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Landau theory of the ferroelastic phase transition in ionic molecular solids: A microscopic approach

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Starting from Bogolyubov's inequality, we derive a variational form for the Helmholtz free energy F to study the ferroelastic phase transitions in simple ionic molecular solids. The coefficients of the Landau expansion of F in terms of the five orientational order parameters (η_i, $i=1,\ldots,5$) are calculated from a rotation-translation Hamiltonian which has been used with reasonable success to explain the thermoelastic anomalies of the orientationally disordered phase. Detailed calculations have been performed for CsCN to understand the first-order phase transition from the pseudocubic ($Pm3m$) to trigonal ($R3m$) phase. Various aspects of this transition resulting from the interplay of direct and lattice-mediated interactions and limitations of the currently used models to describe the physical properties of alkali cyanides are discussed.

I. INTRODUCTION

A general characteristic of a large class of molecular solids is that at high temperatures (T) they possess crystal structures of cubic symmetry and with decreasing temperature undergo ferroelastic phase transitions to structures with lower symmetry. The nature of these structural phase transitions is primarily governed by the orientational degrees of freedom of the molecular species and its coupling to the translational degrees of freedom. At high temperatures, thermal reorientation of molecules makes them effectively spherical so far as the average structure is concerned. Typical examples are alkali cyanides[1] and alkali superoxides[2] which have either pseudocubic NaCl or CsCl structures at high T and undergo ferroelastic phase transitions to (excepting NaO_2) orthorhombic, tetragonal or trigonal structures with decreasing T.

In all these systems, the molecules undergo large-amplitude orientational motion at temperatures of interest,[3] and there is strong coupling between translational and orientational degrees of freedom. The latter results in an effective interorientational interaction which, in most cases, is stronger that the direct interaction between the molecules[1] Competition between (a) direct and lattice-mediated interactions, (b) short-range repulsion and anisotropic electrostatic interaction contributions to rotational-translational coupling, and (c) intermolecular and single-site interactions are some of the interesting features of these systems. The main purpose of the present study is to calculate the free energy of these systems starting from a microscopic Hamiltonian and to make a systematic study of the above-mentioned competing processes. In particular, we relate the coefficients in the Landau free-energy expansion to parameters appearing in the rotational-translational Hamiltonian which has been reasonably successful in understanding the anomalous thermoelastic properties of alkali cyanides.[4-7] The reason for choosing the cyanides instead of the superoxides is that they have not only been thoroughly studied by various experimental techniques[8-10] but also in recent years molecular-dynamics simulations[11] have been performed in these systems. A comparison between simulation studies and those using different theoretical methods can, in principle, shed light on the adequacy of the rotation-translation Hamiltonian and the methods used to solve them.

Until now, there has been only one serious theoretical attempt[12] to understand the structure of the ferroelastic phase of the cyanides starting from a microscopic Hamiltonian. In addition to certain limitations of the theory (to be discussed in detail in Sec. IV) this work was unable to explain the (110) orientational ordering in NaCN and KCN.[1] In this paper we derive a variational form of the free energy starting from Bogolyubov's inequality[13] which differs considerably from that obtained in Ref. 12 and then analyze qualitatively various terms in the free energy that can give rise to the above-mentioned (110) ordering. But for detailed numerical investigation, we have chosen CsCN which shows (111) ordering instead. We hope to go back to the question of (110) ordering in KCN and NaCN after obtaining a better understanding of the microscopic Hamiltonian.

The outline of this paper is as follows. In Sec. II we derive an effective orientational Hamiltonian starting from the translational-rotational Hamiltonian studied in Ref. 6. In Sec. III we briefly describe the order parameters η_i, their symmetry, and the variational principle used to obtain Helmholtz's free energy F. In Sec. IV the expansion of F in powers of η_i's is given and the coefficients are related to second-, third- and fourth-order single-site orientational susceptibilities. Also in this section we compare our theory with that of Ref. 12. Finally in Sec. V we apply our theory to CsCN and discuss the limitations of the present model.

II. EFFECTIVE ORIENTATIONAL HAMILTONIAN

The Hamiltonian, describing the rotational and translational dynamics of the molecular solids, has been studied by many authors[3–7] in the past. For the purpose of the present paper we will use the notations of Ref. 6. The total Hamiltonian H can be written as a sum of translational (H_t), rotational (H_r), and rotational-translational (H_{tr}) parts; these are given by

$$H_t=\sum_{j,\vec{k}} \hbar\omega^0_{j\vec{k}}(b^\dagger_{j\vec{k}}b_{j\vec{k}}+\tfrac{1}{2}) , \tag{2.1}$$

$$H_r=\sum_{\vec{k}}\sum_{\lambda=1}^{2}(1/2I_\lambda)L^\dagger_\lambda(\vec{k})L_\lambda(\vec{k})+\sum_{i=1}^{N}V_0(\hat{n}_i)$$

$$+\tfrac{1}{2}\sum_{\vec{k}}\sum_{\alpha,\beta}D_{\alpha\beta}(\vec{k})Y^\dagger_\alpha(\vec{k})Y_\beta(\vec{k}) , \tag{2.2}$$

$$H_{tr}=i\sum_{\vec{k},j,\alpha}Y^\dagger_\alpha(\vec{k})V_{\alpha j}(\vec{k})(b_{j\vec{k}}+b^\dagger_{j-\vec{k}}) . \tag{2.3}$$

In Eq. (2.1), ω^0_{jk} is the frequency of bare phonons of wave vector $\vec{k}$ and polarization index j; $b_{j\vec{k}}$ ($b^\dagger_{j\vec{k}}$) are the corresponding phonon destruction (creation) operators. In Eq. (2.2), I is the moment of inertia of the molecular ion (treated as a dumbbell) about each of the two principal axes, $\vec{L}(\vec{k})$ is the fourier transform of the angular-momentum operator $\vec{L}_i$, $V_0(\hat{n}_i)$ is the single-site potential as a function of the orientation $\hat{n}_i$ of the ith molecule, $D_{\alpha\beta}(\vec{k})$ is the Fourier transform of the direct intermolecular interaction, and $Y_\alpha(\vec{k})$ ($\alpha=1$–5) are the Fourier transforms of $Y_\alpha(\hat{n}_i)$ which are properly symmetrized linear combinations of spherical harmonics of order 2. In contrast to Refs. 4, 6, and 7, Y_α's in this paper are normalized to unity. The coupling constants $V_{\alpha j}(\vec{k})$ are given by [see Eq. (2.20) of Ref. 6]

$$V_{\alpha j}(\vec{k})=[(1/(2\omega^0_{j\vec{k}})^{1/2}]$$

$$\times\sum_{\mu,\,\kappa=\pm}(1/\sqrt{m_\kappa})e_\mu(\kappa\,|\,\vec{k},j)v_{\mu\alpha}(\kappa\,|\,\vec{k}) , \tag{2.4}$$

where $e_\mu(\kappa\,|\,\vec{k},j)$ is the μth component of the polarization vector associated with the mode $(j,\vec{k})$; m_κ ($\kappa=+,-$) are the ionic masses. The coupling-constant matrix $v_{\mu\alpha}(\kappa\,|\,\vec{k})$ has been worked out in detail in Ref. 6.[14]

For studying the thermodynamics of ferroelastic phase transitions described by the Hamiltonian H, we assume that the rotational degrees of freedom can be treated classically, i.e., we assume that $\vec{L}$ and Y_α's commute and ignore rotational kinetic-energy contributions to the free energy. We then use a canonical transformation to remove the linear coupling H_{tr} and obtain an effective rotational Hamiltonian H_r^{eff} which is given by

$$H_r^{\text{eff}}=\sum_{i=l}^{N}V_0(\hat{n}_i)$$

$$+\tfrac{1}{2}\sum_{\vec{k}}\sum_{\alpha,\beta}[D_{\alpha\beta}(\vec{k})+I_{\alpha\beta}(\vec{k})]Y^\dagger_\alpha(\vec{k})Y_\beta(\vec{k}) , \tag{2.5}$$

where

$$I_{\alpha\beta}(\vec{k})=-\sum_j 2V^*_{\alpha j}(\vec{k})V_{\beta j}(\vec{k})/(\hbar\omega^0_{j\vec{k}}) \tag{2.6}$$

is the Fourier transform of the indirect lattice-mediated interaction between the molecules, j being the summation over acoustic- and optical-phonon branches. The real-space Fourier transform of $I_{\alpha\beta}(\vec{k})$ gives the indirect interaction $I_{\alpha\beta}(\vec{R}_i-\vec{R}_j)=I_{\alpha\beta}(ij)$ between two molecules situated at sites $\vec{R}_i$ and $\vec{R}_j$, respectively. It is well known that the term with $\vec{R}_i=\vec{R}_j$, i.e., the self-term does not vanish[12] and gives rise to a modification of the single-site potential $V_0(\hat{n}_i)$. We can rewrite H_r^{eff} in terms of orientational variables $Y_\alpha(\hat{n}_i)\equiv Y_\alpha(i)$ as

$$H_r^{\text{eff}}=\sum_i[V_0(i)+V_s(i)]+\tfrac{1}{2}\sum_{i,j}{}'\sum_{\alpha\beta}T_{\alpha\beta}(i,j)Y_\alpha(i)Y_\beta(j) , \tag{2.7}$$

where the self-term $V_s(i)$ is given by the equation

$$V_s(i)=\sum_{\alpha,\beta}\sum_{\vec{k}}I_{\alpha\beta}(\vec{k})Y_\alpha(i)Y_\beta(i) \tag{2.8}$$

and possesses cubic symmetry (contains only terms up to fourth order in Kubic harmonics). The prime in Eq. (2.7) implies that $i\neq j$ and the total interaction $T_{\alpha\beta}(ij)$ is a sum of direct $D_{\alpha\beta}(ij)$ and indirect $I_{\alpha\beta}(ij)$ intermolecular interactions. Note that $D_{\alpha\beta}(ii)=0$.

The major contribution to $D_{\alpha\beta}(ij)$ comes from quadrupole-quadrupole (Q-Q) interaction between two $(\mathrm{CN})^-$ molecules. The short-range repulsion and anisotropic dispersion interactions are usually small[15] and can be neglected excepting for maybe NaCN. In the present paper and our earlier work in these systems[6] we have neglected these contributions to $D_{\alpha\beta}(ij)$. Because of the short-range nature of the Q-Q interaction $D_{\alpha\beta}(\vec{k})$ is well behaved as $\vec{k}\to\vec{0}$ [$D_{\alpha\beta}=D_{\alpha\beta}(\vec{k}=\vec{0})$]. For cubic symmetry, $D_{11}=D_{22}$ (e_g symmetry) and $D_{33}=D_{44}=D_{55}$ (t_{2g} symmetry). In contrast, the lattice-mediated interaction $I_{\alpha\beta}(i,j)$ is usually long ranged which is reflected in the nonanalytic behavior of $I_{\alpha\beta}(\vec{k})$ as $\vec{k}\to\vec{0}$ (see Bergman and Halperin[16] and Gehring and Marques[17]). This nonanalytic behavior can be avoided by separating out the long-range strain and considering phonon excitations of the strained lattice.[18] An alternate procedure was pointed out by Elliott *et al.*[19] who found that one could incorporate the effects of strain-mediated interaction by analyzing the negative eigenvalues of $T_{\alpha\beta}(\vec{k})$ matrix in the limit $\vec{k}\to\vec{0}$ and considering the eigenvalue with largest magnitude. In our present calculation we will follow this procedure although the effect of choosing a given direction in $\vec{k}$ space breaks the cubic symmetry. This point will be discussed in detail in Secs. IV and V.

We would like to point out that $I_{\alpha\alpha}(\vec{k}\to\vec{0})$ is always negative, i.e., ferrodistortive, whereas $D_{\alpha\alpha}(\vec{k}\to\vec{0})=D_{\alpha\alpha}$ can be either positive or negative depending on the symmetry of the lattice. For example, for the NaCl structure $D_{11}=D_{22}<0$ and $D_{33}=D_{44}=D_{55}>0$, and for the CsCl structure $D_{11}=D_{22}>0$ and $D_{33}=D_{44}=D_{55}<0$. This leads to different interplay between direct and lattice-mediated interactions in molecular solids with these two different structures.

III. ORDER PARAMETERS AND VARIATIONAL PRINCIPLE

Since we have eliminated the linear rotational-translational coupling by a displaced oscillator transformation,[19] the displaced phonons are still harmonic and the structural phase transition is determined solely by H_r^{eff}. Once there is order in the rotational system, the lattice deformation in the ordered (ferrodistortive) phase will follow the orientational order parameters and can be calculated simply by using the equations of displaced oscillator transformation. We therefore choose the molecular orientations as order parameters. For the ferrodistortive case we choose

$$\langle Y_\alpha(\vec{k})\rangle=\delta_{\vec{k},\vec{0}}\eta_\alpha=\langle Y_\alpha(\hat{n}_i)\rangle \ . \tag{3.1}$$

We next derive a variational form for the free energy (to be denoted as F_{var}) associated with the effective rotational Hamiltonian H_r^{eff} given in Eq. (2.7). We start from the Bogolyubov's variational principle[13] which states that for a given Hamiltonian H,

$$\begin{aligned} F_{\text{exact}} &= -kT\ln \text{Tr}e^{-\beta H} \\ &\le F_{\text{var}}=\text{Tr}(\rho_T H)+kT\,\text{Tr}(\rho_T \ln\rho_T) \end{aligned} \tag{3.2}$$

where ρ_T is a trial density matrix satisfying the equation $\text{Tr}\,\rho_T=1$. If we choose

$$\rho_T=\rho_{\text{exact}}=\exp(-\beta H)/\text{Tr}\exp(-\beta H) \ ,$$

then we have $F_{\text{var}}=F_{\text{exact}}$. For the trial density matrix we choose the form

$$\rho_T=\prod_i \rho_{it} \ , \tag{3.3}$$

$$\rho_{it}=e^{-\beta H_i}/\text{Tr}e^{-\beta H_i} \ , \tag{3.4}$$

$$H_i=V_0(i)+V_s(i)+\sum_\alpha h_\alpha(i)Y_\alpha(i) \ . \tag{3.5}$$

The variational parameters in F_{var} are the ordering fields $h_\alpha(i)$. Instead of $h_\alpha(i)$'s we choose $\eta_{i\alpha}$'s as variational parameters where $\eta_{i\alpha}$'s are related to $h_\alpha(i)$'s by

$$\eta_{i\alpha}=\text{Tr}_i\rho_{it}Y_\alpha(i) \ . \tag{3.6}$$

Thus $\eta_{i\alpha}$'s are functions of $h_\alpha(i)$'s and we formally invert Eq. (3.6) and express F_{var} in terms of $\eta_{i\alpha}$. Since we are dealing with ferroelastic transitions, we choose

$$\eta_{i\alpha}=\eta_\alpha \quad \text{for all } i \ ,$$

and obtain

$$\begin{aligned} F_{\text{var}}=\tfrac{1}{2}&\sum_{i,j}{}' T_{\alpha\beta}(ij)\eta_\alpha\eta_\beta \\ &-N[h_\alpha\eta_\alpha+\tfrac{1}{2}h_\alpha h_\beta\chi^0_{\alpha\beta} \\ &\quad -\tfrac{1}{6}h_\alpha h_\beta h_\gamma\chi^0_{\alpha\beta\gamma}+\tfrac{1}{24}(h_\alpha h_\beta h_\gamma h_\delta\chi^0_{\alpha\beta\gamma\delta} \\ &\quad -3\beta h_\alpha h_\beta h_\gamma h_\delta\chi^0_{\alpha\beta}\chi^0_{\gamma\delta})]+\cdots \ , \end{aligned} \tag{3.7}$$

where the generalized single-site susceptibilities $\chi^0_{\alpha\beta\gamma\delta,\ldots}$ are

$$\chi^0_{\alpha\beta}=\beta\langle Y_\alpha Y_\beta\rangle_0 \ , \tag{3.8a}$$

$$\chi^0_{\alpha\beta\gamma}=\beta^2\langle Y_\alpha Y_\beta Y_\gamma\rangle_0 \ , \tag{3.8b}$$

$$\chi^0_{\alpha\beta\gamma\delta}=\beta^3\langle Y_\alpha Y_\beta Y_\gamma Y_\delta\rangle_0 \ . \tag{3.8c}$$

In Eq. (3.7) and in what follows we use the convention that repeated indices imply summation, and in Eqs. (3.8a)–(3.8c), $\langle\ \rangle_0$ is the thermal average taken over the single-site potential $V_T(i)=V_0(i)+V_s(i)\equiv V_T(\hat{n}_i)=V_T(\Omega)$, i.e.,

$$\langle Q\rangle_0=\int e^{-\beta V_T(\Omega)}Q(\Omega)d\Omega \Big/ \int e^{-\beta V_T(\Omega)}d\Omega \ . \tag{3.9}$$

IV. LANDAU EXPANSION OF FREE ENERGY

In order to obtain a variational form for the free energy F_{var} in terms of the five order parameters $\eta_1,\ldots,\eta_5$, we start from the Eq. (3.7) which gives F_{var} in terms of the ordering fields $h_1,\ldots,h_5$ and eliminate h_α's in favor of η_α's using Eq. (3.6), which (dropping the i suffix for the ferroelastic phase) can be formally inverted to give

$$h_\alpha=\phi^0_{\alpha\delta}\eta_\delta+\phi^0_{\alpha\delta\delta'}\eta_\delta\eta_{\delta'}+\phi^0_{\alpha\delta\delta'\delta''}\eta_\delta\eta_{\delta'}\eta_{\delta''}+\cdots \ . \tag{4.1}$$

Substituting this in the equation

$$\eta_\alpha=\chi^0_{\alpha\beta}h_\beta+\chi^0_{\alpha\beta\gamma}h_\beta h_\gamma+\cdots \ , \tag{4.2}$$

we obtain

$$\phi^0_{\alpha\beta}=-[(\chi^0)^{-1}]_{\alpha\beta} \ , \tag{4.3}$$

$$\phi^0_{\alpha\delta\delta'}=-\tfrac{1}{2}\phi^0_{\alpha\mu}\phi^0_{\delta\gamma}\phi^0_{\delta'\epsilon}\chi^0_{\mu\gamma\epsilon} \ . \tag{4.4}$$

Since we are interested in expanding F_{var} only up to fourth order in η_α's, it turns out that we do not need $\phi^0_{\alpha\delta\delta'\delta''}$. Substituting for h_α in F_{var} and eliminating $\phi^0_{\alpha\delta}$, etc., we obtain

$$\begin{aligned} (1/N)(F_{\text{var}}-F_0)&=\tfrac{1}{2}[T_{\alpha\beta}(\vec{k}\to\vec{0})+1/P_\alpha]\eta_\alpha\eta_\beta-\tfrac{1}{6}(P_\alpha P_\beta P_\gamma)^{-1}\chi^0_{\alpha\beta\gamma}\eta_\alpha\eta_\beta\eta_\gamma \\ &\quad -\tfrac{1}{24}(P_\alpha P_\beta P_\gamma P_\delta)^{-1}[\chi^0_{\alpha\beta\gamma\delta}-3\beta P_\alpha P_\gamma\delta_{\alpha\beta}\delta_{\gamma\delta}-(3/P_\rho)\delta_{\rho\sigma}\chi^0_{\alpha\beta\rho}\chi^0_{\gamma\delta\sigma}]\eta_\alpha\eta_\beta\eta_\gamma\eta_\sigma \\ &=f_2+f_3+f_4 \end{aligned} \tag{4.5}$$

where $P_\alpha=\beta\langle Y_\alpha^2\rangle_0$, F_0 is the free energy in the disordered phase, and

$$T_{\alpha\beta}(\vec{k}\to\vec{0})=D_{\alpha\beta}(\vec{k}=\vec{0})+I_{\alpha\beta}(\vec{k}\to\vec{0})-\sum_{\vec{k}}I_{\alpha\beta}(\vec{k}) \ . \tag{4.6}$$

The last term in Eq. (4.6) is the second self-energy contribution in molecular solids, the first one contributing to the modification of the single-site potential $V_T(i)$. The limit $\vec{k}\to\vec{0}$ is necessary because of the nonanalyticity of $I_{\alpha\beta}(\vec{k})$ in this limit.

Since $V_T(i)$ possesses cubic symmetry, the susceptibilities $\chi^0_{\alpha\beta}$, $\chi^0_{\alpha\beta\gamma}$, $\chi^0_{\alpha\beta\gamma\delta}$, and consequently the third and fourth order terms in $F_{\text{var}}-F_0$, can be considerably simplified. The nonanalyticity of $I_{\alpha\beta}(\vec{k}\to\vec{0})$ breaks the symmetry in the second-order term. As has been discussed earlier, we will choose the direction of $\vec{k}$ and the combination of η_α's which give the lowest eigenvalue of $I_{\alpha\beta}(\vec{k}\to\vec{0})$. Since the third- and fourth-order terms do not depend on $\vec{k}$, we can simplify them by using cubic symmetry. After a considerable amount of algebra we obtain the following results for f_3 and f_4 of Eq. (4.5):

$$f_3=-(\tfrac{1}{6})[A_{3,1}\eta_1(\eta_1^2-3\eta_2^2)+A_{3,2}\eta_3\eta_4\eta_5+A_{3,3}[\eta_1(2\eta_3^2-\eta_4^2-\eta_5^2)+\sqrt{3}\eta_2(\eta_5^2-\eta_4^2)]$$

and

$$\begin{aligned}f_4=(\tfrac{1}{24})[&A_{4,1}(\eta_1^2+\eta_2^2)^2+A_{4,2}(\eta_3^4+\eta_4^4+\eta_5^4)+A_{4,3}(\eta_3^2\eta_4^2+\eta_4^2\eta_5^2+\eta_5^2\eta_3^2)+B_{4,1}\eta_1^2\eta_3^2+B_{4,2}\eta_1^2(\eta_4^2+\eta_5^2)\\&+B_{4,3}\eta_2^2\eta_3^2+B_{4,4}\eta_2^2(\eta_4^2+\eta_5^2)+B_{4,5}\eta_1\eta_2(\eta_4^2-\eta_5^2)]\ ,\end{aligned}\tag{4.8}$$

where the coefficients $A_{3,i}$ and $B_{4,i}$ are given in Table I. Cubic symmetry requires that the coefficients $B_{4,1},\ldots,B_{4,5}$ must satisfy certain symmetry conditions which are discussed in Appendix A. These symmetry relations provide strong checks not only the correctness of Eq. (4.8), but also on the numerical evaluation of these coefficients which will be presented in Sec. V. The susceptibilities that determine these Landau coefficients are given in Appendix B.

A. Comparison with earlier theory

The only other attempt to understand the low-temperature structure in the ferroelastic phase of alkali cyanides starting from a microscopic Hamiltonian has been made recently by deRaedt, Binder, and Michel (DBM).[12] The approach of the present paper differs from that of DBM in two essential ways. The first is related to the form of the Landau free energy used in the minimization procedure and the second is related to the averaging procedure used to take into consideration the long-range nature of the indirect lattice-mediated interaction and its shape dependence. We will discuss these two points separately.

DBM start from a Hamiltonian of the form given in Eq. (2.5) (they assume the direct interaction to be unimportant) and obtain an effective mean-field Hamiltonian H_r^{eff} which is given by

$$\begin{aligned}H_r^{\text{eff}}=H_r^0-&\sum_i\langle Y_\alpha(i)\rangle C_{\alpha\beta}Y_\beta(i)\\&+\tfrac{1}{2}\sum_i\langle Y_\alpha(i)\rangle C_{\alpha\beta}\langle Y_\beta(i)\rangle\ ,\end{aligned}\tag{4.9}$$

where

$$C_{\alpha\beta}=\sum_{j\neq i}I_{\alpha\beta}(i,j)\tag{4.10}$$

and H_r^0 is the single-site Hamiltonian $\sum_i V_T(i)$. The free energy is calculated using the equation

$$F_{\text{MF}}=-kT\ln\text{Tr}\,e^{-\beta H_r^{\text{eff}}}\ .\tag{4.11}$$

Instead of calculating $\langle Y_\alpha(i)\rangle$ from the self-consistency equation

$$\langle Y_\alpha(i)\rangle=\text{Tr}[e^{-\beta H_r^{\text{eff}}}Y_\alpha(i)]/\text{Tr}e^{-\beta H_r^{\text{eff}}}\tag{4.12}$$

and substituting it in Eq. (4.11) to obtain the free energy

TABLE I. Third- ($A_{3,i}$) and fourth- ($A_{4,i}$ and $B_{4,i}$) order Landau coefficients in terms of generalized free-molecule susceptibilities: $\chi^0_{\alpha\beta}\equiv(\alpha\beta)$, $\chi^0_{\alpha\beta\gamma}\equiv(\alpha\beta\gamma)$, $\chi^0_{\alpha\beta\gamma\delta}=(\alpha\beta\gamma\delta)$, and $\beta=1/kT$.

Coefficient	Expression
$A_{3,1}$	$(111)/(11)^3$
$A_{3,2}$	$6(345)/(33)^3$
$A_{3,3}$	$(3/2)(331)/(11)(33)^2$
$A_{4,1}$	$-(1111)/(11)^4+3\beta(11)^2+3(111)^2/(11)^5$
$A_{4,2}$	$-(3333)/(33)^4+3\beta/(33)^2+3(331)^2/(11)(33)^4$
$A_{4,3}$	$-6(3344)/(33)^4+6\beta/(33)^2+3[4(345)^2/(33)-(331)^2/(11)]/(33)^4$
$B_{4,1}$	$-6(1133)/(11)^2(33)^2+6\beta/(11)(33)+[3/(11)^2(33)^2][2(111)(331)/(11)+4(331)^2/(33)]$
$B_{4,2}$	$-6(1144)/(11)^2(33)^2+6\beta/(11)(33)+[3/11)^2(33)^2][(331)^2/(33)-(331)(111)/(11)]$
$B_{4,3}$	$-6(2233)/(11)^2(33)^2+6\beta/(11)(33)-[6/(11)^2(33)^2](331)(111)/(11)$
$B_{4,4}$	$-6(2244)/(11)^2(33)^2+6\beta/(11)(33)+[3/(11)^2(33)^2][(111)(331)/(11)+3(331)^2/(33)]$
$B_{4,5}$	$-12(1244)/(11)^2(33)^2+[6\sqrt{3}/(11)(33)][(111)(331)/(11)+(331)^2/(33)]$

in the mean-field approximation, DBM expand $F_{\rm MF}$ in powers of $\{\eta_\alpha\}$ which are related to $\{\langle Y_\alpha\rangle\}$ and minimize it with respect to $\{\eta_\alpha\}$. The free energy thus obtained (which we denote as $F_{\rm DBM}$) differs from that obtained by minimizing $F_{\rm var}$ discussed in Sec. III.

To see whether $F_{\rm DBM}$ and $F_{\rm var}$ give the same free energy after minimization, we have considered a simple Ising system with nearest-neighbor ferromagnetic interactions described by the Hamiltonian $H=-J\sum_{\langle ij\rangle}\sigma_i\sigma_j$. We denote by $f_{\rm DBM}$ and $f_{\rm var}$ as the change in free energies (per spin) from the noninteracting value obtained by methods similar to that used by DBM and the present paper, respectively. After expanding the free energy up to fourth power in the order parameters $\langle\sigma_i\rangle=m$, we obtain

$$f_{\rm DBM}/Jz=\tfrac{1}{2}(1-\beta Jz)m^2+\tfrac{1}{12}(\beta Jz)^3m^4$$

and

$$f_{\rm var}/kT=\tfrac{1}{2}(1-\beta Jz)m^2+\tfrac{1}{12}m^4\ ,$$

where z is the number of nearest neighbors. Note that the fourth-order term in $f_{\rm var}$ does not depend on the interaction parameter J. Minimizing $f_{\rm DBM}$ and $f_{\rm var}$ with respect to m, we find that both give the same equation for the transition temperature, i.e., $1-\beta_cJz=1$. However, for $T<T_C$, i.e., for $\beta Jz>1$, the order parameter m and the corresponding free energies differ. For example,

$$m_{\rm DBM}=-3(1-\beta Jz)/(\beta Jz)^3\ ,$$

$$f_{\rm DBM}^{\rm min}=-\tfrac{3}{4}kT(1-\beta Jz)^2/(\beta Jz)^2\ ,$$

whereas

$$m_{\rm var}=-3(1-\beta Jz),\quad f_{\rm var}^{\rm min}=-\tfrac{3}{4}kT(1-\beta Jz)^2\ ,$$

and clearly for $\beta Jz>1$, $m_{\rm var}>m_{\rm DBM}$ and $f_{\rm var}^{\rm min}<f_{\rm var}^{\rm min}$. Thus the free energy obtained from the variational principle is lower.

An advantage of using $f_{\rm var}$ instead of $f_{\rm DBM}$ to calculate the free energy is that in the former, the interaction matrix $T_{\alpha\beta}(\vec{k}\to\vec{0})$ appears only in the second order and higher-order terms are determined by the single-site potential $V_T(\hat{n}_i)$ which has cubic symmetry. This is extremely helpful when one is dealing with lattice-mediated interaction because the nonanalyticity of $I_{\alpha\beta}(\vec{k}\to\vec{0})$ appears only in the second order. Thus one can calculate and compare the free energies for various $\vec{k}\to\vec{0}$ limits with relative ease because the higher-order terms are independent of $\vec{k}$ and have to be calculated only once.

The second point that we wish to discuss is the way in which the long-range nature of the lattice-mediated interaction is handled in the theory. DBM make an interesting suggestion to handle the long-range elastic forces or equivalently the $\vec{k}\to\vec{0}$ limit of $I_{\alpha\beta}(\vec{k})$. They suggest that one should choose a crystal with length L_x,L_y,L_z such that $L_x=L_y\ll L_z$. This implies that one should consider $\vec{k}=(p,p,0)$ and take $p\to 0$ limit. In fact they evaluate the free energy which is an average of the free energies associated with $\vec{k}=p(1,1,0)$ and $\vec{k}=p(1,-1,0)$ directions. This averaging incorporates the fourfold rotation symmetry of the entire crystal about the z axis. Since these two directions give orderings appropriate for two different domains and since no domain-wall energy is included in the present theory, we prefer to calcuate the free energy for a single-domain configuration, i.e., break the degeneracy between the (1,1,0) and (1,−1,0) directions by an appropriate choice of L_x,L_y,L_z. We believe, however, that the inclusion of different domains and domain-wall energies may eventually be necessary to have a true picture of phase transition in these molecular solids. Another point in reference to the form of free energy obtained by DBM needs mention; for $\vec{k}=(k_x,0,0)$, DBM find that the third-order term in the Landau expansion vanishes and the transition is be necessity continuous (unless the fourth-order term is negative). In contrast, within our formalism, the third-order coefficients are independent of $\vec{k}$ and it is possible to have a first-order transition for $\vec{k}=(k_x,0,0)$.

Finally we would like to make some general remarks about the variational free energy $f=f_2+f_3+f_4$ given in Eqs. (4.5), (4.7), and (4.8). Because of the coupling between η_1,η_2 and η_3,η_4,η_5 in third and fourth order, it is possible that the system can undergo a phase transition to a structure where the order parameter has both e_g and t_{2g} components. This is possible if the indirect and direct interactions are such that the eigenvalues of $T_{\alpha\beta}(\vec{k}\to\vec{0})$ associated with e_g and t_{2g} symmetries are close to each other. Another possibility is that the lowest eigenvalue of $T_{\alpha\beta}(\vec{k}\to\vec{0})$ is itself of mixed symmetry due to large off-diagonal terms. We believe that both the possibilities mentioned above can in principle explain the (110) ordering found in NaCN and KCN. Which of these two is actually operative in KCN and NaCN can be seen only after a careful numerical analysis of the free energy. But before getting into the complications associated with mixed t_{2g}-e_g ordering, we discuss the results of ferroelastic ordering only in the t_{2g} manifold, as seen in CsCN.

V. FERROELASTIC PHASE TRANSITION IN CsCN

CsCN exists in the usual cesium halide crystal structure $[Pm3m(O_h^1)]$ at room temperature and undergoes a first-order phase transition[20] at 193 K to a slightly distorted cubic structure of trigonal $[R3m\ (C_{3v}^5)]$ symmetry in which the $(\mathrm{CN})^-$ ions are aligned along the threefold axes corresponding to the (111) axes of the high-T cubic structure. In the trigonal phase the $(\mathrm{CN})^-$ ions are still disordered with respect to their head and tail and there is a residual entropy of $\sim R\ln 4$ in the low-T phase. We next discuss the nature of phase transition in CsCN using the theoretical methods developed in earlier sections.

A. Orientational ordering in the absence of translation-rotation coupling

Because of the direct intermolecular interaction $D_{\alpha\beta}(\vec{k})$, the $(\mathrm{CN})^-$ molecules can undergo an orientational order-disorder transition. In the CsCl structure, $(\mathrm{CN})^-$ molecules from a cubic lattice. One has $D_{\alpha\beta}(\vec{k}=\vec{0})=\delta_{\alpha\beta}D_{\alpha\alpha}$; $D_{33}=D_{44}=D_{55}<0$ and $D_{11}=D_{22}>0$. Thus a ferrorotational ordering with $\eta_3=\eta_4=\eta_5=\eta$ and $\eta_1=\eta_2=0$ is possible. In fact, the ground-state structure for such a system has been studied using Luttinger-Tisza[21] method by Nagai and Nakamura[22] who find a (111) ferrorotational ordering characterized by $\eta \neq 0$. This contrasts with the ground state associated with NaCl structure which is of antiferrorotational type. Thus the (111) ferrorotational ordering is consistent with a quadrupole-dominated direct interaction. Using the free-ion quadrupole moment, we find that $D_{11}=D_{22}=5919$ K and $D_{33}=D_{44}=D_{55}=-3943$ K, which clearly indicates that ordering will be in the t_{2g} manifold. Putting $\eta_1=\eta_2=0$ and $\eta_3=\eta_4=\eta_5=\eta$ and using Eqs. (4.5)–(4.8), we obtain the following for $(1/N)(F_{\text{var}}-F_0)=f_{\text{var}}$:

$$f_{\text{var}}=\frac{3}{2}\left[D_{33}+\frac{1}{P_3}\right]\eta^2-\frac{1}{6}A_{3,2}\eta^3+\frac{1}{8}(A_{4,2}+A_{4,3})\eta^4 . \tag{5.1}$$

f_{var} given in Eq. (5.1) can be rewritten in the usual form as

$$f_{\text{var}}=\frac{1}{2}C_2\eta^2+\frac{1}{3}C_3\eta^3+\frac{1}{4}C_4\eta^4 . \tag{5.2}$$

We then minimize f_{var} with respect to η to obtain the transition temperature T_c and the order parameter η for $T \leq T_c$.

The transition temperature T_c and the strength of the first-order transition as measured by the discontinuity $\Delta\eta$ in the order parameter η at T_c depend on the Landau coefficients C_2, C_3, and C_4. In Figs. 1 and 2 we have plotted these coefficients as a function of T in the neighborhood of transition. The single-site potential tends to reduce the temperature where C_2 becomes zero. However, at these high temperatures the major effect of the single-site potential is to shift the three coefficients by constant amount without changing their T dependence appreciably. The coefficient C_4 is an order of magnitude larger than C_3.

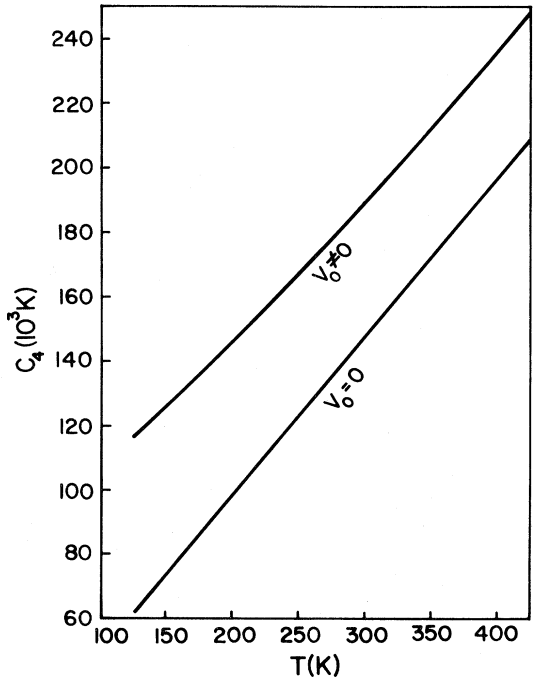

FIG. 2. Temperature dependence of fourth-order Landau coefficient [see Eq. (5.2)] in the presence ($V_0 \neq 0$) and absence ($V_0=0$) of a single-site potential. Only short-range repulsion contribution to V_0 has been considered.

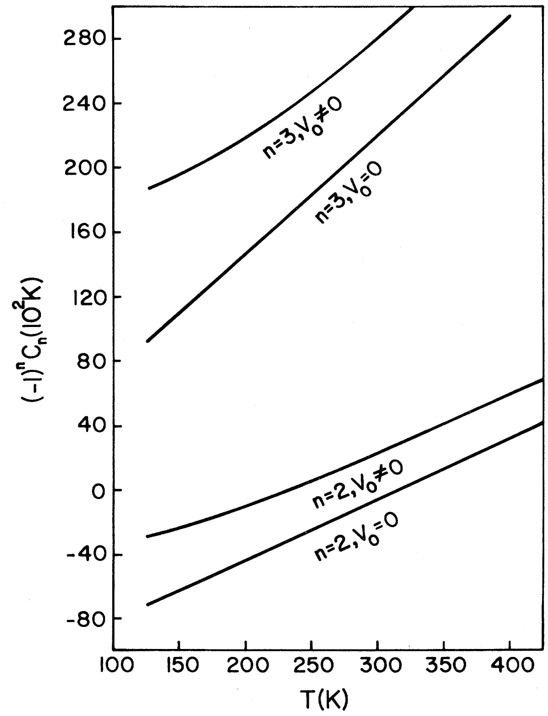

FIG. 1. Temperature dependence of second- and third-order Landau coefficients [see Eq. (5.2)] in the presence ($V_0 \neq 0$) and absence ($V_0=0$) of a single-site potential. Only short-range repulsion contribution to V_0 has been considered.

After minimizing f_{var} numerically to take into account the T dependence of C_3 and C_4, we find that for $V_0(\hat{n}_i)=0$, $T_c=335$ K and $\Delta\eta=0.274\eta_0$ where $\eta_0=\frac{1}{3}\sqrt{15/4\pi}$. When $V_0(\hat{n}_i)\neq 0$, $T_c=255$ and $\Delta\eta=0.271\eta_0$. The reason $\Delta\eta$ does not change much is due to a simultaneous increase in C_3 and C_4 and $\Delta\eta \propto C_3/C_4$. The experimental transition temperature $T_c^{\text{expt}}=193$ K. Since the present calculation is mean field in nature, the agreement between theoretical (255 K) and experimental (193 K) transition temperatures appear reasonable.

The above result suggests that considering the direct quadrupole-quadrupole interaction alone is sufficient to explain the ferroelastic phase transition reasonably well. The ferroelastic distortions observed in the ordered phase (trigonal structure) can be understood in terms of a weak coupling between the order parameters (η_3,η_4,η_5) of t_{2g} symmetry and the strains of the same symmetry. However, as discussed in the next paragraph, such a simple picture does not explain the observed[23] anomalous thermoelastic softening in the high-T pseudocubic phase as one approaches the transition temperature from above.

The thermoelastic softening in the orientationally disordered phase of alkali cyanides have been explained reasonably well within the translation-rotation (TR) model by several authors.[4,5,6,9] In a recent paper[7] we have investigated the elastic softening in CsCN using the TR model. In this work we found that if we assumed the quadrupole moment of the (CN)$^-$ ion to be unchanged from its free-ion value Q_0, then the rotation-translation coupling parameter of t_{2g} symmetry (denoted as B_{eff}) was extremely small due to a near cancellation between short-range repulsion (B_R) and quadrupolar (B_Q) contributions to B_{eff} (see Refs. 6 and 7). As a result, the total intermolecular interaction is dominated by the direct interaction $D_{\alpha\beta}(0)$, since the indirect interaction is proportional to B_{eff}^2. However, there is a basic difficulty with this choice of the quadrupole moment. The experimentally observed thermoelastic anomaly cannot be explained with a small B_{eff}. It was necessary in Ref. 7 to reduce the free-ion quadrupole moment by about 85% to fit the high-T elastic constant data. This reduction in the quadrupole-moment value leads to a large B_{eff} and a small $D_{\alpha\beta}(0)$. As a result the total interaction between the (CN)$^-$ ions is drastically different from that given by $D_{\alpha\beta}(\vec{k}=0)$ alone. Consequently, the orientational phase transition has to be investigated when both direct and indirect interactions are present.

B. Orientational ordering in the presence of both direct and lattice-mediated interactions

Following the results of thermoelastic anomaly study[7] we use the quadrupole moment $Q=0.15Q_0$ for the following calculations. The self-energy corrections $V_s(i)$ and $\sum_{\vec{k}} I_{\alpha\beta}(\vec{k})$ discussed in Secs. II and IV have been neglected. We do not believe that this will change our essential conclusions. Their quantitative importance will be studied after some of the other fundamental difficulties (to be discussed at the end of this section) have been sorted out. In Table II we give the direct $D_{\alpha\beta}(0)$ and indirect $I_{\alpha\beta}(\vec{k}\to 0)$ interaction matrices, the latter for three symmetry directions (001), (110), and (111). Certain general observations can be made by looking at parts (a)–(d) of Table II. Reducing Q to $0.15Q_0$ reduces the strength of the direct-interaction matrix by 0.0225. The lattice-mediated interaction breaks the cubic symmetry and we find $T_{11}\neq T_{22}$ and $T_{33}\neq T_{44}=T_{55}$. Except for the (001) direction $T_{\alpha\beta}(\vec{k})$ is rather complicated.

Diagonalizing the total interaction matrix $T_{\alpha\beta}(\vec{k})$ for the three symmetry directions, we find that the lowest eigenvalue (-2590 K) is associated with both (110) and (001) directions. The corresponding eigenvectors have only nonzero η_4 and η_5 components. This means that if we assume the order parameter to have only nonzero η_4 and η_5 components, then the third-order term in the free energy will not contribute and one will have a second-order transition at $T^*=175$ K with $\eta_4=\eta_5>0$ for $T<T^*$. However, the third-order term will tend to make $\eta_3\neq 0$, whereas the second-order term η_3^2 will oppose this. The final result will depend on the third-order coefficient and the splitting between the lowest eigenvalue of $T_{\alpha\beta}(\vec{k})$ and the eigenvalue associated with η_3 ordering. For the (001) direction, the eigenvalue associated with this ordering is -631 K, whereas for the (110) direction the corresponding eigenvalue is -1448 although there is a small ($\sim 2\%$) η_1 component mixed with η_3 Thus the lower free energy is expected for the (110) direction and therefore we minimize f_{var} as a function of η_3,η_4,η_5. Our results are the following.

TABLE II. Direct $D_{\alpha\beta}(\vec{k}=\vec{0})$ and indirect $I_{\alpha\beta}(\vec{k}\to\vec{0})$ interaction matrices, the latter for three symmetry directions $\hat{k}$. Matrix elements were calculated by fitting the high-T thermoelastic data. Parameters used in the calculation of matrix elements are (1) $Q=0.15Q_0$, Q_0 being the free-ion quadrupole moment; (2) $C_{11}^0=2.2327\times 10^{11}$ dyn/cm^2, $C_{44}^0=1.6800\times 10^{11}$ dyn/cm^2, and $C_{12}^0=1.1867\times 10^{11}$ dyn/cm^2; and (3) $B_{\text{eff}}=2749$ K/Å and $A_{\text{eff}}=-79$ K/Å. In order to take into account anharmonicity effects, we have assumed T-dependent bare elastic constants of the form $C_{ij}^0(T)=C_{ij}^0-\gamma_{ij}T$, where $\gamma_{11}=0.116\times 10^9$ dyn/cm^2/K, $\gamma_{44}=0.106\times 10^9$ dyn/cm^2/K, and $\gamma_{12}=0.044\times 10^9$ dyn/cm^2/K. This assumption makes the indirect-interaction terms T dependent. Entries in the table correspond to $T=200$ K.

$$\text{(a)}\ D_{\alpha\beta}(000)=\left[\begin{array}{ccccc} 133 & 0 & 0 & 0 & 0 \\ 0 & 133 & 0 & 0 & 0 \\ 0 & 0 & -89 & 0 & 0 \\ 0 & 0 & 0 & -89 & 0 \\ 0 & 0 & 0 & 0 & -89 \end{array}\right]$$

$$\text{(c)}\ I_{\alpha\beta}(110)=\left[\begin{array}{ccccc} -1 & 0 & +33 & 0 & 0 \\ 0 & -13 & 0 & 0 & 0 \\ +33 & 0 & -1625 & 0 & 0 \\ 0 & 0 & 0 & -1671 & -1671 \\ 0 & 0 & 0 & -1671 & -1671 \end{array}\right]$$

$$\text{(b)}\ I_{\alpha\beta}(001)=\left[\begin{array}{ccccc} -4 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -3345 & 0 \\ 0 & 0 & 0 & 0 & -3345 \end{array}\right]$$

$$\text{(d)}\ I_{\alpha\beta}(111)=\left[\begin{array}{ccccc} -5 & 0 & +83 & -42 & -42 \\ 0 & -5 & 0 & -72 & +72 \\ +83 & 0 & -2030 & +43 & +43 \\ -42 & -72 & +43 & -2030 & +43 \\ -42 & +72 & +43 & +43 & -2030 \end{array}\right]$$

We find that $\eta(=\eta_4=\eta_5)$ becomes nonzero at $T_c=175$ K where the second-order Landau coefficient changes sign. This suggests that the splitting between the lowest eigenvalue (-2590 K) associated with $\eta_3=0$, $\eta_4=\eta_5=\eta\neq 0$ and that with only η_3 ordering, i.e., $\eta_3\neq 0$, $\eta_4=\eta_5=0$ is sufficiently large for the third-order term to make the transition first order. But once $\eta_4=\eta_5\neq 0$, the η_3 order parameter becomes nonzero because the cubic term $(\eta^2\eta_3)$ acts like a field as far as the η_3 ordering is concerned. One can think of η_3 as a passive order parameter. In the neighborhood of transition, η_4 and $\eta_5\sim(T_c-T)^{1/2}$ and $\eta_3\sim(T_c-T)$. However, the true nature of the transition in the presence of anisotropy of second-order Landau coefficents and the third-order term can be obtained by going beyond the simple mean-field theory, preferably by using a renormalization-group analysis.

From our numerical study of the free energy for CsCN we find that the parameters of the TR Hamiltonian that can explain the high-T thermoelastic softening lead to a continuous phase transition from the orientationally disordered pseudocubic phase to the trigonal ferroelastic phase. This does not agree with the observed first-order transition. This suggests that the TR-model Hamiltonian that we have used in the present study is not adequate and needs further improvement.

Recently, Lasaar and Gordon[24] have calculated the different multipole moments of the $(CN)^-$ ion in different ionic environments using a density-functional theory. They find that the $(CN)^-$ ion has a large hexadecapole moment (HDM) and also the different multipole moments are rather insensitive to the different environments. A large HDM can not only contribute to the single-site cubic potential but also to the rotation-translation coupling and direct intermolecular interaction. We believe that a proper counteraction of the effect of HDM's on both elastic softening and ferroelastic order should remove the difficulties encountered in the present study where only the effects of quadrupole moment have been considered.

ACKNOWLEDGMENTS

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APPENDIX A: SYMMETRY ANALYSIS

A general Landau expansion of the free energy f_{var} in terms of the tensor order parameters η_i is an infinite sum of products of all invariants of the high-symmetry phase.[25] Thus the individual terms in the sum are polynomial invariants (PI's). For the following discussion we refer the reader to the paper by Smith *et al.*[26] In general a PI can be reduced, i.e., it can be expressed as a polynomial of other lower-order invariants. If it cannot be reduced then we denote it as an irreducible PI (IPI). A set of IPI's which has the property that any PI can be expressed in terms of the members of this set is called an integrity basis or an irreducible set of polynomial basis.

Smith and Rivlin[27] have shown that for an elastic tensor order parameter (a symmetric second-rank tensor g_{ij}, $i,j=x,y,z$), the elastic energy W can be expressed in the form

$$W=C_{ij,\ldots,k}I_1^iI_2^j\cdots I_n^k\ , \tag{A1}$$

where $I_1,I_2,\ldots,I_n$ are elements of the polynomial basis associated with a given crystal class. Since the second-rank tensor g_{ij} has only six independent components, there exist polynomial relations (syzygies) among $I_1,I_2,\ldots,I_n$. These relations can be utilized to further restrict the form of W. Smith[28] has shown that W is uniquely expressible in the form

$$W=S_0+\sum_{i=1}^{n-1}S_iL_i+\sum_{i,j=1}^{n-6}S_{ij}L_iL_j\ , \tag{A2}$$

where $S_0,S_i,\ldots,S_{ij}$ are polynomials in six functionally independent invariants $K_1,K_2,\ldots,K_6$ chosen from the PI basis set $\{I_1,I_2,\ldots,I_n\}$ and $L_1,\ldots,L_{n-6}$ are the remaining $(n-6)$ elements of this set.

For our present problem the order parameters $\eta_1,\ldots,\eta_5$ are related to a symmetric second-rank tensor g_{ij} with the additional constraint $g_{xx}=g_{yy}+g_{zz}=1$. The integrity basis for the full cubic group[26] consists of nine members which are

$$I_1=g_{xx}+g_{yy}+g_{zz}=1,\ \ I_2=g_{xx}g_{yy}+g_{yy}g_{zz}+g_{zz}g_{xx}\ ,$$

$$I_3=g_{xx}g_{yy}g_{zz},\ \ I_4=g_{xy}^2+g_{yz}^2+g_{zx}^2\ ,$$

$$I_5=g_{xy}^2g_{xz}^2+g_{yz}^2g_{xy}^2+g_{zx}^2g_{zy}^2,\ \ I_6=g_{xy}g_{yz}g_{zx}\ ,$$

$$I_7=g_{xx}g_{yz}^2+g_{yy}g_{zx}^2+g_{zz}g_{xy}^2\ ,$$

$$I_8=g_{xx}(g_{zx}^2g_{xy}^2)+g_{yy}(g_{yz}^2g_{yx}^2)+g_{zz}(g_{zx}^2g_{zy}^2)\ ,$$

$$I_9=g_{xx}g_{yy}g_{xy}^2+g_{yy}g_{zz}g_{yz}^2+g_{zz}g_{xx}g_{zx}^2\ .$$

Defining $K_i=I_i$ for $i=1,\ldots,6$ and $L_1=I_7$, $L_2=I_8$, and $L_3=I_9$, we obtain the invariant form of the free energy as

$$W=S_0(K_1,\ldots,K_6)+(S_1L_1+S_2L_2+S_3L_3)+\sum_{i,j=1}^{3}S_{ij}L_iL_j\ . \tag{A3}$$

We utilize Eq. (A3) to obtain symmetry checks on the free energy f_{var} that we derive from the variational principle. For example, let us consider the fourth-order contribution to f_{var} arising from the second order in both e_g order parameters (η_1 and η_2) and t_{2g} order parameters (η_3, η_4, η_5). Contributions in this order come from S_0 through the product I_2I_4 and from S_3L_3 with $S_3=$const. Note that although the product S_1L_1 can contribute by taking $S_1=I_1$, for our case $I_1=1$ and therefore this does not contribute. Thus the fourth-order e_g-t_{2g} coupling terms can be written down in general as $a\times I_2I_4+b\times I_9$ where a and b are arbitrary temperature-dependent constants. If we define another polynomial invariant I_{10} as

$$I_{10}=g_{xx}g_{yy}(g_{xz}^2+g_{yz}^2)+g_{yy}g_{zz}(g_{xy}^2+g_{zx}^2)+g_{zz}g_{xx}(g_{xy}^2+g_{zy}^2)\ ,$$

then we see that $I_2I_4=I_9+I_{10}$. Therefore the free energy $a\times I_2I_4+b\times I_9$ should have the form const$(I_9+R\times I_{10})$ where R is some temperature-dependent constant. Using the relations

$$g_{xx}\frac{1-\eta_1}{3}+\frac{\eta_2}{\sqrt{2}},\quad g_{zz}=\frac{1+2\eta_1}{3}\ ,$$

$$g_{yy}=\frac{1-\eta_1}{3}-\frac{\eta_2}{\sqrt{2}},\quad g_{xy}=\eta_3,\quad g_{yz}=\eta_4,\quad g_{zx}=\eta_5\ ,$$

we obtain (keeping only the cross e_g-t_{2g} coupling terms)

$$\begin{aligned} I_9+RI_{10}=&B_{4,1}\eta_1^2\eta_3^2+B_{4,2}\eta_1^2(\eta_4^2+\eta_5^2)\\ &+B_{4,3}\eta_2^2\eta_3^2+B_{4,4}\eta_2^2(\eta_4^2+\eta_5^2)\\ &+B_{4,5}\eta_1\eta_2(\eta_4^2-\eta_5^2)\ , \end{aligned} \tag{A4}$$

where

$$\begin{aligned} &B_{4,4}/B_{4,3}=R,\quad B_{4,2}/B_{4,3}=\tfrac{2}{3}+\tfrac{1}{3}R\ ,\\ &B_{4,1}/B_{4,3}=-\tfrac{1}{3}+\tfrac{4}{3}R,\quad B_{4,5}/B_{4,3}=-(2/\sqrt{3})(1-R)\ . \end{aligned} \tag{A5}$$

Thus knowing only two coefficients, $B_{4,3}$ and $B_{4,4}$, we can calculate all the rest. Furthermore, the relations (A5) provide a strong check on the accuracy of Landau coefficients that we have obtained in terms of parameters of the Hamiltonian H_r^{eff} in Sec. IV.

APPENDIX B: NONVANISHING SINGLE-SITE GENERALIZED SUSCEPTIBILITIES

In the following x, y, and z are the Cartesian components of a unit vector $\hat{n}$ and $\langle\ \rangle_0$ refers to the thermal average taken over the single-site cubic potential $V_T(\hat{n})$. For convenience, we use a simple notation for the susceptibilites of different orders, i.e., $\chi^0_{\alpha\beta}=(\alpha\beta)$; $\chi^0_{\alpha\beta\gamma}=(\alpha\beta\gamma)$; $\chi^0_{\alpha\beta\gamma\delta}=(\alpha\beta\gamma\delta)$ (see Table I). Also $\beta=1/kT$, $e=\sqrt{5/16\pi}$, and $t=\sqrt{15/4\pi}$; $A_4=\langle x^4+y^4+z^4\rangle_0$, $A_6=\langle x^2y^2z^2\rangle_0$, and $A_{4s}=\langle(x^4+y^4+z^4)^2\rangle_0$.

(I) Second order—$\chi^0_{\alpha\beta}$. We have, for e_g,

$$(11)=(22)=\beta e^2(3A_4-1)\ , \tag{B1}$$

and for t_{2g},

$$(33)=(44)=(55)=\beta\frac{t^2}{6}(1-A_4)\ . \tag{B2}$$

(II) Third order—$\chi^0_{\alpha\beta\gamma}$. We have, for e_g,

$$(111)=-(122)=\tfrac{1}{2}\beta^2e^3(54A_6+9A_4-5)\ , \tag{B3}$$

for t_{2g},

$$(345)=\beta^2t^3A_6\ , \tag{B4}$$

and for e_g-t_{2g},

$$\begin{aligned} &(331)=\tfrac{1}{6}\beta^2et(18A_6+A_4-1)\ ,\\ &(441)=(551)=-\tfrac{1}{2}(331)\ ,\\ &(442)=-(552)=-\frac{\sqrt{3}}{2}(331)\ , \end{aligned} \tag{B5}$$

(III) Fourth order—$\chi^0_{\alpha\beta\gamma\delta}$. We have, for e_g,

$$(1111)=(2222)=3(1122)=\beta^3e^4(\tfrac{3}{2})(9A_{4s}-6A_4+1)\ , \tag{B6}$$

for t_{2g},

$$\begin{aligned} &(3333)=(4444)=(5555)=\beta^3t^4(\tfrac{1}{12})(A_{4s}-2A_4-8A_6+1)\ ,\\ &(3344)=(4455)=(5533)=\beta^3t^4(\tfrac{1}{3})A_6\ , \end{aligned} \tag{B7}$$

and for e_g-t_{2g},

$$\begin{aligned} &(1133)=\beta^3(et)^2(\tfrac{1}{6})(1-A_4-18A_6)\ ,\\ &(1144)=(1155)\\ &\qquad=\beta^3(et)^2(\tfrac{1}{12})(13A_4-9A_{4s}+18A_6-4)\ ,\\ &(2233)=\beta^3(et)^2(\tfrac{1}{2})(3A_4-2A_{4s}+6A_6-1)\ ,\\ &(2244)=(2255)=\beta^3(et)^2(\tfrac{1}{4})(A_4-A_{4s}-6A_6)\ ,\\ &(1244)=-(1255)\\ &\qquad=\beta^3(et)^2(\sqrt{3}/12)(3A_{4s}-5A_4-18A_6+2)\ . \end{aligned} \tag{B8}$$

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$\int |Y_\alpha|^2 d\Omega=1$, whereas in Refs. 4–7, Y_2, Y_3, Y_4, and Y_5 were not normalized. This leads to some modifications in the coupling-constant matrices $v_{\alpha\mu}(\vec{k})$, single-site susceptibilities $\chi^0_{\alpha\alpha}$, and Fourier transform of the direct interaction matrix $D_{\alpha\beta}(\vec{k})$. If we define the various quantities obtained with *unnormalized* Y_α's by a tilde, then the following relations hold: $v_{1\mu}=\tilde{v}_{1\mu}$, $v_{2\mu}=\sqrt{3}\tilde{v}_{2\mu}=\sqrt{2}\tilde{v}_{\alpha\mu}$, $\alpha=3,4,5$; $\chi^0_{11}=\tilde{\chi}^0_{11}$, $\chi^0_{22}=3\chi^0_{22}$, and $\chi^0_{\alpha\alpha}=2\tilde{\chi}^0_{\alpha\alpha}$, $\alpha=3,4,5$; $D_{11}(\vec{k}=\vec{0})=\tilde{D}_{11}(\vec{k}=\vec{0})$, $D_{22}(\vec{k}=\vec{0})=3\tilde{D}_{22}(\vec{k}=\vec{0})$, and $D_{\alpha\alpha}(\vec{k}=\vec{0})=2\tilde{D}_{\alpha\alpha}(\vec{k}=\vec{0})$, $\alpha=3,4,5$.

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