (3.11) to higher-order Green's functions and obtain

$$[\omega^2-\omega_0^2-\Sigma_{j\vec{k}}(\omega)]\langle\langle\phi_{j\vec{k}};\phi^\dagger_{j\vec{k}}\rangle\rangle_\omega = 2\omega_0 , \tag{3.12}$$

where the phonon self-energy $\Sigma_{jk}(\omega)$ is given by

$$\Sigma_{j\vec{k}}(\omega) = 2\omega_0 \sum_{\alpha\beta} V^*_{\alpha j}(k)V_{\beta j}(\vec{k})\sum_{r=1}^{\infty}\frac{1}{\omega^{r+1}}\langle[Y_{r,\alpha}(\vec{k}),Y^\dagger_\beta(\vec{k})]\rangle . \tag{3.13}$$

We will now relate the phonon self-energy to the frequency and wave-vector-dependent rotational susceptibility $\chi_{\alpha\beta}(\vec{k},\omega)$.

The rotational susceptibility is defined by a related orientational Green's function,

$$\chi_{\alpha\beta}(\vec{k},t-t') = -\frac{1}{i}\langle[Y_\alpha(\vec{k},t),Y^\dagger_\beta(\vec{k},t')]\rangle\Theta(t-t') . \tag{3.14}$$

The time Fourier transform of $\chi_{\alpha\beta}(\vec{k},t-t')$ is given by the equation

$$\chi_{\alpha\beta}(\vec{k},\omega) = -\langle\langle Y_\alpha(\vec{k});Y_\beta(\vec{k})\rangle\rangle_\omega = -\frac{1}{i}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\Theta(t-t')\langle[Y_\alpha(\vec{k},t),Y^\dagger_\beta(\vec{k},t')]\rangle , \tag{3.15}$$

$$\omega\langle\langle Y_\alpha(\vec{k});Y_\beta(\vec{k})\rangle\rangle_\omega = \langle\langle Y_{1,\beta}(\vec{k}),Y^\dagger_\beta(\vec{k})\rangle\rangle_\omega . \tag{3.16}$$

Let us assume that the rotational response is determined by H_{rot} alone. With this approximation, which is equivalent to the assumption that rotational dynamics has a faster time scale compared to translation,[31] we obtain

$$\omega\langle\langle Y_{1,\alpha};Y^\dagger_\beta\rangle\rangle_\omega = \langle[Y_{1,\alpha},Y^\dagger_\beta]\rangle + \langle\langle Y_{2,\alpha};Y^\dagger_\beta\rangle\rangle_\omega . \tag{3.17}$$

Generalizing this procedure to higher-order Green's functions, we obtain

$$\langle\langle Y_\alpha;Y^\dagger_\beta\rangle\rangle_\omega = \sum_{r=1}^{\infty}\langle[Y_{r,\alpha}(\vec{k}),Y^\dagger_\beta(\vec{k})]\rangle\frac{1}{\omega^{r+1}} . \tag{3.18}$$

Using Eqs. (3.18) and (3.15) in Eq. (3.13) we get

$$\Sigma_{j\vec{k}}(\omega) = -2\omega_0\sum_{\alpha,\beta} V^*_{\alpha j}(\vec{k})V_{\beta j}(\vec{k})\chi_{\alpha\beta}(\vec{k},\omega) . \tag{3.19}$$

Thus from (3.11) and (3.18) and noting that the renormalized phonon frequencies $\omega_{j\vec{k}}$ are obtained from the poles of the Green's function $\langle\langle\phi_{j\vec{k}};\phi^\dagger_{j\vec{k}}\rangle\rangle_\omega$, we get

$$\omega^2_{j\vec{k}} = \omega^{0^2}_{j\vec{k}} - 2\omega^0_{j\vec{k}}\sum_{\alpha,\beta} V^*_{\alpha j}(\vec{k})\chi_{\alpha\beta}(\vec{k},\omega)V_{\beta j}(\vec{k}) . \tag{3.20}$$

The above equation ignores vertex corrections and is not adequate when the time scales of rotational and translational dynamics are comparable. However, we are primarily interested in the elastic softening ($\omega_{j\vec{k}} \to 0$) at relatively high temperatures where the rotational motion is rapid and the above approximation is quite reasonable. For the calculation of phonon frequencies at finite $\vec{k}$ particularly when $\omega_{jk} \sim \omega_{\text{rot}}$, where ω_{rot} is a characteristic rotational frequency, one has to consider the frequency dependence[31] of $\chi_{\alpha\beta}(\vec{k},\omega)$ and also include vertex corrections.

From Eq. (3.20) one can easily obtain the effect of rotational-translational coupling on the elastic constants by choosing $\vec{k}$ along several symmetry directions and studying the frequencies of longitudinal and transverse phonons in the limit $\vec{k},\omega \to 0$. The details of the calculation of $\chi_{\alpha\beta}(\vec{k},0)$ are discussed in Sec. IV and in Sec. V, we will give explicit expressions for the renormalized elastic constants.

IV. ROTATIONAL SUSCEPTIBILITY $\chi_{\alpha\beta}(\vec{k},\omega=0)$

For the calculation of elastic constants and phonon frequencies we replace $\chi_{\alpha\beta}(\vec{k},\omega)$ by its static values $\chi_{\alpha\beta}(\vec{k})\equiv\chi_{\alpha\beta}(\vec{k},\omega=0)$. This is adequate for the elastic constants and the limitations for phonon frequency calculation will be discussed in Sec. VI E. $\chi_{\alpha\beta}(\vec{k})$ is the static susceptibility of an isolated system subjected to an adiabatic perturbation. Following the commonly made approximation for large systems we replace $\chi_{\alpha\beta}(\vec{k})$ by the isothermal susceptibility $\chi^T_{\alpha\beta}(\vec{k})$, i.e., we assume that $\chi_{\alpha\beta}(\vec{k})\approx\chi^T_{\alpha\beta}(\vec{k})$ even though the differences between the two need not be zero in general.[32] Next we calculate $\chi^T_{\alpha\beta}(\vec{k})$ in the presence of only the direct intermolecular interaction $D_{\alpha\beta}(\vec{k})$ using a molecular field approximation.

The rotational response is determined by H_{rot}, which is replaced by its mean-field value H_{MF}:

$$H_{\text{MF}}=\sum_{\alpha,\beta,\vec{k}} D_{\alpha\beta}(\vec{k})Y_\alpha(\vec{k})m_\beta(\vec{k})+\sum_i V_0(\hat{n}_i)\ , \tag{4.1}$$

where

$$m_\beta(\vec{k})=\langle Y_\beta(\vec{k})\rangle\ . \tag{4.2}$$

We apply a staggered external field $h_\beta(\vec{k})$ which adds a term H_{ext} to the Hamiltonian H_{MF},

$$H_{\text{ext}}=-\sum_\beta h_\beta(\vec{k})Y_\beta(\vec{k})\ , \tag{4.3}$$

and calculate the susceptibility χ in the limit when the external field vanishes. In the presence of $h_\beta(\vec{k})$

$$m_\alpha(\vec{k}')=\frac{\text{Tr}e^{-(1/k_BT)(H_{\text{MF}}+H_{\text{ext}})}Y^\dagger_\alpha(\vec{k}')}{\text{Tr}e^{-(1/k_BT)(H_{\text{MF}}+H_{\text{ext}})}}\ . \tag{4.4}$$

The generalized susceptibility matrix $\chi_{\alpha\beta}(\vec{k},\vec{k}')$, defined by the equation

$$\chi_{\alpha\beta}(\vec{k}',\vec{k})\equiv\lim_{h_\beta\to0}\frac{\partial}{\partial h_\beta(\vec{k})}m_\alpha(\vec{k}')\ , \tag{4.5}$$

is found to satisfy the matrix integral equation,

$$\begin{aligned}\chi_{\alpha\beta}(\vec{k}',\vec{k})&\\ =\chi^0_{\alpha\beta}(\vec{k}',\vec{k})-&\sum_{\alpha'\beta'\vec{k}''}\chi^0_{\alpha\alpha'}(\vec{k}',\vec{k}'')\\ &\times D_{\alpha'\beta'}(\vec{k}'')\chi_{\beta'\beta}(\vec{k}'',\vec{k})\ ,\end{aligned} \tag{4.6}$$

where

$$\chi^0_{\alpha\beta}(\vec{k},\vec{k}')=\frac{1}{k_BT}[\langle Y^+_\alpha(\vec{k}')Y_\beta(\vec{k})\rangle-\langle Y^+_\alpha(\vec{k}')\rangle\langle Y_\beta(\vec{k})\rangle]\ , \tag{4.7}$$

the thermal averages being taken in the absence of H_{ext}. For the disordered phase $\langle Y^+_\alpha(\vec{k})\rangle=0$ and $H_{\text{MF}}=\sum_i V_0(\hat{n}_i)$ and we have

$$\chi^0_{\alpha\beta}(\vec{k}',\vec{k})=\chi^0_{\alpha\beta}\,\delta_{\vec{k},\vec{k}'}\ , \tag{4.8}$$

where $\chi^0_{\alpha\beta}$ is the $\vec{k}$-independent single-site susceptibility.[16] In this case $\chi_{\alpha\beta}(\vec{k},\vec{k}')$ is diagonal in the $\vec{k}$ index and defining $\chi_{\alpha\beta}(\vec{k})\equiv\chi_{\alpha\beta}(\vec{k},\vec{k})$, we obtain

$$\chi_{\alpha\beta}(\vec{k})=\chi^0_{\alpha\beta}-\sum_{\alpha'\beta'}\chi^0_{\alpha\alpha'}D_{\alpha'\beta'}(\vec{k})\chi_{\beta'\beta}(\vec{k})\ . \tag{4.9}$$

From Eq. (4.9) one obtains, symbolically, the formal solution

$$\chi=(1+\chi^0D)^{-1}\chi^0\ . \tag{4.10}$$

As shown in Ref. 16 because of cubic symmetry χ^0 is a diagonal matrix with

$$\chi^0_{\alpha\alpha}=(\chi^0_{11},3\chi^0_{11},\chi^0_{33},\chi^0_{33},\chi^0_{33})\ , \tag{4.11}$$

where the first two quantities have e_g symmetry and the last three have t_{2g} symmetry. Similarly in the $\vec{k}\to0$ limit $D(\vec{k})$ is diagonal with

$$D_{\alpha\alpha}(\vec{k}\to0)=(D^0_{11},\tfrac{1}{3}D^0_{11},D^0_{33},D^0_{33},D^0_{33})\ . \tag{4.12}$$

From (4.8)–(4.10) it follows that in the $\vec{k}\to0$ limit χ is diagonal with

$$\chi_{\alpha\alpha}=(\chi_{11},3\chi_{11},\chi_{33},\chi_{33},\chi_{33})\ .$$

The $\vec{k}$-independent susceptibility $\chi^0_{\alpha\beta}(T)$ is calculated from

$$\chi^0_{\alpha\beta}(T)=\frac{1}{k_BT}\frac{\int e^{-V_0(\theta,\phi)/k_BT}Y^*_\alpha(\theta,\phi)Y_\beta(\theta,\phi)\sin\theta\,d\theta\,d\phi}{\int e^{-V_0(\theta,\phi)/k_BT}\sin\theta\,d\theta\,d\phi}\ . \tag{4.13}$$

V. ROTATIONAL-TRANSLATIONAL COUPLING COEFFICIENTS

As discussed in the Introduction, there are two main physical sources that contribute to the rotational-translational coupling matrix $v_{\alpha\mu}(\kappa\,|\,\vec{k})$ and we write down this as a sum of two parts,

$$v_{\alpha\mu}(\kappa\,|\,\vec{k})=v^{R}_{\alpha\mu}(\kappa\,|\,\vec{k})+v^{\mathrm{EFG}}_{\alpha\mu}(\kappa\,|\,\vec{k})\quad(\kappa=\pm)\,, \tag{5.1}$$

where $v^{R}_{\alpha\mu}(\kappa\,|\,\vec{k})$ denotes the short-range repulsion contribution and $v^{\mathrm{EFG}}_{\alpha\mu}(\kappa\,|\,\vec{k})$ denotes the contribution coming from the interaction between electric quadrupole moment of the $(\mathrm{CN})^{-}$ ion and the fluctuating EFG produced at its site by all the other ions (taken to be point charges). We denote by 1,2,3,... the contributions from first, second, third, etc., ... neighbors, respectively, which have charges +, −, +, and so on. Then

$$v^{i}_{\alpha\mu}(+\,|\,\vec{k})=v^{i}_{\alpha\mu}(+\,|\,\vec{k})_1+v^{i}_{\alpha\mu}(+\,|\,\vec{k})_3+\cdots\quad(i=R,\ \mathrm{EFG})\,, \tag{5.2a}$$

$$v^{i}_{\alpha\mu}(-\,|\,\vec{k})=v^{i}_{\alpha\mu}(-\,|\,\vec{k})_2+v^{i}_{\alpha\mu}(-\,|\,\vec{k})_4+\cdots\quad(i=R,\ \mathrm{EFG})\,. \tag{5.2b}$$

Following Michel and Naudts[16] we will take $v^{R}_{\alpha\mu}(\kappa\,|\,\vec{k})=v^{R}_{\alpha\mu}(+\,|\,\vec{k})_1$ because the short-range repulsion falls off rapidly with distance. In calculating $v^{\mathrm{EFG}}_{\alpha\mu}(\kappa\,|\,\vec{k})$ we include contributions up to fourth neighbors only, further neighbors making insignificant contributions since the interaction falls off as $1/r^4$.

A. Short-range repulsion contribution $v^{R}_{\alpha\mu}(+\,|\,\vec{k})_1$

The coefficients v^R in $\vec{k}$ space can be obtained from their $\vec{r}$-space values through the relation

$$v^{R}_{\alpha\mu}(+\,|\,\vec{k})_1=\sum_{nn}v^{R}_{\alpha\mu}(+\,|\,\vec{R}^{0}_{ij})e^{i\vec{k}\cdot\vec{R}^{0}_{ij}}\,, \tag{5.3}$$

where the sum is to be carried over all the NN positions $\vec{R}^{0}_{ij}$ given by $(\pm a\hat{x},0,0)$, $(0,\pm a\hat{y},0)$, $(0,0,\pm a\hat{z})$. From Ref. 16 we have

$$v^{R}_{\alpha\mu}(+\,|\,a\hat{x})_1=\begin{bmatrix}A_R & -A_R & 0 & 0 & 0\\ 0 & 0 & B_R & 0 & 0\\ 0 & 0 & 0 & B_R & 0\end{bmatrix}\,,$$

$$v^{R}_{\alpha\mu}(+\,|\,a\hat{y})_1=\begin{bmatrix}0 & 0 & B_R & 0 & 0\\ A_R & A_R & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & B_R\end{bmatrix}\,, \tag{5.4}$$

$$v^{R}_{\alpha\mu}(+\,|\,a\hat{z})_1=\begin{bmatrix}0 & 0 & 0 & B_R & 0\\ 0 & 0 & 0 & 0 & B_R\\ -2A_R & 0 & 0 & 0 & 0\end{bmatrix}\,.$$

The quantities A_R and B_R depend on C_1, C_2, d, and a. They are explicitly given in Eqs. (A13) and (A15) of Ref. 16. The values of C_1, C_2, d, and a for the cyanides are given in Table III and the values of A_R and B_R are given in Table IV. The Fourier-transformed quantities $v^{R}_{\alpha\mu}(+\,|\,\vec{k})_1$ are then

$$v^{R}_{\alpha\mu}(+\,|\,\vec{k})_1=2\begin{bmatrix}A_RS_x & -A_RS_x & B_RS_y & B_RS_z & 0\\ A_RS_y & A_RS_y & B_RS_x & 0 & B_RS_z\\ -2A_RS_z & 0 & 0 & B_RS_x & B_RS_y\end{bmatrix}\,, \tag{5.5}$$

where

$$S_i=\sin k_ia,\quad C_i=\cos k_ia\quad(i=x,y,z)\,. \tag{5.6}$$

B. Calculation of $v^{\mathrm{EFG}}_{\alpha\mu}(\kappa\,|\,\vec{k})$

As the lattice vibrates there is deviation from the local cubic symmetry at the positions of the molecules and the resulting EFG couples to Q. To the lowest order in displacement this leads to an additional coupling between rotation and translation with strength given by $v^{\mathrm{EFG}}_{\alpha\mu}(\kappa\,|\,\vec{k})$. Depending on the sign of the quadrupole moment Q the net rotation translation coupling is either enhanced or suppressed.

TABLE III. Repulsion parameters (C_1,C_2), lattice constant (a), molecular size $(2d)$, and free-ion quadrupole moment value (Q_0). See Eq. (2.11) for A_0^{QQ}.

	NaCN	KCN	RbCN
C_1 (10^7 K)	1.013	2.347	3.421
C_2 (Å^{-1})	3.3382	3.3382	3.3382
a (Å)	2.944	3.250	3.415
d (Å)	0.615	0.600	0.575
Q_0 (10^{-10} esu Å^2)	−4.64	−4.64	−4.64
A_0^{QQ} (K)	1870	1143	892

TABLE IV. Repulsion (A_R, B_R) and quadrupolar (A_Q, B_Q) contributions to the translation-rotation coupling.

	NaCN	KCN	RbCN
$Q=$	$0.6Q_0$	$0.6Q_0$	$0.6Q_0$
A_R (K/Å)	5578	4379	3323
B_R (K/Å)	−1390	−988	−713
A_Q (K/Å)	−3065	−2064	−1693
B_Q (K/Å)	2503	1685	1382
B_R/A_R	−0.249	−0.226	−0.215
B_Q/A_Q	−0.816	−0.816	−0.816

The quadrupole EFG interaction can be written as[33]

$$H'=\frac{1}{6}\sum_i\sum_{\mu,\nu}Q^i_{\mu\nu}U^i_{\mu\nu}\ , \tag{5.7}$$

where the Cartesian components of the quadrupole moment and the field gradient tensor at site i are

$$Q^i_{\mu\nu}=\int(3x_{i\mu}x_{i\nu}-\delta_{\mu\nu}r_i^2)\rho(\vec{r}_i)\,d\vec{r} \qquad (\mu,\nu=x,y,z;\vec{r}_i=\vec{r}-\vec{R}_i)\ , \tag{5.8}$$

$$U^i_{\mu\nu}=\frac{\partial}{\partial X_\mu}\frac{\partial}{\partial X_\nu}U(\vec{X}) =\frac{\partial}{\partial X_\mu}\frac{\partial}{\partial X_\nu}\sum_j{}'\frac{q_j}{|\vec{R}_i-\vec{R}_j|}\quad(\vec{X}\in\vec{R}_i)\ . \tag{5.9}$$

Here $\rho(\vec{r}_i)$ is the charge density at the site i and $U(\vec{R}_i)$ is the electrostatic potential at the ith site due to all other charges q_j at the $\vec{R}_j$. We can express $Q^i_{\mu\nu}$ as a linear combination of spherical quadrupole moment tensors of rank 2 defined by

$$Q^i_{2m}=\int r_i^2 Y_{2m}(\hat{r}_i)\rho(\vec{r}_i)\,d\vec{r} \tag{5.10}$$

so that Eq. (5.7) can be rewritten as

$$H'=\sum_i\sum_{m=-2}^{2}Q^i_{2m}U_2^{-m}(i)\ , \tag{5.11}$$

where U_2^{-m}'s are appropriate linear combinations of $U^i_{\mu\nu}$'s. Since Q is measured with respect to molecular axes (MA) one should transform from the lab axes to the molecular axes, i.e.,

$$Q^i_{2m}=Y_{2m}(\hat{n}_i)Q\ , \tag{5.12}$$

$$Q=\int\left[\left[\frac{3z^2-r^2}{2}\right]\rho(\vec{r})\,d\vec{r}\right]_{\text{MA}}\ . \tag{5.13}$$

Using (5.11) and (5.12) we can write

$$H'=Q\sum_i\sum_{\alpha=1}^{5}Y_\alpha(\hat{n}_i)U^i_\alpha\ , \tag{5.14}$$

where (dropping the superscript i in U^i_α)

$$\begin{aligned} U_1&=\sqrt{\pi/5}\,U_{zz}\ ,\\ U_2&=\sqrt{\pi/45}\,(U_{xx}-U_{yy})\ ,\\ U_3&=-\sqrt{2\pi/15}\,U_{xy}\ ,\\ U_4&=-\sqrt{2\pi/15}\,U_{xz}\ ,\\ U_5&=-\sqrt{2\pi/15}\,U_{yz}\ . \end{aligned} \tag{5.15}$$

The components $U_{\mu\nu}$ are obtained from Eq. (5.9), i.e.,

$$U^i_{\mu\nu}=\sum_j\frac{3q_j}{X^4_{ij}}\left[(\hat{X}_{ij\nu}u_{j\mu}+\hat{X}_{ij\mu}u_{j\nu}) -(5\hat{X}_{ij\mu}\hat{X}_{ij\nu}-\delta_{\mu\nu})\vec{X}_{ij}\cdot\vec{U}_j\right]\ , \tag{5.16}$$

where $\vec{X}_{ij}=\vec{R}^0_j-\vec{R}^0_i$, $\hat{X}_{ij}=\vec{X}_{ij}/X_{ij}$, and $X_{ij\nu}$ is the νth component of $\hat{X}_{ij}$. In obtaining Eq. (5.16), because of inversion symmetry the $\vec{u}_i$ terms drop out when the sum over j is carried out. Finally one obtains the coefficients $v^{\text{EFG}}_{\alpha\mu}(\kappa\,|\,\vec{X}_{ij})$ and its Fourier components from the identity

$$\begin{aligned} H'&=\sum_i Y_\alpha(\hat{r}_i)U^i_\alpha\\ &\equiv\sum_{i,j,\alpha,\mu}Y_\alpha(\hat{n}_i)v^{\text{EFG}}_{\alpha\mu}(\vec{X}_{ij})u_{j\mu}\\ &\equiv i\sum_{\vec{k},\mu,\kappa}Y^\dagger_\alpha(\vec{k})v^{\text{EFG}}_{\alpha\mu}(\kappa\,|\,\vec{k})u_\mu(\kappa\,|\,\vec{k})\ . \end{aligned} \tag{5.17}$$

The quantities $v^{\text{EFG}}_{\alpha\mu}(\kappa\,|\,\vec{k})$ have been explicitly calculated in Appendix A.

C. Elastic limit

To extract information regarding the elastic constants C_{ij}, we take the long-wavelength limit ($\vec{k}\rightarrow 0$) and retain the leading terms in sines and cosines and obtain

$$v_{\alpha\mu}(+\,|\,\vec{k})+v_{\alpha\mu}(-\,|\,\vec{k})=2a\begin{bmatrix} A_{\text{eff}}k_x & -A_{\text{eff}}k_x & B_{\text{eff}}k_y & B_{\text{eff}}k_z & 0\\ A_{\text{eff}}k_y & A_{\text{eff}}k_y & B_{\text{eff}}k_x & 0 & B_{\text{eff}}k_z\\ -2A_{\text{eff}}k_z & 0 & 0 & B_{\text{eff}}k_x & B_{\text{eff}}k_y \end{bmatrix}\ , \tag{5.18}$$

where

$$A_{\mathrm{eff}}=A_R+\alpha A_Q\ , \tag{5.19a}$$

$$B_{\mathrm{eff}}=B_R+\alpha B_Q\ , \tag{5.19b}$$

and

$$A_Q=\sqrt{9\pi/5}\,\frac{Q\,|e|}{a^4}=-\sqrt{3/2}B_Q\ ,$$

$$\alpha=1+1/(4\sqrt{2})-8/(27\sqrt{3})-\tfrac{1}{16}+\cdots\ . \tag{5.20}$$

1. Case 1

For a wave along [001] direction we take $k_x=k_y=0$ and $k_z=k$ and consider the frequencies of LA and TA branches.[34] The longitudinal acoustic (LA) frequency in the limit $\vec{k}\rightarrow 0$ is given by

$$\omega_{\mathrm{LA}}^2=(C_{11}/\rho)k^2 \tag{5.21a}$$

and the polarization of the vibration is

$$e_\mu(\kappa\,|\,\vec{k})=\sqrt{m_\kappa/m}\begin{bmatrix}0\\0\\1\end{bmatrix}\ , \tag{5.21b}$$

where m_κ is the mass of the κ-type ion, $m=m_{+}+m_{-}$, and ρ is the mass density $(m/2a^3)$. Substituting (5.18) and (5.21) in (2.20) and using (3.20) we obtain

$$C_{11}=C_{11}^0-\frac{8}{a}A_{\mathrm{eff}}^2\chi_{11}(T)\ . \tag{5.22}$$

Similarly for the transverse acoustic branch (TA), using

$$\omega_{\mathrm{TA}}^2=(C_{44}/\rho)k^2$$

and

$$e_\mu(\kappa\,|\,\vec{k})=\sqrt{m_\kappa/m}\begin{bmatrix}1\\0\\0\end{bmatrix}\ ,$$

we obtain

$$C_{44}=C_{44}^0-\frac{2}{a}B_{\mathrm{eff}}^2\chi_{44}(T)\ . \tag{5.23}$$

2. Case 2

For a wave propagating along the [110] direction, we take $k_x=k_y=k/\sqrt{2}$, $k_z=0$. For a TA wave in the xy plane, using

$$\omega_{\mathrm{TA}}^2=k^2(C_{11}-C_{12})/(2\rho)$$

and

$$e_\mu(\kappa\,|\,\vec{k})=\sqrt{m_k/m}\;1/\sqrt{2}\begin{bmatrix}1\\-1\\0\end{bmatrix}\ ,$$

we obtain

$$C_{12}=C_{12}^0+\frac{4}{a}A_{\mathrm{eff}}^2\chi_{11}(T)\ . \tag{5.24}$$

Equations (5.22)–(5.24) are in agreement with the results of Ref. 16 when $Q=0$, although they have been derived in a completely different way. These equations will be used in the next section to study the T dependence of the elastic constants for the cyanides.

VI. RESULTS AND DISCUSSION

The temperature dependence of elastic constants C_{11}, C_{44}, and C_{12} given in Eqs. (5.22)–(5.24) depend upon (i) the short-range repulsion (A_R,B_R) and quadrupole contributions (A_Q,B_Q) to the translational rotational coupling, and (ii) the rotational susceptibility $\chi_{\alpha\beta}(\vec{k})$ obtained in the presence of direct interaction $D_{\alpha\beta}(\vec{k})$. The T dependence of $\chi_{\alpha\beta}(\vec{k})$ comes from that of $\chi_{\alpha\beta}^0$, the single-site susceptibility. From Eq. (4.13) we see that apart from the $1/k_BT$ factor, the T dependence of $\chi_{\alpha\beta}^0(\vec{k})$ is determined by the single-site potential $V_0(\hat{n}_i)$. In the cubic phase, the electric field and the electric field gradient vanish at the lattice sites and therefore the only contribution to $V_0(\hat{n}_i)$ comes from the repulsive (steric) forces and because of the short-range nature of the latter only the neighboring cations contribute to $V_0(\hat{n}_i)$. In Fig. 1 we give the (θ,ϕ) dependence of $V_0(\hat{n}_i)$ for KCN which shows the four minima along the [111] and equivalent body-diagonal directions. The maxima are along the [±100], [0±10], [00±1], and the saddle points are along the [110] and its equivalent directions. The values and the T dependence of the different components of the single-site susceptibility χ_{ii}^0 are determined by the strength of the repulsion and will be discussed in detail later. For the superoxides, there is an additional contribution to $V_0(\hat{n}_i)$ which comes from the splitting of the orbital degeneracy of the $O_2{}^-$ ion as the molecule orients away from the symmetry directions.[20]

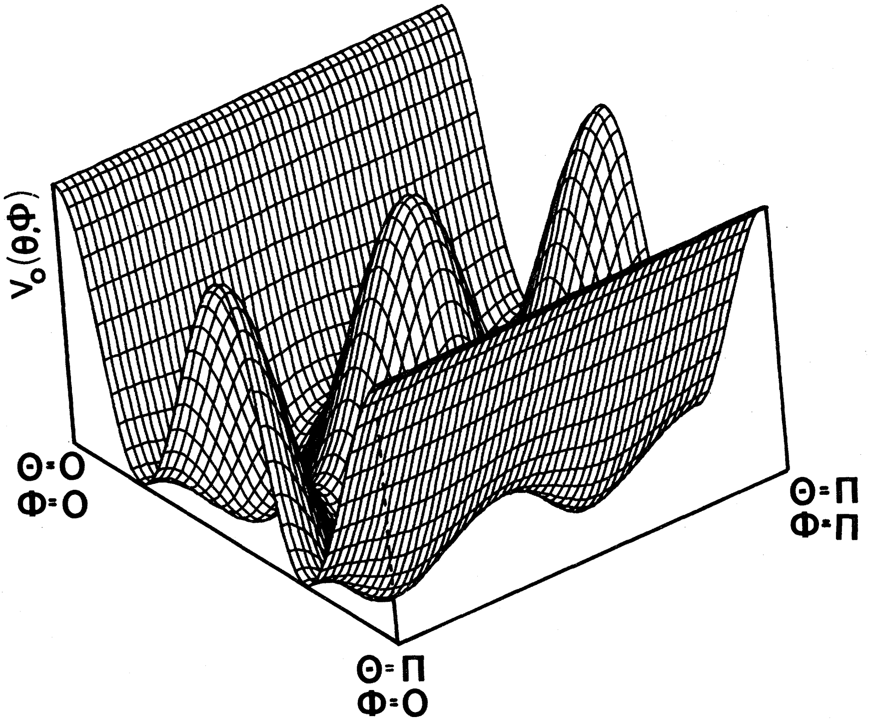

FIG. 1. Single-site potential $V_0(\theta,\phi)$ for KCN. $V_0(0,0)=9914$ K (max); $V_0(\theta_0,\pi/4)=8350$ K (min), where $\theta_0=54°$; $V_0(\pi/2,\pi/4)=8387$ K (saddle point). θ is measured from the [001] and ϕ from the [100] axis.

A. Repulsion parameters and quadrupole moment

In the present and all earlier[16,21] calculations, C and N atoms of the $(\mathrm{CN})^-$ molecule have been assumed to be equivalent so far as the strength of atom-atom repulsion is concerned. In other words, the repulsion parameter between a positive ion M and any one atom of the CN molecule is given by

$$C_1=\sqrt{(C_1)_{M\text{-C}}(C_1)_{M\text{-N}}}\ ,$$
$$C_2=\tfrac{1}{2}[(C_2)_{M\text{-C}}+(C_2)_{M\text{-N}}]\ . \tag{6.1}$$

Using Tosi-Fumi[24] parameters for metal ions and the parameters of Mirsky *et al.*[25] for CC and NN, we have calculated C_1 and C_2 and the values are given in Table III. Bound *et al.*[21] have used the same values (excepting for a few minor differences) in their molecular dynamic (MD) study. Actually there are two sets of parameters given in the paper by Tosi and Fumi; our final results are not very sensitive to the choice of these two different sets. The value[21] of the quadrupole moment (Q_0) of the free $(\mathrm{CN})^-$ ion is given in Table III. In their MD study involving KCN molecules confined to a finite cube, Bound *et al.*[21] found that in order to explain the orientational probability distribution function (OPDF) they had to reduce the value of Q by a factor $f=0.5$, i.e., $Q=fQ_0$. They argued that such a reduction could arise from the charge redistribution of $(\mathrm{CN})^-$ ion when it is placed in a solid environment. While this is an important physical effect, the precise value of f depends on the nature of the approximations made in obtaining the OPDF. In particular, Bound *et al.* considered a small system and did not allow for volume fluctuations. Instead of using their value of f, we have used a slightly different value, i.e., $f=0.6$ to fit the long-wavelength elastic constant data for the three compounds NaCN, KCN, and RbCN.

For the superoxides we find that the repulsive forces are slightly stronger compared to cyanides whereas the free-ion quadrupole moment[20] is about a factor of 2 smaller. These differences along with the orbital degeneracy of the $O_2{}^-$ ion are primarily responsible for the experimentally observed[8,5] qualitative differences between the cyanides and superoxides as regards the nature of structural phase transition in these systems is concerned. In Table III we also give the values of a quantity $A_0^{QQ}=(24\pi/5)Q_0^2(\sqrt{2a})^5$ which measures the strength of the direct intermolecular quadrupole interaction. The repulsion and anisotropic dispersion contribution to the direct interaction which was found[20] to be important for NaO_2 are not so important for the cyanides because of large Q and for the other superoxides because of a large value of a. In the present calculation, repulsion and anisotropic dispersion contributions to the direct intermolecular interaction are ignored.

We would like to make a few comments about the effect of the nonzero electric dipole moment ($\vec{\mathscr{D}}$) of the $(CN)^-$ ion on the elastic softening at high temperatures. Taking the calculated value[21] of $|\vec{\mathscr{D}}|=0.3D$, we find that the strength of the dipole-dipole interaction measured by the quantity $\epsilon_d=\mathscr{D}^2/(a\sqrt{2})^3\approx 10$ K which is a factor of 10 smaller than the quadrupole-quadrupole interaction energy measured by $\epsilon_Q=Q_0^2/(a\sqrt{2})^5\cong 100$ K. Therefore the dipole-dipole interaction can be neglected while calculating $\chi_{\alpha\beta}$. The coupling between $\vec{\mathscr{D}}$ and the fluctuating electric field $\vec{E}$ can soften the phonons just like the coupling between Q and the fluctuating EFG. But we have found that for symmetry reasons the former does not contribute to the softening of the elastic constants because in the presence of this coupling only $\omega^2-\omega_0^2\propto k^4$ for $k\rightarrow 0$.

B. Rotational-translational coupling A_R, B_R, A_Q, B_Q

Knowing C_1 and C_2 for the various compounds we have calculated A_R and B_R using the expressions of Michel and Naudts (MN).[16] For the sake of completeness we have reproduced their expressions for A_R and B_R in Appendix B. Our values of A_R and B_R (see Table IV) for KCN are about a factor of 2 larger than that given by MN and this difference is due to the large value of C_1 given by Tosi-Fumi parameters. An important quantity that determines the nature of the ferroelastic instability, i.e., which of the two elastic constants C_{11} or C_{44} softens first, is the ratio B_R/A_R. This ratio (see Appendix B) is given by

$$\delta_R=\frac{B_R}{A_R}=-\sqrt{6}\left[\frac{d}{a}\right]\left[(f_1-f_3)\Big/\left[3f_2-f_0+\frac{d}{a}(f_1-3f_3)\right]\right] \tag{6.2}$$

and depends upon the parameters (d/a) and (C_2a). For the cyanides $\delta_R\simeq -0.25$ (see Table IV) and it turns out that if one considers repulsion alone, C_{11} goes to zero at a higher temperature than C_{44}.

The parameters A_Q and B_Q depend on the values of the quadrupole moment of the $(CN)^-$ ion in the solid. As has been pointed out before, there is some evidence from the molecular dynamic studies[21] of rotational autocorrelation functions in the cubic phase of KCN that $Q_{\text{solid}}<Q_0$, the free-ion value. For the entries in the Table IV, we have used the value $Q=0.6Q_0$; this value was obtained by making a reasonable fit to the experimental values of elastic constants C_{11} and C_{44} over a large temperature range. With $Q=0.5Q_0$ (a value suggested by Bound *et al.*) we were unable to obtain a decent fit over the entire experimental temperature range. Of course it is possible to change the value of repulsion parameters slightly and obtain a different value for Q which gives an equally good fit. However, our main purpose is to point out the important role of the quadrupole-fluctuating EFG interaction on the elastic softening rather than to obtain a very good fit to the experiment. It will be pointed out later that anharmonicity and non-mean-field effects are important and should be taken into account for a better quantitative understanding of the experiment.

It turns out that the dominant contribution to A_Q and B_Q comes from the nearest-neighbor positive ion. This is because the second and third neighbors [see Eqs. (5.19a) and (5.19b)] make contributions of opposite sign and almost equal (within 0.1%) magnitude to A_Q and B_Q. The fourth neighbor's contribution is $\lesssim 7\%$ of that of the nearest neighbor. For the quadrupolar contribution we find that

$$\delta_Q=B_Q(1+\cdots)/A_Q(1+\cdots)=B_Q/A_Q=-\sqrt{2/3}\ . \tag{6.3}$$

The large value of $|\delta_Q|$ compared to $|\delta_R|$ causes $C_{44}\rightarrow 0$ at a higher temperature than C_{11} if we consider the quadrupole contribution to the translational-rotational coupling alone. The above analysis concerning the competition between quadrupolar and repulsive forces in determining the effective rotation-translation coupling suggests that there should be interesting pressure effects because of the different volume dependences of A_R,B_R and A_Q,B_Q. Such a study is under present investigation.

C. Isothermal rotational susceptibility $\chi_{\alpha\beta}$

The temperature dependences of C_{11} and C_{44} are determined by $\chi_{\alpha\beta}(\vec{k})$. For the symmetry direction $\vec{k}=[0\,0\,k]$ that we are interested in, $\chi_{\alpha\beta}(\vec{k})=\delta_{\alpha\beta}\chi_{\alpha\alpha}(\vec{k})$ and furthermore in the limit $k\to 0$, which is relevant for the calculation of elastic constants

$$\chi_{ii}(0)=\chi_{ii}^{0}/[1+D_{ii}(\vec{k}=0)\chi_{ii}^{0}]\ , \tag{6.4}$$

where χ_{ii}^{0} is defined in Eq. (4.13). As has been discussed in the first paragraph of this subsection, the T dependence of χ_{ii}^{0} is determined by the single-site potential $V_0(\hat{n}_i)$. Because of cubic symmetry $\chi_{11}^{0}=3\chi_{22}^{0}=\chi_{e_g}$ and $\chi_{33}^{0}=\chi_{44}^{0}=\chi_{55}^{0}=\chi_{t_{2g}}$ and the quantities $T\chi_{11}^{0}$ and $T\chi_{44}^{0}$ are given in Figs. 2(a) and 2(b). Our results differ from that of MN even if we use their C_1 and C_2 parameters and this difference is due to a factor of 2 error in the calculation of their $V_0(\hat{n}_i)$. In fact, their numerical values of $T\chi_{11}^{0}$ and $T\chi_{44}^{0}$ given in Figs. 1 and 2 are appropriate for a system for which $C_1\cong 2C_1^{\mathrm{MN}}$, a value much closer to that obtained from Tosi-Fumi parameters. However, for this stronger repulsion, A_R and B_R should be increased by a factor of 2. This will change their results on T dependence of C_{11} and C_{44} drastically and spoil the agreement with the experiment that they found.

In Figs. 2(a) and 2(b) we also give $R_1=\chi_{11}/\chi_{11}^{0}$ and $R_4=\chi_{44}/\chi_{44}^{0}$, χ_{11} and χ_{44} being the e_g and t_{2g} susceptibilities obtained in the presence of direct quadrupole-quadrupole interaction. Using the value of $Q=0.6Q_0$, we find that $D_{11}(\vec{k}=0)=-704$ K and $D_{44}(\vec{k}=0)=235$ K. From Eq. (6.4) we immediately see that $\chi_{11}/\chi_{11}^{0}>1$ and $\chi_{44}/\chi_{44}^{0}<1$ which indicates that direct intermolecular interaction enhances C_{11} softening and suppresses C_{44} softening. Over the temperature range of interest $100\ \leq T<500$ K, $1.08<\chi_{11}/\chi_{11}^{0}<1.13$, and $0.6\leq\chi_{44}/\chi_{44}^{0}<0.9$. Thus effect of the direct interaction on elastic softening is quite important for C_{44} and not so for C_{11} which is essentially due to the fact that $\chi_{44}^{0}/\chi_{11}^{0}\approx 10$ in the temperature range of interest. From Eqs. (5.22) and (5.23) we see that the effect of direct molecular interaction is to decrease T_{44} and increase T_{11}, the actual amount of decrease will depend upon other parameters like C_{44}^{0},C_{11}^{0} and values of $\chi_{11}^{0},\chi_{44}^{0}$. The maximum effect of direct interaction on T_{ii} in cyanides is found to be $\sim$20%.

D. Elastic constants C_{11} and C_{44} and transition temperature

Before presenting the results on the T dependence of $C_{11}(T)$ and $C_{44}(T)$ and the temperature where they approach zero, we would like to discuss the importance of anharmonic effects on C_{11} and C_{44}. It is well known[23] that anharmonic effects give rise to phonon-phonon interaction and renormalize the elastic constants, i.e.,

$$C_{ii}(T)=C_{ii}^{0}+\delta C_{ii}^{\mathrm{an}}(T)\ . \tag{6.5}$$

At high temperatures $\delta C_{ii}^{\mathrm{an}}(T)=-\gamma_i T$. For alkali-halide crystals careful elastic constant measurements[35-37] have been made and it is found that $\gamma_1\gg\gamma_4$. In order to incorporate anharmonicity effects in our calculation, we assume that

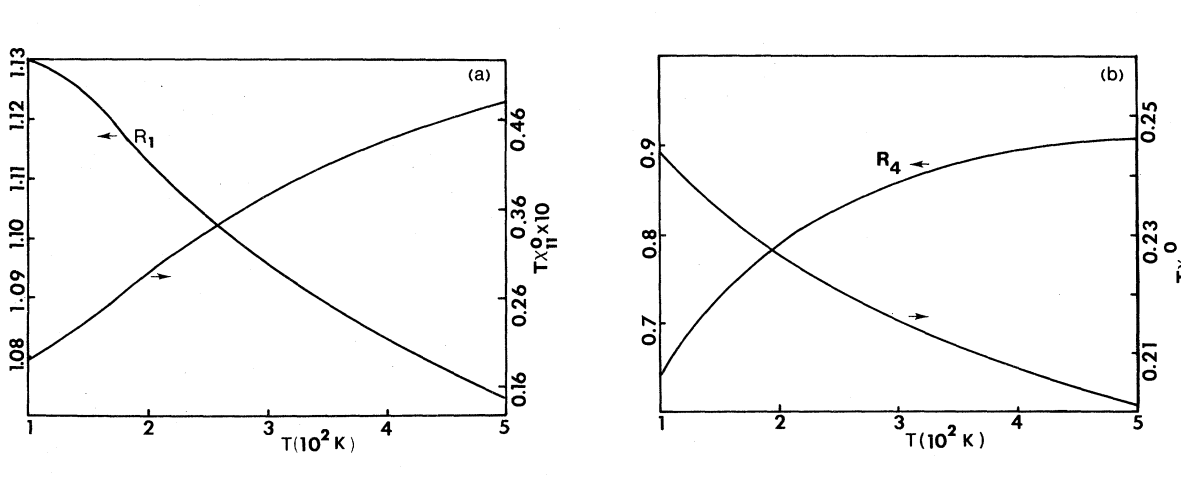

FIG. 2. Single-site susceptibility $\chi_{11}^{0}T$ and enhancement factor $R_1=\chi_{11}(T)/\chi_{11}^{0}(T)$ for e_g symmetry (KCN). (b) Single-site susceptibility $\chi_{44}^{0}T$ and enhancement factor $R_4=\chi_{44}(T)/\chi_{44}^{0}(T)$ for t_{2g} symmetry (KCN).

cyanides are equivalent to bromides[26] excepting for the nonzero translational-rotation coupling in the former and therefore use

$$\gamma_i(M\mathrm{CN})=\gamma_i(M\mathrm{Br}),\quad M=\mathrm{Na}\ ,\mathrm{K}\ ,\mathrm{Rb}\ . \qquad (6.6)$$

The values of γ_1 and γ_4 are given in Table V.

In the presence of both translational-rotational (tr-rot) coupling and anharmonicity effects, we then have

$$C_{ii}(T)=C_{ii}^0+\delta C_{ii}^{\mathrm{an}}(T)+\delta C_{ii}^{\text{tr-rot}}(T)\ , \qquad (6.7)$$

where $\delta C_{ii}^{\text{tr-rot}}(T)$ is given by Eqs. (5.22) and (5.23).

To calculate $C_{11}(T)$ and $C_{44}(T)$ we need to know the values of bare elastic constants C_{11}^0 and C_{44}^0. In their calculation[16] MN obtained C_{11}^0 and C_{44}^0 by fitting to the experimental value of the transition temperatures T_{44} and T_{11}. Since the present theory is of mean-field nature and therefore does not include fluctuation effects, we have obtained C_{11}^0 and C_{44}^0 by fitting to the experimental values of C_{11} and C_{44} at temperatures T_{fit} far above the transition temperature T_c. The values of T_{fit} are given in Table V and those of T_c in Table I.

As has been pointed out earlier, the value of the quadrupole moment that we have used in our calculation is $0.6Q_0$ compared to $0.5Q_0$ used by Bound *et al.* in their MD study. In Fig. 3 we give $C_{44}(T)$ vs T for three values of Q, i.e., $Q=0.5Q_0$, $0.6Q_0$, $0.75Q_0$ in the absence of anharmonicity effects. We find that the temperature at which $C_{44}\to 0$ are <100, 200, 300, respectively. Inclusion of anharmonicity effects reduces the transition temperatures further although by only a few percent. Since our theory of phonon softening is of mean-field nature, we expect that inclusion of fluctuation effects will reduce the transition temperature still further for $Q=0.5Q_0$ (away from the experimental value $T^*=156$ K). The choice $Q=0.6Q_0$ gives $T^*_{\mathrm{theor}}\gtrsim T^*_{\mathrm{expt}}$ and a reasonable fit over the entire range of the experiment. For $Q=0.75Q_0$ the agreement between theory and experiment for $T \gg T^*$ is rather poor. For all the cyanides, instead of choosing different values of Q to obtain an optimum fit, we have chosen $Q=0.6Q_0$. The overall agreement between theory and experiment (to be discussed shortly) using this value is quite good.

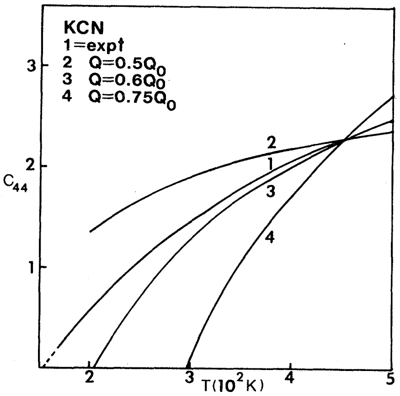

FIG. 3. T dependence of C_{44} (in units of 10^{11} dyn/cm^2) for KCN for different values of the (CN$^-$) quadrupole moment $Q=fQ_0$, where Q_0 is the free-ion value.

TABLE V. Anharmonicity parameters (γ_1,γ_4) bare elastic constants (C_{11}^0,C_{44}^0) and temperature T_{fit} where theoretical and experimental values are fitted.

	NaCN	KCN	RbCN
γ_1 (10^9 dyn/cm^{2}K)	0.26	0.27	0.28
γ_4 (10^9 dyn/cm^{2}K)	0.019	0.013	0.008
C_{11}^0 (10^{11} dyn/cm^2)	5.749	5.115	4.022
C_{44}^0 (10^{11} dyn/cm^2)	0.752	0.470	0.411
T_{fit} (K)	473	453	380

Before discussing individual systems separately we make a few general remarks. If we consider only the repulsion contribution to the translation-rotation coupling, i.e., $A_Q=B_Q=0$, then we find that $C_{11}\to 0$ at temperature T_{11} which is higher than T_{44} where $C_{44}\to 0$. Thus the repulsive forces tend to soften C_{11} much more than C_{44}. Since C_{11} couples to order parameter Y_1, one expects that $C_{11}\to 0$ will imply a nonzero $\langle Y_1\rangle$ in the ferroelastic phase. This corresponds to molecules orienting along the z axis with a concomitant tetragonal structure. Such a structure is not seen in the cyanides but in the superoxides. If on the other hand, we choose $A_R=B_R=0$ and $A_Q,B_Q\neq 0$, then we find that $T_{44}>T_{11}$ which is observed in the cyanides. Of course as can be seen from the Table IV, A_R, B_R, A_Q, and B_Q are all important for the cyanides. The fact that in these systems $T_{44}>T_{11}$ is due to the dominance of B_Q over B_R and a significant reduction in A_R caused by negative A_Q. Since the quadrupole moment of the O_2^- ion is about a factor of 2 smaller than that of (CN)$^-$ and since the short-range repulsion is stronger in the superoxides, we believe that the qualitative features of the ferroelastic instability in superoxides is determined by the short-range repulsive forces. However, for a quantitative understanding of the transition temperatures in superoxides, one has to include anisotropic (quadrupolar) electrostatic forces and the effect of orbital degen-

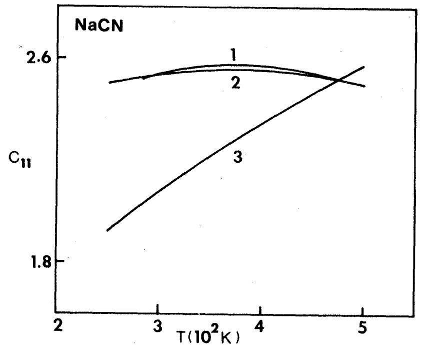

FIG. 4. T dependence of C_{11} (in units of 10^{11} dyn/cm^2) for NaCN. 1: experiment, 2: theory with anharmonicity, 3: theory without anharmonicity.

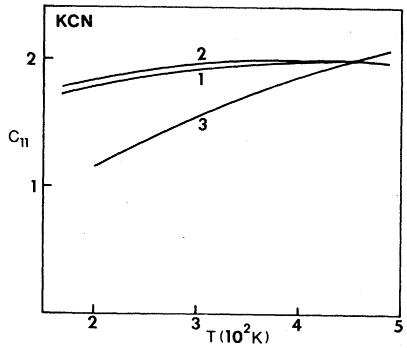

FIG. 6. T dependence of C_{11} (in units of 10^{11} dyn/cm^2) for KCN. 1: experiment, 2: theory with anharmonicity, 3: theory without anharmonicity.

eracy of the superoxide ion.

In Figs. 4–9, we give the T dependence of C_{11} and C_{44} with and without the inclusion of anharmonicity effect and compare with the experimental result. For NaCN and KCN, the overall agreement appears to be very good. In particular the peak in $C_{11}(T)$ is understood in terms of a competition between the two contributions to the renormalization of the elastic constants $\delta C_{11}^{\text{an}}$ and $\delta C_{11}^{\text{tr-rot}}$. For a proper understanding of the T dependence of C_{11} it is important to include the anharmonicity effect whereas for $C_{44}(T)$ this is not so. For RbCN, inclusion of anharmonicity effects in C_{11} gives a peak but at a much lower temperature than that seen experimentally. Our feeling is that although our calculations bring out the importance of various physical effects it is necessary to go beyond a simple mean-field theory for a complete understanding of the elastic softening in the orientationally disordered phases of molecular crystals. In this regard we propose to extend the work of Naudts and Mahanti[38] on spin-phonon systems and apply to molecular crystals.

The value of T_{44} is given in Table I. The effect of including anharmonicity is to reduce T_{44} by ~ 10 K. Comparing the theoretical values of T_{44} with T^* (see Table I), we see that the agreement is reasonably good in view of the mean-field nature of the present theory. Particularly remarkable is the trend in T_{44} in going from NaCN to RbCN. The T dependence of elastic constants in CsCN are not available but they will provide an additional test of the present microscopic theory.

E. Softening of phonons over the entire Brillouin zone

Strauch *et al.*[39] have used the translation-rotation (tr-rot) coupling model to calculate the phonon frequencies of NaCN and KNC at 300 K for the three symmetry directions [ζ00], [0$\zeta\zeta$], and [$\zeta\zeta\zeta$]. For the bare phonon frequencies which are determined by the dynamic matrix M^0, they have used a 10-parameter shell model. Translation-

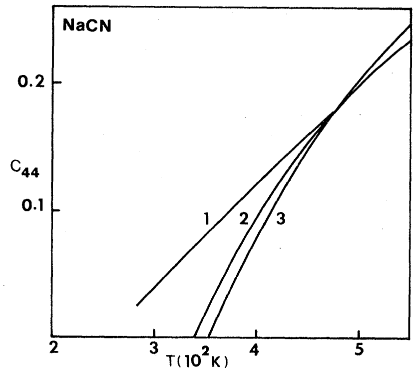

FIG. 5. T dependence of C_{44} (in units of 10^{11} dyn/cm^2) for NaCN. 1: experiment, 2: theory with anharmonicity, 3: theory without anharmonicity.

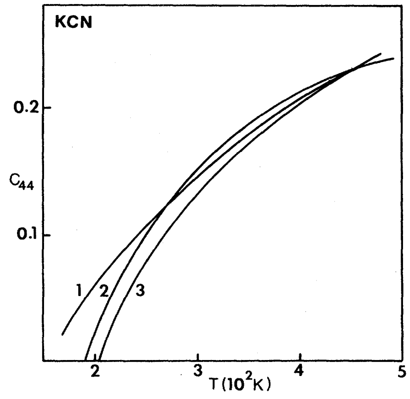

FIG. 7. T dependence of C_{44} (in units of 10^{11} dyn/cm^2) for KCN. 1: experiment, 2: theory with anharmonicity, 3: theory without anharmonicity.

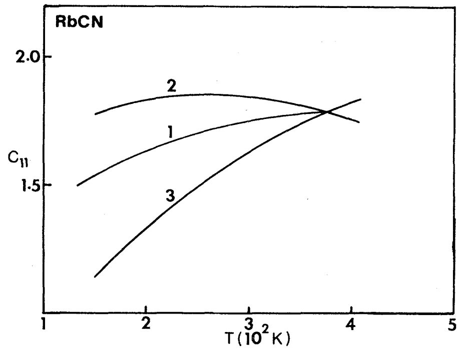

FIG. 8. T dependence of C_{11} (in units of 10^{11} dyn/cm^2) for RBCN. 1: experiment, 2: theory with anharmonicity, 3: theory without anharmonicity.

rotation coupling is incorporated by adding to M^0 a contribution δM given by

$$\delta M=\begin{bmatrix}\delta M_+ & 0\\ 0 & 0\end{bmatrix}, \tag{6.8}$$

where

$$\delta M_+ = -v\chi^0 v^\dagger , \tag{6.9}$$

where v and χ^0 are the tr-rot coupling and rotational susceptibility matrices discussed in Sec. III of this paper. Only the nearest-neighbor contributions to v, i.e., the interaction between a (CN)$^-$ ion and its nearest-neighbor M^+ ion was considered in Ref. 39 just as in Ref. 16. Strauch *et al.* did not include the direct interaction between the (CN)$^-$ molecules and therefore their renormalized phonon frequencies are the same as those given in Eq. (3.20) of this paper with $\chi_{\alpha\beta}(\vec{k},\omega)$ replaced by $\chi^0_{\alpha\beta}$, the single-site static susceptibility. Thus our results can be thought of as a generalization of their work.

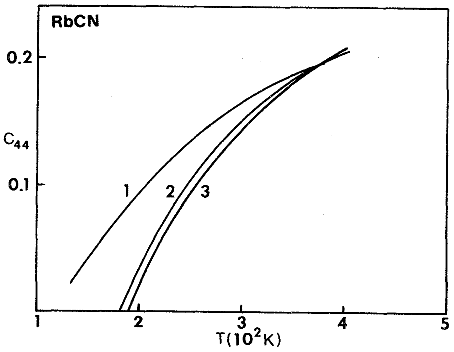

FIG. 9. T dependence of C_{44} (in units of 10^{11} dyn/cm^2) for RBCN. 1: experiment, 2: theory with anharmonicity, 3: theory without anharmonicity.

Since in the limit $\vec{k}\rightarrow 0$, δM_+ gives the renormalization of elastic constants, the latter completely determines δM_+ provided only nearest neighbors contribute to $v_{\alpha\mu}(\vec{k})$. Then knowing δC_{11} and δC_{44} at $T=300$ K, one can calculate $\omega^2_{j\vec{k}}-\omega^{02}_{j\vec{k}}$ for all values of $j\vec{k}$ at this temperature. Strauch *et al.* had to use values of δC_{11} and δC_{44} different from those obtained by Michel and Naudts[16] to fit to the experimental data. In our analysis of the short-range repulsion and quadrupole contribution to $v^{\pm}_{\alpha\mu}(\vec{k})$ we found that because of near perfect cancellation between second- and third-neighbor contributions to $v_{\alpha\mu}(\vec{k})$, considering only the nearest-neighbor contribution to $v_{\alpha\mu}(\vec{k})$, is an excellent approximation. However, both the above mechanisms contribute to $v^{+}_{\alpha\mu}(\vec{k})$. As we discuss below our present calculations provide a microscopic justification of the values of δC_{11} and δC_{44} chosen by Strauch *et al.* to fit to the experiment. Since these authors, with their phenomenological choice of δC_{11} and δC_{44}, found excellent agreement with experiment we will use their calculated values of $\omega^2_{j\vec{k}}-\omega^{02}_{j\vec{k}}$ as an experimental measure of the phonon renormalization.

We define a quantity $\Gamma^{j\vec{k}}=(\omega^{02}_{jk}-\omega^{2}_{jk})^{1/2}/10^{13}$ cps which is a measure of phonon renormalization. We have calculated $\Gamma^{j\vec{k}}$ for phonons propagating along the $[00k]$ direction by using Eq. (3.20) and noting that the tr-rot coupling matrix (including both short-range and quadrupole contributions) has typically a form like Eq. (5.5) with $k_x=k_y=0$ and $k_z=k$. In Table VI the results of our calculation of $\Gamma^{j\vec{k}}$ are given along with those obtained from the Fig. 1 of Ref. 39 where the phonon frequency $\nu=\omega/2\pi$ is given in units of THz. Using the appropriate polarization vectors of phonons given in Sec. V C it is easy to see that $\Gamma^{j\vec{k}}$ for the LA and TA phonons are determined by the rotational susceptibilities of e_g and t_{2g} symmetries, respectively. These susceptibilities in turn depend on the direct Q-Q interaction $D_{\alpha\beta}(\vec{k})$ through Eq. (4.10). We find that at $T\cong 300$ K inclusion of direct interaction affects LA phonon softening by about 7% whereas the TA phonons are affected by 5–25%. The TA phonons are influenced more strongly by direct interaction because at this temperature $\chi^0_{t_{2g}}/\chi^0_{e_g}\approx 10$, in spite of the fact that $D_{11}(k)$ is -704 K at $k=0$ and 1955 K at $k=k_{\text{BZ}}$ and that $D_{44}(k)$ is 235 K at $k=0$ and -652 K at $k=k_{\text{BZ}}$. As can be seen from Table VI, for LA modes our calculated values of $\Gamma^{j\vec{k}}$ are about 15–30% higher than experiment. This difference is due to the fact that for a proper calculation of phonon

TABLE VI. Renormalization of TA and LA phonons along [00k] direction; $\Gamma^i[(\omega_0^i)^2-(\omega^i)^2]^{1/2}/10^{13}$ cps; i = LA, TA.

$k/k_{\max}$	Γ^{TA} (present)	Γ^{TA} (Ref. 39)	Γ^{LA} (present)	Γ^{LA} (Ref. 39)
0	0	0	0	0
0.2	0.24	0.35(5)	0.71	0.61(5)
0.4	0.42	0.52	1.12	0.88
0.6	0.49	0.53	1.11	0.87
0.8	0.35	0.38(5)	0.71	0.56
1.0	0	0	0	0

softening one has to include the frequency dependence of $\chi_{\alpha\beta}(\vec{k},\omega)$. If one is far away from the phase transition temperature, i.e., $T > T_c$ (this may not be true for NaCN) then the frequency dependence of $\chi_{\alpha\beta}(\vec{k},\omega)$ is determined primarily by that of $\chi^0_{\alpha\beta}(\omega)$. The rotational dynamics at $T \cong 300$ K will be almost diffusive with a frequency scale $\Gamma_{\mathrm{rot}} \sim 0.5\times 10^{13}$ cps, i.e.,

$$\chi(\vec{k},\omega) \sim \chi(\vec{k},0)\frac{\Gamma^2}{\Gamma^2+\omega^2} \;.$$

On physical grounds[40] one expects that for high-frequency phonons ($\omega > \omega_{\mathrm{rot}}, \Gamma_{\mathrm{rot}}$) the effect of tr-rot coupling will be reduced from the values given in Table VI. This will improve agreement between theoretical and experimental values of $\omega_{\mathrm{LA}}(\vec{k})$.

On the other hand, for TA phonons one finds from Table VI that our calculated values of $\Gamma^{j\vec{k}}$ are smaller than the experimental values by about 7–32%, the large discrepancy being in the low-k region. However, because of the direct interaction, the agreement with experiment ($\sim$ Strauch *et al.*'s work) is fairly good for large values of k. Therefore, for the low-frequency TA phonons, if one approximates the rotational dynamics by a resonant-type behavior, i.e., by

$$\chi(\vec{k},\omega) \sim \chi(\vec{k},0)\frac{\Gamma^2}{\Gamma^2+(\omega-\omega_{\mathrm{rot}})^2}$$

with $\Gamma \sim \omega_{\mathrm{rot}}$, then one can improve the agreement between experiment and present theory. There is some evidence of the behavior of the form given above from the MD calculation.[21] For the high-frequency TA phonons though, the quantity $\Gamma^{j\vec{k}}$ may depend sensitively on the values of $\chi^0_{t_{2g}}$, $D_{44}(\vec{k})$, and the frequency scales involved and the above-mentioned quantitative agreement should be reexamined carefully. A quantitative study of the phonon softening including the proper frequency dependence of $\chi_{\alpha\beta}(\vec{k},\omega)$ is beyond the scope of the present work.

F. Conclusion

In summary, we believe that the anomalous thermoelastic properties and softening of phonons in the orientationally disordered phase of the cyanides can be adequately described by the tr-rot coupling model.[16,17] The physics of these systems depends sensitively on the competition between the short-range repulsive and anisotropic electrostatic (predominantly quadrupole-EFG interaction) forces.[17] Furthermore, anharmonicity effects are also important for a proper understanding of the T dependence of C_{11}. For the phonons in general, it is necessary to include the retardation effects by considering the frequency dependence of the rotational susceptibility $\chi_{\alpha\beta}(\vec{k},\omega)$. Fluctuation effects not included in the present mean-field theory approach should be considered for a better quantitative understanding. We propose to extend our theory to CsCN which has a different high-T cubic structure and see if we can understand the large ferroelastic transtition temperature[41] $T_{\mathrm{CsCN}} \simeq 200$ K. Finally for the alkali superoxides (which will be discussed in detail in a separate paper) short-range repulsion dominates over the quadrupole coupling and the orbital degeneracy of the superoxide ion plays an important role.

ACKNOWLEDGMENTS

We thank Dr. G. Kemeny and Dr. J. Naudts for helpful discussions. This work was partially supported by NSF Grant No. DMR 81-17297.

APPENDIX A: ROTATIONAL-TRANSLATIONAL COUPLING FROM QUADRUPOLE EFG INTERACTIONS

In this appendix we evaluate the coupling constant matrices arising from the contribution of various NN's to the electric field gradient. We explicitly consider the cases $\alpha = 1$ and $\alpha = 4$, other terms being readily obtainable from these by symmetry considerations.

1. First NN contribution

From (5.16), choosing the origin at $\vec{R}_i^0$

$$U_{zz}(a\hat{z})=-U_{zz}(-a\hat{z})=-\frac{3|e|}{a^4}2u_{jz},\ldots . \tag{A1}$$

We use (5.6), (5.15), (5.17), and (A1) and express the displacements $\vec{u}_j$ in terms of their Fourier components and obtain for $\alpha=1$ [see Eq. (5.6) for the definition of S_x, C_x, etc.]. We have

$$\sum_i QY_1(\hat{n}_i)U_1^i=2iA_Q\sum_{\vec{k}}Y_1^\dagger(\vec{k})[u_x(\vec{k})S_x+u_y(\vec{k})S_y -2u_z(\vec{k})S_z] , \tag{A2}$$

where

$$A_Q=\sqrt{9\pi/5}\frac{Q|e|}{a^4} \tag{A3}$$

so that

$$v_{1\mu}^{\mathrm{EFG}}(+|\vec{k})_1=2A_Q\begin{bmatrix} S_x \\ S_y \\ -2S_z \end{bmatrix} . \tag{A4}$$

Similarly for $\alpha=4$,

$$U_{xz}(a\hat{z})=-U_{xz}(-a\hat{z})=\frac{3|e|}{a^4}u_{jx},\ldots , \tag{A5}$$

$$\sum_i QY_4(\hat{n}_i)U_4^i=2iB_Q\sum_{\vec{k}}Y_4^\dagger(\vec{k})[u_x(\vec{k})S_z+u_z(\vec{k})S_x] , \tag{A6}$$

where

$$B_Q=-\sqrt{2/3}A_Q , \tag{A7}$$

and therefore,

$$v_{4\mu}^{EFG}(+|\vec{k})_1=2B_Q\begin{bmatrix} S_z \\ 0 \\ S_x \end{bmatrix} . \tag{A8}$$

Hence we obtain

$$v_{\alpha\mu}^{\mathrm{EFG}}(+|\vec{k})_1=2\begin{bmatrix} A_QS_x & -A_QS_x & B_QS_y & B_QS_z & 0 \\ A_QS_y & A_QS_y & B_QS_x & 0 & B_QS_z \\ -2A_QS_z & 0 & 0 & B_QS_x & B_QS_y \end{bmatrix} . \tag{A9}$$

2. Second NN contribution

From (5.16) we again obtain

$$U_{zz}(a\hat{x}+a\hat{y})=-U_{zz}(-a\hat{x}-a\hat{y}) =-\frac{3|e|}{2^{5/2}a^4}(u_{jx}+u_{jy}) , \tag{A10}$$

$$U_{zz}(a\hat{x}-a\hat{y})=-U_{zz}(-a\hat{x}+a\hat{y}) =-\frac{3|e|}{2^{5/2}a^4}(u_{jx}-u_{jy}) ,$$

and

$$\sum_i QY_1(\hat{n}_i)U_1^i =i2\bar{A}_Q\sum_{\vec{k}}Y_1^\dagger(\vec{k})[u_x(\vec{k})S_x(3C_z-2C_y) +u_y(\vec{k})S_y(3C_z-2C_x) +u_z(\vec{k})S_z(C_x+C_y)] , \tag{A11}$$

where

$$\bar{A}_Q=\frac{1}{4\sqrt{2}}A_Q \tag{A12}$$

so that

$$v_{1\mu}^{\mathrm{EFG}}(-|\vec{k})_2=2\bar{A}_Q\begin{bmatrix} S_x(3C_z-2C_y) \\ S_y(3C_z-2C_x) \\ -S_z(C_x+C_y) \end{bmatrix} . \tag{A13}$$

Similarly with

$$\bar{B}_Q=\frac{1}{4\sqrt{2}}B_Q , \tag{A14}$$

we obtain

$$v_{2\mu}^{\mathrm{EFG}}(-|\vec{k})_2=\tfrac{2}{3}\bar{A}_Q\begin{bmatrix} S_x(C_z-4C_y) \\ S_y(4C_x-C_z) \\ 5S_z(C_x-C_y) \end{bmatrix} ,$$

$$v_{3\mu}^{\mathrm{EFG}}(-|\vec{k})_2=2\bar{B}_Q\begin{bmatrix} S_y(3C_x-2C_z) \\ S_x(3C_y-2C_z) \\ 0 \end{bmatrix} , \tag{A15}$$

$$v_{4\mu}^{\mathrm{EFG}}(-\,|\,\vec{\mathrm{k}})_2=2\bar{B}_Q\begin{bmatrix}S_z(3C_x-2C_y)\\0\\S_x(3C_x-2C_y)\end{bmatrix},$$

and

$$v_{5\mu}^{\mathrm{EFG}}(-\,|\,\vec{\mathrm{k}})_2=2\bar{B}_Q\begin{bmatrix}0\\S_z(3C_y-2C_x)\\S_y(3C_z-2C_x)\end{bmatrix}.$$

3. Third NN contribution

Defining

$$\bar{\bar{A}}=-\frac{8}{27\sqrt{3}}A_Q\,, \tag{A16}$$

$$\bar{\bar{B}}=-\frac{8}{27\sqrt{3}}B_Q\,, \tag{A17}$$

we obtain the following terms for the coupling constant matrix:

$$v_{1\mu}^{\mathrm{EFG}}(+\,|\,\vec{\mathrm{k}})_3=2\bar{\bar{A}}_Q\begin{bmatrix}S_xC_yC_z\\S_yC_xC_z\\-2S_zC_xC_y\end{bmatrix},$$

$$v_{2\mu}^{\mathrm{EFG}}(+\,|\,\vec{\mathrm{k}})_3=2\bar{\bar{A}}_Q\begin{bmatrix}-S_xC_yC_z\\S_yC_zC_x\\0\end{bmatrix},$$

$$v_{3\mu}^{\mathrm{EFG}}(+\,|\,\vec{\mathrm{k}})_3=2\bar{\bar{B}}_Q\begin{bmatrix}S_yC_zC_x\\S_xC_yC_z\\-\tfrac{5}{2}S_xS_yS_z\end{bmatrix}, \tag{A18}$$

$$v_{4\mu}^{\mathrm{EFG}}(+\,|\,\vec{\mathrm{k}})_3=2\bar{\bar{B}}_Q\begin{bmatrix}S_zC_xC_y\\-\tfrac{5}{2}S_xS_yS_z\\S_xC_yC_z\end{bmatrix},$$

$$v_{5\mu}^{\mathrm{EFG}}(+\,|\,\vec{\mathrm{k}})_3=2\bar{\bar{B}}_Q\begin{bmatrix}-\tfrac{5}{2}S_xS_yS_z\\S_zC_xC_y\\S_yC_zC_x\end{bmatrix}.$$

APPENDIX B: ROTATIONAL-TRANSLATIONAL COUPLING FROM SHORT-RANGE REPULSION

Equations (A13) and (A15) of Ref. 16 are correct. There is an error of a factor of $1/\sqrt{2}$ in Eq. (A14) where $B_R\equiv B$ is expressed in terms of $\vec{\mathrm{P}}^{(1)}(a_z;\Omega)$, but the other equations are correct. The parameters A and B (which are A_R and B_R in the present paper) are

$$A_R\equiv A=\sqrt{5\pi}C_1C_2(d^2+a^2)^{-1/2}\times[a(3f_2-f_0)+d(f_1-3f_3)]\,, \tag{B1}$$

$$B_R\equiv B=-\sqrt{30\pi}C_1C_2(d^2+a^2)^{-1/2}d(f_1-f_3)\,, \tag{B2}$$

where

$$f_n=g^{-(n+1)}\int_{\sqrt{1-g}}^{\sqrt{1+g}}(1-y^2)^ne^{-hy}dy \tag{B3}$$

and

$$h=C_2(d^2+a^2)^{1/2}\,, \tag{B4}$$

$$g=2da/(d^2+a^2)\,. \tag{B5}$$

In the above equations C_1,C_2 are the repulsion parameters discussed in Sec. VI A of the text , $2d$ is the internuclear separation, and a is the distance between the (CN)$^-$ ion and its nearest M^+ ion.

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