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Theory of the orientational glass state in mixed crystals $M(\mathrm{CN})_xX_{1-x}$. I. Statics

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A microscopic model of mixed crystals with orientational disorder and translation-rotation coupling is proposed. The substitutional atoms act as static impurity centers which generate random strain fields. The static strains play the role of external random fields which couple to the orientational order parameter. In addition, the orientational modes couple to thermal lattice vibrations. The thermodynamics is studied within mean-field theory. Above a certain concentration of substitutional atoms, the system does not undergo anymore a transition to a phase with long-range orientational order. The theory accounts for experimental properties which are characteristic of the quadrupolar orientational glass state.

I. INTRODUCTION

Mixed crystals $(M\mathrm{CN})_x(MX)_{1-x}$, where M is an alkali metal and X a halogen ion, have attracted much experimental and theoretical interest. While the alkali cyanides MCN, with $M=$Na, K, Rb, exhibit a characteristic phase transition[1] from the high-temperature orientationally disordered phase with cubic symmetry, to orientationally ordered phases with crystal structures of lower symmetry, no such transition occurs in mixed crystals[2] above some critical value of the concentration $(1-x)$ of halogen atoms. For a review, see Lüty.[3] Most remarkable is the temperature (T) dependence of the transverse-acoustic phonons or shear-elastic constants in mixed crystals.[4–6] While in KCN, the elastic constants become soft by approaching the ferroelastic phase transition,[7] in mixed crystals, above the critical concentration of halogens, the transverse-acoustic phonon energy passes through a minimum at $T=T_f$ and increases again at lower T.[4,5] At the same time, a large central component[4,8] at zero energy transfer grows strongly at low T. The central component is elastic within the best attainable resolution of neutron scattering experiments;[8,9] its intensity has a characteristic shape in Q space.[8,10] The absence of long-range order and the appearance of the central peak have been related[8] to the possible existence of a "dipole glass".[11] It has been shown in Ref. 12 that a freezing in of orientational modes implies a concomitant freezing in of translational modes (lattice strains). The bilinear coupling of these modes produces the asymmetries of equal intensity contours of the elastic line in Q space. These features are consistent with the hypothesis of an orientational glass state. Additional indications that the phenomena in $M(\mathrm{CN})_x\,X_{1-x}$ are related to glasses have been obtained from calorimetric measurements.[13,14]

Nonwithstanding recent work on the theory of quadrupole glasses,[15,16] the experimental phenomena have not yet found a coherent explanation. Some of the open problems have been discussed in Ref. 17.

The result of Refs. 2, 3, 17, and 18 show that the critical concentration of X ions which is necessary for the absence of long-range order at low T is twice as large in bromide as in chloride mixed crystals, $(1-x)$ is equal to 42% and 20%, respectively. We therefrom conclude that the interaction between the halogen ions and the CN molecular ions is an essential mechanism for the existence of the orientational glass state.

The content of the present paper is as follows. In Sec. II it is shown that the substitution of CN molecular ions by spherical X ions leads to additional strain fields in the crystal. These strain fields couple to the orientational degrees of freedom of the molecules or molecular ions (Sec. III). This interaction plays the role of an external random field. In Sec. IV we calculate the free energy from a microscopic model by including the random field. The method is based on mean-field theory. Above a certain critical value of the concentration of X ions, the collective orientational susceptibility is no longer divergent but exhibits a smooth maximum at low T. In Sec. **V** we study various properties which are associated with the onset of the orientational glass state.

II. STATIC STRAINS

We take explicitly into account the influence of the substitutional X impurities in mixed crystals $M(\mathrm{CN})_xX_{1-x}$. The forces exerted by the X^- ion on the surrounding lattice are different from the forces exerted by the substituted CN^- molecular ion. In the pure crystal MCN, the equilibrium positions of the CN^- ions at lattice sites $\mathbf{n}$ are denoted by $\mathbf{X}(\mathbf{n})$. Each CN^- is surrounded by six M^+ in octahedral positions:

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

here $\tau(l)=(a,0,0)$ etc., with a half the cubic lattice constant. We assume that the mixed crystal still has the the average cubic structure. We want to investigate the inhomogeneous static lattice deformations which are induced by the concentration fluctuations of impurities.[19] To each lattice site $\mathbf{n}$, we assign a variable $\sigma(\mathbf{n})$ with value $+1$ if the site is occupied by a CN^-, and value 0 if the site is occupied by a X^-. For a given configuration $\{\sigma(\mathbf{n})\}$, the interaction of the concentration fluctuations of X^- ions with neighboring M^+ ions is written as

$$V^X=\sum_{\mathbf{n}}\sum_{\kappa}[1-\sigma(\mathbf{n})-(1-x)]V^X(\,|\mathbf{R}(\mathbf{n})-\mathbf{R}(\mathbf{n},\kappa)|\,)\ , \tag{2.2}$$

with

$$\mathbf{R}(\mathbf{n})=\mathbf{X}(\mathbf{n})+\mathbf{u}^X(\mathbf{n})\ , \tag{2.3a}$$

$$\mathbf{R}(\mathbf{n},\kappa)=\mathbf{X}(\mathbf{n},\kappa)+\mathbf{u}^M(\mathbf{n},\kappa)\ . \tag{2.3b}$$

Here u^X and u^M are lattice displacements. V^X is a sum of atom-atom potentials. Expansion up to first order in the displacements yields

$$V^X=V^X\Big|_{u=0}+\sum_{n}\sum_{\kappa}[x-\sigma(\mathbf{n})]v_i^X(\kappa)[u_i^X(\mathbf{n})-u_i^M(\mathbf{n},\kappa)]\ , \tag{2.4a}$$

where

$$v_i^X(\kappa)=\frac{\partial V^X}{\partial X_i}(\mathbf{X}(\mathbf{n})-\mathbf{X}(\mathbf{n},\kappa))\ . \tag{2.4b}$$

In Eq. (2.4a), we have used the summation convention for repeated Cartesian indices i. Cubic symmetry implies

$$v_i^X(\kappa)=-v_i^X(\kappa+3) \tag{2.5a}$$

and

$$v_i^X(\kappa)\equiv F^X\delta_{i\kappa}\ ,\quad \kappa=1,2,3\ . \tag{2.5b}$$

Defining the Fourier transform

$$u_i^M(\mathbf{n},\kappa)=\frac{1}{(Nm_M)^{1/2}}\sum_{\mathbf{k}}u_i^M(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{X}(\mathbf{n},\kappa)}\ , \tag{2.6}$$

and taking into account Eqs. (2.5a), (2.5b), and (2.1), we rewrite Eq. (2.4a) as

$$V^X=-i\frac{2}{(m_M)^{1/2}}\sum_{\mathbf{k}}\rho(-\mathbf{k},\{\sigma\})F^X\sin(k_ia)u_i^M(\mathbf{k})\ . \tag{2.7a}$$

The first term on the right-hand side of Eq. (2.4a) is an irrelevant constant and has been dropped. In Eq. (2.7a), we have defined

$$\rho(\mathbf{k},\{\sigma\})=\frac{1}{N}\sum_{n}[x-\sigma(\mathbf{n})]e^{-i\mathbf{k}\cdot\mathbf{X}(\mathbf{n})}\ , \tag{2.7b}$$

Where N is the total number of unit cells (also equal to the sum of CN$^-$ and X^- ions in the crystal). Since the X^- ions are located in CN$^-$ sites, we have to subtract from expression (2.7a) the effect of the substituted CN$^-$ ions in spherical approximation. This operation leads to the replacement of F^X by

$$\Delta F^X=F^X-F^{\mathrm{CN}}\ , \tag{2.8a}$$

where

$$F^{\mathrm{CN}}=\frac{1}{4\pi}\int d\mathbf{\Omega}\frac{\partial V^{\mathrm{CN}}}{\partial X_i}(\mathbf{X}(\mathbf{n})-\mathbf{X}(\mathbf{n},\kappa),\mathbf{\Omega})\delta_{\kappa i}\ . \tag{2.8b}$$

Here V^{CN} stands for the interaction of the CN$^-$ molecular ion with the surrounding M^+ ions,[20] $\mathbf{\Omega}\equiv(\theta,\varphi)$ accounts for the orientation of the CN$^-$ ion. In order to calculate the strain induced in the crystal by the substitutional X^- ions, we transform Eq. (2.7a), with $F^X\rightarrow\Delta F^X$, to acoustic displacements $s_i(\mathbf{k})$. The result reads as

$$V_{\mathrm{ac}}^{\Delta X}=\sum_{\mathbf{k}}v_i^X(\mathbf{k})\rho(-\mathbf{k},\{\sigma\})s_i(\mathbf{k})\ , \tag{2.9a}$$

with

$$v_i^X(\mathbf{k})=-2i\frac{\Delta F^X}{\sqrt{m}}\sin(k_ia)\ . \tag{2.9b}$$

Here $m=m_M+m_\Delta$ is the average mass per unit cell, with $m_\Delta=xm_{\mathrm{CN}}+(1-x)m_X$. The static lattice strains are obtained by minimizing the total elastic interaction

$$V_{\mathrm{el}}=V^{TT}+V_{\mathrm{ac}}^{\Delta X}\ . \tag{2.10}$$

Here

$$V^{TT}=\tfrac{1}{2}\sum_{\mathbf{k}}M_{ij}(\mathbf{k})s_i^\dagger(\mathbf{k})s_j(\mathbf{k})\ , \tag{2.11}$$

M represents the corresponding dynamical matrix. The minimization yields

$$s_i(\mathbf{k},\{\sigma\})=A_i(\mathbf{k})\rho(\mathbf{k},\{\sigma\})\ , \tag{2.12a}$$

where $\mathbf{A}(\mathbf{k})$ represents the amplitude vector of the displacement wave:

$$A_i(\mathbf{k})=[M^{-1}(\mathbf{k})]_{ij}v_j^X(\mathbf{k})\ . \tag{2.12b}$$

Expressions of the form (2.12a) are well known from the theory of imperfections in crystals.[19] As a consequence of the elastic anisotropy of the crystal, $\mathbf{A}(\mathbf{k})$ is in general, except for high-symmetry directions in the cubic crystal, *not* parallel to the direction of the wave vector $\mathbf{k}$. The corresponding displacements $s_i(\mathbf{k},\{\sigma\})$ are transverse. This point is essential for the existence of a coupling between acoustic lattice displacements and orientational modes of T_{2g} symmetry.

III. STRAIN-ORIENTATION COUPLING

The interaction of an orientational mode Y_α at lattice site $\mathbf{r}$ with acoustic displacements reads[20] as

$$V^{TR}=\sum_{\mathbf{r}}\sum_{\mathbf{k}}\frac{1}{\sqrt{N}}\sigma(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{X}(\mathbf{r})}Y_\alpha(\mathbf{r})v_{\alpha i}(\mathbf{k})s_i(\mathbf{k})\ . \tag{3.1}$$

While the potential V^{TR} was originally derived for the dynamic coupling of orientational modes with lattice vibrations, we will use it here for the coupling V^{SR} of orientational modes with the static lattice strains $s_i(\mathbf{k},\{\sigma\})$, which are generated by the substitutional halogens X. In Eq. (3.1) we consider the three orientational modes with $l=2$ of T_{2g} symmetry. (See Ref. 21 for additional details.) These modes are relevant for the ferroelastic transition at 168 in KCN, they are also characteristic for the orientational glass state.[12] The coupling matrix $(v_{\alpha i})$ is given by[21]

$$(v_{\alpha i}(\mathbf{k}))=-2i\frac{B}{\sqrt{m}}\begin{vmatrix}\sin(k_ya) & \sin(k_xa) & 0\\ 0 & \sin(k_za) & \sin(k_ya)\\ \sin(k_za) & 0 & \sin(k_xa)\end{vmatrix}\ . \tag{3.2}$$

Defining a local displacement field

$$h_\alpha(\mathbf{r},\{\sigma\})=\frac{1}{N}\sum_{\mathbf{n}}\sum_{\mathbf{k}}[x-\sigma(\mathbf{n})]R_\alpha(\mathbf{k}) \times \cos\{\mathbf{k}\cdot[\mathbf{X}(\mathbf{r})-\mathbf{X}(\mathbf{n})]\} , \tag{3.3}$$

where

$$R_\alpha(\mathbf{k})=v_{\alpha i}(\mathbf{k})A_i(\mathbf{k}) . \tag{3.4}$$

We get from Eqs. (3.1), (2.12a) and (2.7b)

$$V^{SR}(\{\sigma\})=\sum_{\mathbf{r}}\sigma(\mathbf{r})Y_\alpha(\mathbf{r})h_\alpha(\mathbf{r},\{\sigma\} . \tag{3.5}$$

The static strains, which are generated by the substitutional ions, act as local fields on the orientational motion of the CN^- molecular ion at site $\mathbf{r}$. Expression (3.2) for the matrix $\underline{v}(\mathbf{k})$ implies that only transverse displacements $A_i(\mathbf{k})$ couple to the orientational modes of T_{2g} symmetry. The field $h_\alpha(\mathbf{r},\{\sigma\})$ at site $\mathbf{r}$ is due to the superposition of strains from all substitutional halogens $\{\sigma\}$. Denoting the configurational average by an overbar, we have $\bar{\sigma}=x$ and consequently,

$$\bar{h}_\alpha=0 . \tag{3.6}$$

On the other hand, using $\sigma^2=\sigma$, and neglecting correlations between impurity positions, we obtain from Eq. (2.7b)

$$\overline{\rho(\mathbf{k},\{\sigma\})\rho(\mathbf{k}',\{\sigma\})}\sim x(1-x)\delta_{\mathbf{k}\mathbf{k}'} . \tag{3.7}$$

Therefore we conclude that

$$\overline{h_\alpha h_\beta}=x(1-x)h^2\delta_{\alpha\beta} , \tag{3.8a}$$

where as an approximation

$$h^2\sim\frac{1}{N}\sum_{\mathbf{k}}[R_\alpha(\mathbf{k})]^2 . \tag{3.8b}$$

Cubic symmetry implies that all three components α are equal. In addition, we have assumed statistical independence of different components α,β. Properties (3.6) and (3.8a) suggest to consider $h_\alpha(\mathbf{r})$ as a random field with a Gaussian distribution at each molecular site $\mathbf{r}$. Experimental evidence for the existence of local strain fields in mixed crystals is provided by ultrasonic (Ref. 17), x rays (Refs. 22 and 23), and NMR (Ref. 24) data. In Sec. IV we will apply concepts from the statistical mechanics of random field systems[25,26] and calculate the free energy.

So far we have considered the coupling of random strains to orientational modes of T_{2g} symmetry, i.e., quadrupoles. However, there exists also a coupling between acoustic strains and orientational modes of T_{1u} symmetry, i.e., dipoles.[21] Replacing $\underline{v}(\mathbf{k})$ in Eq. (3.4) by the corresponding coupling matrix $\underline{v}^u(\mathbf{k})$ for the three orientational modes Y_α^u, $\alpha=1,2,3, l=1$, we obtain immediately the corresponding random field $\mathbf{h}^u$. Since $\underline{v}^u(\mathbf{k})$ is quadratic in $\mathbf{k}$ (Ref. 21) for small $\mathbf{k}$, while $\underline{v}(\mathbf{k})$[Eq. (3.2)] is linear in $\mathbf{k}$, terms of small $\mathbf{k}$ have less weight in the $\mathbf{k}$ sum (3.3) in the case of dipolar modes. On the other hand, the amplitude $\mathbf{A}(\mathbf{k})$[Eq. (2.12b)] is proportional to $\underline{M}^{-1}(\mathbf{k})$ and this quantity is most important at small $\mathbf{k}$. We therefore conclude that the $\mathbf{k}$ sums in Eqs. (3.3) and (3.8b) give smaller contributions in the case of dipolar modes than of quadrupolar modes. In other words, the orientational freezing effects exist also for dipolar modes, but they are less pronounced than in the case of quadrupolar modes, in particular, the corresponding freezing temperature should be lower. There exists a large amount of results from dielectric measurements in mixed crystals.[3,27-30] In particular, the dielectric loss data reflect the existence of a wide spectrum of relaxation times in the mixtures,[3,29] a feature which is related to the distribution of local random strain fields. It has been suggested[31] that the energy barriers to dipolar orientations depend on the local deformations of the single ion potential through quadrupolar interaction forces. In our opinion, the relation between the dipolar freezing and the quadrupolar freezing is due to the fact that both processes have the same physical origin, namely the strain due to the substitutional halogens. However the coupling $\underline{v}$ and $\underline{v}^u$ are different and therefore the corresponding random fields have a different strength.

IV. FREE ENERGY

We consider a crystal $M(CN)_xX_{1-x}$, where the substitutional impurities X have a random distribution. The total potential is given by

$$V=V^{TT}+V^{TR}+V^R+V^{RR}+V^{SR} . \tag{4.1}$$

The first four terms, on the right-hand side have been considered previously[21] for the case $x=1$. The last term V^{SR} accounts for the coupling of the rotational modes with the random strain fields. The harmonic lattice potential V^{TT} is given by Eq. (2.11) and the bilinear interaction V^{TR} by Eq. (3.1). Here we treat the acoustic displacements $s_i(\mathbf{k})$ as dynamic variables. In contradistinction, the displacements $s_i(\mathbf{k},\{\sigma\})$ which determine the random fields are static [see Eq. (2.12a)]. The term V^R stands for the single particle potential

$$V^R=\sum_{\lambda_0}\sum_{\mathbf{r}}\sigma(\mathbf{r})a_{\lambda_0}Y_{\lambda_0}(\mathbf{r}) . \tag{4.2}$$

The functions Y_{λ_0} have the symmetry of the undeformed crystal site (A_{1g}). The term V^{RR} represents a direct orientation-orientation interaction

$$V^{RR}=\tfrac{1}{2}\sum_{\mathbf{k}}Y_\alpha(\mathbf{k})J_{\alpha\beta}(\mathbf{k})Y_\beta^\dagger(\mathbf{k}) , \tag{4.3a}$$

where

$$J_{\alpha\beta}(\mathbf{k})=\sum_{\mathbf{r}}J_{\alpha\beta}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{X}(\mathbf{r})} , \tag{4.3b}$$

and

$$Y_\alpha(\mathbf{k})=\frac{1}{\sqrt{N}}\sum_{\mathbf{r}}\sigma(\mathbf{r})Y_\alpha(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{X}(\mathbf{r})} . \tag{4.3c}$$

With definition (4.3c), we have introduced distribution weighted Fourier transforms. We rewrite Eq. (3.1) as

$$V^{TR}=\sum_{\mathbf{k}}v_{\alpha i}(\mathbf{k})Y_\alpha(-\mathbf{k})s_i(\mathbf{k}) , \tag{4.4}$$

and Eq. (3.5) as

$$V^{SR}(\{\sigma\}) = \sum_{\mathbf{k}} Y_\alpha(\mathbf{k}) h_\alpha(-\mathbf{k},\{\sigma\}) \;, \tag{4.5a}$$

where

$$h_\alpha(\mathbf{k},\{\sigma\}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{r}} h_\alpha(\mathbf{r},\{\sigma\}) e^{-i\mathbf{k}\cdot\mathbf{X}(\mathbf{r})} \;. \tag{4.5b}$$

In order to obtain the thermodynamic properties of the model, one must first calculate the thermodynamic quantity for a given random distribution $\{\sigma\}$ of impurities i.e., of fields, and then take the configurational average.[25,26] Details of the calculation are found in the Appendix. Up to second order in the order parameter variables $\mathbf{s}^e$ and $\mathbf{Y}^e$, we obtain for the configurational averaged free energy

$$\bar{F} = \bar{F}_W + \sum_{\mathbf{k}} \{ \tfrac{1}{2} \bar{\mathbf{s}}^{\dagger e}(\mathbf{k}) \underline{M}(\mathbf{k}) \bar{\mathbf{s}}^e(\mathbf{k}) + \bar{\mathbf{Y}}^{e\dagger}(\mathbf{k}) \underline{v}(\mathbf{k}) \bar{\mathbf{s}}^e(\mathbf{k})$$
$$+ \tfrac{1}{2} [(\underline{\chi}^0)^{-1} + \underline{J}(\mathbf{k}) + \underline{1} C^s] \bar{\mathbf{Y}}^{e\dagger}(\mathbf{k}) \bar{\mathbf{Y}}^e(\mathbf{k}) \} \;. \tag{4.6}$$

Here $\bar{F}_W$ stands for the single particle orientational free energy:

$$\bar{F}_W = -xNT \ln \mathrm{Tr}[\, \exp(-\beta W^R)] \;, \tag{4.7a}$$

with

$$W^R = \left[\sum_{\lambda_0} \alpha_{\lambda_0} Y_{\lambda_0}(\mathbf{r}) - C^s \sum_{\alpha} Y_\alpha^2(\mathbf{r}) \right] \;. \tag{4.7b}$$

The last term on the right-hand side represents the self-energy correction[21]

$$\underline{1} C^s = \frac{1}{N} \sum_{\mathbf{k}} \underline{C}(\mathbf{k}) \;, \tag{4.8a}$$

where $\underline{C}(\mathbf{k})$ is the lattice mediated orientational interaction[20]

$$\underline{C}(k) = \underline{v}(\mathbf{k}) \underline{M}^{-1}(\mathbf{k}) \underline{v}^{\tau}(\mathbf{k}) \;. \tag{4.8b}$$

In Eq. (4.6), $\underline{\chi}^0 = \underline{1}\chi^0$ stands for the local orientational susceptibility

$$\chi^0 = x (y_W/T)[1 - x(1-x)\xi_W h^2/T^2] \;. \tag{4.9}$$

Here y_W is the single particle expectation value

$$y_W \equiv \langle Y_\alpha^2 \rangle_W = \mathrm{Tr}[\rho_W Y_\alpha^2] \;, \tag{4.10a}$$

$$\rho_W = [\, \exp(-\beta W^R)] / \mathrm{Tr} \exp(-\beta W^R) \;. \tag{4.10b}$$

The coefficient ξ_W in Eq. (4.9) is given by

$$\xi_W = \frac{1}{2 y_W} [3 y_W^2 - \langle Y_\alpha^4 \rangle_W$$
$$+ 2 (y_W^2 - \langle Y_\alpha^2 Y_\beta^2 \rangle_W)(1 - \delta_{\alpha\beta})] \;. \tag{4.11}$$

The functions $\xi_W(T)$ and $y_W(T)$ have to be evaluated by numerical integrations. Following Ref. 21, we have used an expansion of W^R in terms of cubic harmonics K_{41} and K_{61} with coefficients α_{41} and α_{61} having the values of 23.8 and -88.5 K, respectively. We find that $\xi_W(T)$ increases monotonically from a value 0.057 at $T = 300$ K to 0.074 at $T = 30$ K; simultaneously $y_W(T)$ increases from a value of 0.080 at $T = 300$ K to 0.096 at $T = 30$ K. With decreasing T, the random-field contribution $-(h^2/T^2)$ plays an increasing role in Eq. (4.9). At very low T, our expression for χ^0 becomes negative. This is an artifact due to the approximations we had to make in calculating the free energy, in particular the series expansions of Eq. (A16). In addition, the present theory is no longer valid at low temperature where a quantum-mechanical treatment is required. Since the rotational constant of the CN molecular ion is large and since the local orientational potentials are relatively weak,[32] we expect that a classical treatment is valid above $T \approx 30$ K. We notice that in a two-state Ising system, (h^2/T^2) has to be replaced by $\tanh^2(h/T)$, as follows from Refs. 25 and 26. For a given configuration of orientations $\{\overline{Y_{\underline{\alpha}}^e}(\mathbf{k})\}$, we minimize $\bar{F}$ with respect to the displacements $s_i^e(\mathbf{k})$ and obtain

$$\overline{s_i^e}(\mathbf{k}) = -[\underline{M}^{-1}(\mathbf{k})]_{ij} v_{j\alpha}(-\mathbf{k}) \overline{Y_\alpha^e}(\mathbf{k}) \;. \tag{4.12}$$

Substitution into Eq. (4.6) yields

$$\bar{F} = \bar{F}_W + \sum_{\mathbf{k}} \tfrac{1}{2} [(\underline{\chi}^0)^{-1} + \underline{J}(\mathbf{k})$$
$$+ \underline{1} C^s - \underline{C}(\mathbf{k})] \overline{\mathbf{Y}^{e\dagger}(\mathbf{k}) \bar{\mathbf{Y}}^e(\mathbf{k})} \;. \tag{4.13}$$

Expressions (4.6), (4.9), and (4.13) constitute the main results of the present theory. Their physical meaning will be discussed in Sec. V.

V. ORIENTATIONAL FREEZING

Using a well-known procedure of statistical mechanics,[33] we derive by means of Eq. (4.13) the collective orientation-orientation susceptibility

$$\chi_{\alpha\beta}(\mathbf{k}) \equiv \overline{\langle Y_\alpha^e(\mathbf{k}) Y_\beta^e(-\mathbf{k}) \rangle} / T = \chi^0 [\underline{1} - \chi^0 \underline{L}(\mathbf{k})]_{\alpha\beta}^{-1} \;, \tag{5.1}$$

where

$$\underline{L}(\mathbf{k}) = \underline{C}(\mathbf{k}) - \underline{1} C^s - \underline{J}(\mathbf{k}) \;. \tag{5.2}$$

The orientational interaction matrix $\underline{L}(\mathbf{k})$ has its largest eigenvalue δ for $\mathbf{k} \to 0$ along one of the cubic crystal axes.[34] Then $\underline{\chi}(\mathbf{k})$ is also diagonal. We choose $\mathbf{k} = (k,0,0,)$ and obtain for the largest elements of $\underline{\chi}$ in the limit $k \to 0$, $\chi_{22}(k) = \chi_{33}(k)$, with

$$\chi_{22}(\mathbf{k}) = \frac{\chi^0}{1 - \delta\chi^0} \;. \tag{5.3}$$

Here the subscript 2 refers to the function $Y_2 \equiv Y_2^{1,c}(\Omega)$, with $l = 2$ and T_{2g} symmetry. The eigenvalue δ is given by

$$\delta = \frac{2B^2}{a c_{44}^0} - C^s - J \;. \tag{5.4}$$

Here c_{44}^0 is the bare shear-elastic constant, which is obtained from the dynamical matrix $\underline{M}$ in the long-wavelength regime. The constant B accounts for the bilinear interaction (3.2). Using results of Ref. 21, we take for δ the value 2375 K. In the pure crystal MCN, $\chi_{22}(\mathbf{k})$ diverges at a transition temperature T_C, where $\delta\chi^0(T_C) \simeq 1$. In mixed crystals $M(\mathrm{CN})_x X_{1-x}$ this condition is equivalent to the existence of a common solution T_C of the system of equations

$$\varphi_1(T)=T \ , \tag{5.5a}$$

$$\varphi_2(T)=x\,\delta y_W(T)[1-x(1-x)\xi_W h^2/T^2] \ . \tag{5.5b}$$

If condition $\varphi_1=\varphi_2$ is realized, the coefficient of the second-order term on the right-hand side of Eq. (4.13) vanishes and there occurs a second-order phase transition. (For a more complete discussion, see Ref. 34.) While in the case of *M*CN, the system (5.5a) and (5.5b) has always a solution $T_C \neq 0$, this is no longer so for mixed crystals. In particular, for sufficiently large values of h, the functions $\varphi_1(T)$ and $\varphi_2(T)$ have no intersection. A graphical discussion as a function of concentration and temperature is given in Fig. 1.

For a given value of the random field h, we determine the critical concentration x_c of CN^- below of which there is no phase transition to an ordered state. We require that the tangent of the curve $\varphi_2\,(x_c,T)$ for $T=T_0$ coincides with the straight line $\varphi_1=T$. This solution is stable, i.e., corresponds to a minimum of the free energy if $\partial\chi(x_c,T)/\partial T=0$. Assuming that the slow varying functions y_W and ξ_W are constants, we obtain

$$T_0=[3x_c(1-x_c)\xi]^{1/2}h \ . \tag{5.6a}$$

The angular coefficient of the tangent at φ_2 in the point (x_c,T_0) satisfies the condition

$$2x_c^2(1-x_c)\,\delta y_W\,\xi\frac{h^2}{T_0^3}=1 \ . \tag{5.6b}$$

Eliminating T_0 from these two equations, we obtain

$$\frac{x_c}{[x_c(1-x_c)]^{1/2}}=2.6\frac{\sqrt{\xi}}{\delta y_W}h \ . \tag{5.6c}$$

On the other hand, elimination of ξh^2 yields

$$T_0=\tfrac{2}{3}x_c\,\delta y_W \ . \tag{5.6d}$$

This condition shows that T_0 depends also on the effective interaction δ. For $x<x_c$, the curve $\varphi_2(T,x)$ in Fig. 1 lies below the straight line $\varphi_1=T$. The minimum of the free energy or equivalently the maximum of the susceptibility $\chi(x,T)$, determines the freezing temperature $T_f(x)$. We find from $\partial\chi/\partial T=0$,

$$T_f=\sqrt{3x(1-x)\xi}h \ , \quad x<x_c \ . \tag{5.7}$$

In Fig. 2 we have plotted the collective orientational susceptibility χ_{22} ($k=0$) as a function of temperature for various concentrations $x<x_c$. Notice that the curves have a smooth maximum at $T_f(x)$ and not a cusp as would be expected from spin-glass theory. A maximum in the orientational susceptability of T_{2g} symmetry corresponds to a minimum in the transverse-acoustic-phonon frequency.[12] (A detailed discussion of these effects is found in the following paper by the present author.)

The single particle (i.e., local) susceptibility χ^0, given by Eq. (4.9) plays the essential role in determining the temperature behavior of the collective orientational susceptability at low T. The effective orientational interaction which is obtained from Eq. (5.3) can be rewritten as

$$\varphi_2(x,T)=x\,\delta y_W\left[1-\frac{1}{3}\left[\frac{T_f}{T}\right]^2\right] \ , \quad x<x_c \ . \tag{5.8}$$

The decrease of φ_2 with decreasing temperature is in qualitative agreement with experiment.[9] The local susceptibility (4.9) is given by

$$\chi^0=\frac{xy_W}{T}\left[1-\frac{1}{3}\left[\frac{T_f}{T}\right]^2\right] \ , \tag{5.9}$$

it reaches its maximum at $T=T_f$ and also decreases for $T<T_f$. Although the orientational freezing process is not a phase transition in the proper sense, T_f is a characteristic temperature where the freezing process becomes effective. From the previous discussion one sees that the effect of the random field in establishing the glass state is

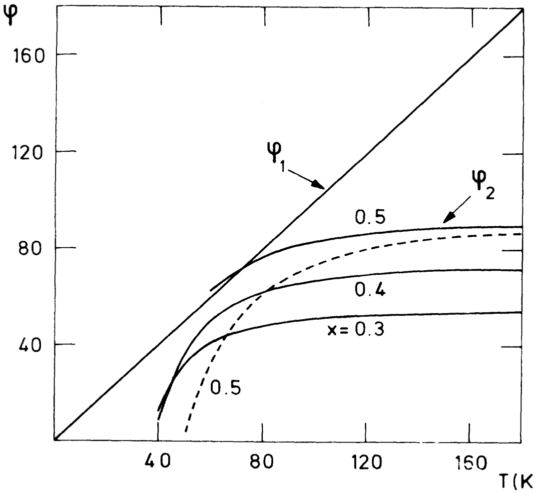

FIG. 1. Temperature dependence of functions φ_1 and φ_2 for several values of h and x: $h=300$ K for solid curves; $h=400$ K for dashed curve. CN concentrations x as indicated.

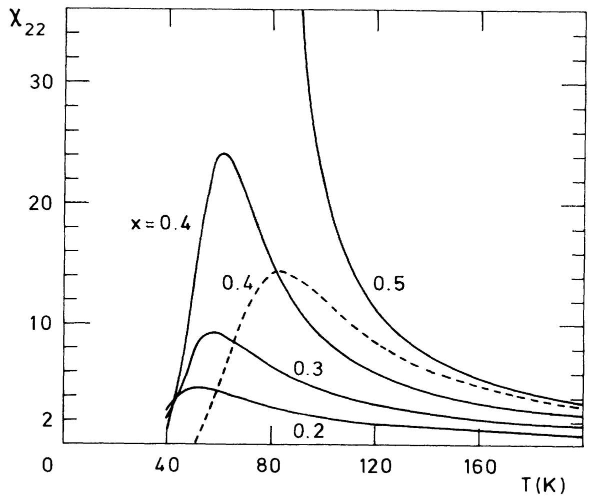

FIG. 2. Collective orientational susceptibility χ_{22} as function of temperature; $h=300$ K for solid curves; $h=400$ K for dashed curve. CN concentrations x as indicated.

twofold. First it leads to a reduction of the ferroelastic interaction such that $\varphi_2(x,T) < T$ for $x < x_c$, and secondly the random field favors the local freezing as follows from the decrease of the local susceptibility for $T < T_f$. If x increases towards x_c, T_f approaches T_0, the lowest temperature where χ_{22} diverges.

For $x > x_c$, the present theory leads to a second-order phase transition, the transition temperature $T_C(x)$ follows from Eqs. (5.5a) and (5.5b) by solving

$$\varphi_1(T_C,x)=\varphi_2(T_C,x)\ , \quad x \geq x_c\ . \tag{5.10}$$

For $x \to x_c$, one obtains by means of Eqs. (5.9) and (5.6b) that $T_C \to T_0$. For $x \geq x_c$ and $T < T_C(x)$, the crystal is in a low-symmetry, orientationally ordered phase. Using Eqs. (5.7) and (5.10), we have calculated the phase diagram which is shown in Fig. 3. Its overall aspect is reasonably consistent with experiment.[22]

The transition from the high-temperature cubic to the low-temperature ordered phase(s) is in reality of first order, while we obtain a second-order transition line $T_C(x)$. This discrepancy is due to the fact that we have neglected third-order terms in the order-parameter expansion of the free energy (4.13). Previously it has been shown that third-order terms lead to cubic invariants which are responsible for the first-order character of the ferroelastic phase transition in pure KCN.[34] Combining these concepts with the present model, it is possible to extend the calculation of the free energy for mixed crystals to third- and fourth-order terms. Since here we want to restrict ourselves to the presentation of a new model and its most simple consequences, we have deferred the derivation and the discussions of higher-order terms to a separate publication.[35]

The strength of the random field h^2 is determined by Eq. (3.8b). Using Eqs. (3.4), (2.12b), (2.9b), and (3.2), we write

$$h^2=(\Delta F^X B)^2 S\ , \tag{5.11}$$

where we have defined

$$S=\frac{1}{N}\sum_{\mathbf{k}}\{[\mathbf{w}_1(\mathbf{k})]^\tau \underline{M}^{-1}(\mathbf{k})\mathbf{w}^X(\mathbf{k})\}^2\ , \tag{5.12}$$

$$[\mathbf{w}_1(\mathbf{k})]^\tau=(2/\sqrt{m}\,)(\sin(k_y a), \sin(k_x a),0)\ , \tag{5.13a}$$

$$[\mathbf{w}^X(\mathbf{k})]^\tau=(2/\sqrt{m}\,)(\sin(k_x a), \sin(k_y a), \sin(k_z a))\ . \tag{5.13b}$$

In Eq. (5.12), $\underline{M}(\mathbf{k})$ stands for the acoustic bare dynamical matrix. The values of the cubic bare elastic constants are $c_{44}^0=0.5$, $c_{11}^0=4.0$, $c_{12}^0=1.2$ in units 10^{11} dyn/cm^2. The quantity S is evaluated by numerical integration over the Brillouin zone. We obtain $S=1.0\times 10^{-7}$ Å^4/K^2, where K stands for Kelvin. The force constants ΔF^X and B are calculated from the interatomic potential by taking into account Born-Mayer, Coulomb, and van der Waals terms. From Ref. 21 we have $B=1460$ K/Å. A reliable numerical estimate of ΔF^X, Eq. (2.8a), is a difficult problem of quantum chemistry. The determination of the microscopic potential parameters bears some uncertainties, in particular the electronic charge distribution of the CN$^-$ ion in the crystal is not well known.[21,36,37] Assuming that for the Coulomb forces, $\Delta F_c^X=0$, for both $X=\mathrm{Cl}$ and $X=\mathrm{Br}$, we retain only the Born-Mayer and van der Waals forces. Taking the force constants from Ref. 38, we estimate

$$\Delta F^{\mathrm{Br}}=(406-87)\ \mathrm{K/Å}\ , \tag{5.14a}$$

$$\Delta F^{\mathrm{Cl}}=(1083-79)\mathrm{K/Å}\ . \tag{5.14b}$$

The first number between parentheses refers to the Born-Mayer forces and the second to the van der Waals forces. Here we have taken the distance $a=3.26$ for the interaction K-CN and, $a=3.298$ for K-Br, and $a=3.147$ for K-Cl. From Eq. (5.6) we then find $h=150$ K in case of the bromide mixed crystal and $h=450$ K in case of the chloride. Although one should not consider these values as exact numbers, we estimate that they have the correct order of magnitude and that $h(\mathrm{Cl}) > h(\mathrm{Br})$.

Since the overall symmetry of the crystal is cubic, our considerations hold also for $\mathbf{k}=(0,k,0)$ and $(0,0,k)$.[34] These cases lead to a freezing in of the orientational modes described by $Y_1=Y_2^{1,s}$ and $Y_3=Y_2^{2,s}$. As a consequence of the local breaking of symmetry of the lattice due to the random strains, the local values of the orientational quadrupoles $\langle Y_\alpha(\mathbf{r})\rangle$ are different from zero and proportional to the corresponding random field $h_\alpha(\mathbf{r})$. From relations (3.6) and (3.8a) we then deduce

$$\overline{\langle Y_\alpha(\mathbf{r})\rangle}=0\ , \quad \overline{(\langle Y_\alpha(\mathbf{r})\rangle)^2}\neq 0\ . \tag{5.15}$$

These properties justify the basic assumptions made in Ref. 12 about the existence of the elastic central peak.[8]

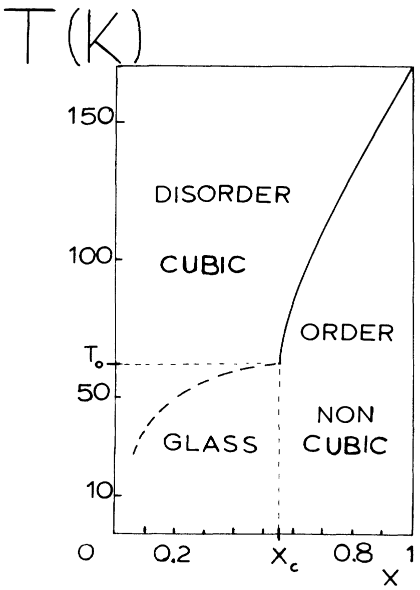

FIG. 3. Phase diagram for K(CN)$_x$Br$_{1-x}$ as a function of concentration and temperature, with values $\xi=0.06$, $h=294$ K chosen as parameters. To be compared with Fig. 1 of Ref. 22. The broken line represents curve $T_f(x)$.

VI. CONCLUDING REMARKS

Starting from the observation that the quadrupolar freezing occurs for different concentrations of halogens X in chloride and in bromide mixed crystals $M(\mathrm{CN})_x X_{1-x}$, we have studied the coupling of the orientational modes to random strain fields. The random strain fields are generated by the substitutional halogens. The free energy has been derived for a system of interacting orientational quadrupoles, coupled to dynamic lattice vibrations and to the random strain fields. The local orientational susceptibility becomes a function of the random field. The interplay of local and collective properties leads to a decrease of the effective orientational interaction $\varphi_2(x,T)$ with decreasing temperature (see Fig. 1). Above a certain value of the concentration $(1-x)$ of substitutional halogens, the ferroelastic phase transition is suppressed. The collective orientational susceptibility does not diverge but exhibits a smooth maximum at low temperature. The position of the maximum determines the freezing temperature T_f. With decreasing concentration of cyanides, T_f shifts to lower values. The theory is in qualitative agreement with many experimental features, in particular, the local breaking of cubic symmetry induced by the random strain fields implies the existence of an elastic central peak. The temperature dependence of the central peak, the temperature and frequency dependence of the phonon energy and of the phonon damping can also be accounted for. These problems will be treated in a separate paper.

The present treatment is based on classical statistical mechanics, therefore it is not valid at very low T where a quantum-mechanical version is required. However the physical mechanism which is based on the existence of random strain fields due to substitutional impurities, should remain valid in a quantum-mechanical treatment. It is tempting to assume that the ideas and concepts of the present paper are of interest for the understanding of other orientational glass systems such as *ortho*-H_2/para-H_2,[39] $(N_2)_x\mathrm{Ar}_{1-x}$[40] and $\mathrm{Rb}_{1-x}(\mathrm{NH}_4)_x\mathrm{H}_2\mathrm{PO}_4$.[41]

Most interesting are recent investigations on $(\mathrm{KCN})_x$ $(\mathrm{NaCN})_{1-x}$ crystals.[28,42] It is not difficult to reformulate the present theory in terms of the random strain fields which are generated by the substitutional counterions in $(\mathrm{NaCN})_{1-x}$ $(\mathrm{KCN})_x$ crystals. An essential difference however consists in the fact that the concentration of molecular ions is unity. Therefore the effective interaction between cyanides is given by

$$\varphi(T)=\delta y_W(T)[1-x(1-x)\xi_W h^2/T^2] , \tag{6.1}$$

instead of Eq. (5.5b). The results are symmetric in x and $(1-x)$, a feature which is borne out by the variation of $T_c(x)$ in Fig. 3 of Ref. 28. On the other hand, in $(\mathrm{KCN})_x$ $(\mathrm{KBr})_{1-x}$ crystals, this symmetry between substituted and substitutional units is spoiled, as follows from the first factor x on the right-hand side of expression (5.5b) for the effective interaction.

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APPENDIX

Starting from the potential (4.1), $V(\{\sigma\})$, we first calculate the corresponding free energy $F(\{\sigma\})$ by following and extending the method of Refs. 43 and 44. We have

$$F(\{\sigma\})=\mathrm{Tr}(\rho V+T\rho\ln\rho) , \tag{A1}$$

where V and the density matrix ρ depend on the quenched configuration $\{\sigma\}$ of impurities. The instantaneous expectation values of displacive and rotational modes are defined as

$$\mathbf{s}^e(\mathbf{k})=\mathrm{Tr}[\rho\mathbf{s}(\mathbf{k})] , \quad \mathbf{Y}^e(\mathbf{k})=\mathrm{Tr}[\rho\mathbf{Y}(\mathbf{k})] . \tag{A2}$$

The density matrix ρ satisfies $\mathrm{Tr}\rho=1$. Under the conditions (A2), the density matrix is obtained as

$$\rho=(1/Z)\,\mathrm{Tr}\exp(-\beta\mathscr{V}) , \quad Z=\mathrm{Tr}\exp(-\beta\mathscr{V}) , \tag{A3}$$

with $\beta=T^{-1}$ and

$$\mathscr{V}=V-\sum_{\mathbf{k}}[\boldsymbol{\lambda}^\dagger(\mathbf{k})\mathbf{s}(\mathbf{k})+\gamma^\dagger(k)Y(\mathbf{k})] . \tag{A4}$$

Here the Lagrange multipliers λ and γ play the role of external fields.[43] We rewrite (A1) as

$$F=F^e+\sum_{\mathbf{k}}[\boldsymbol{\lambda}^\dagger(\mathbf{k})\mathbf{s}^e(\mathbf{k})+\gamma^\dagger(\mathbf{k})\mathbf{Y}^e(\mathbf{k})] . \tag{A5}$$

Following Ref. 43, we obtain after some transformations

$$F^e=F_R(\mathbf{B},\mathbf{h})-\tfrac{1}{2}\sum_{\mathbf{k}}\boldsymbol{\lambda}^\dagger(\mathbf{k})\underline{M}^{-1}(\mathbf{k})\boldsymbol{\lambda}(\mathbf{k}) , \tag{A6}$$

with

$$\boldsymbol{\lambda}(\mathbf{k})=\underline{M}(\mathbf{k})\mathbf{s}^e(\mathbf{k})+\underline{v}^\tau(\mathbf{k})\mathbf{Y}^e(\mathbf{k}) , \tag{A7}$$

where the superscript τ stands for transposed. Here $F_R(\mathbf{B},\mathbf{h})$ is defined as

$$F_R(\mathbf{B},\mathbf{h})=-T\ln\mathrm{Tr}\exp[-\beta W^{RR}(\mathbf{B},\mathbf{h})-\beta W^R(\{\sigma\})] , \tag{A8}$$

with

$$W^{RR}(\mathbf{B})=\sum_{\mathbf{k}}[-\tfrac{1}{2}\mathbf{Y}^\dagger(\mathbf{k})\underline{L}(\mathbf{k})\mathbf{Y}(\mathbf{k}) + \mathbf{B}^\dagger(\mathbf{k})\mathbf{Y}(\mathbf{k})+\mathbf{h}^\dagger(\mathbf{k})\mathbf{Y}(\mathbf{k})] \tag{A9}$$

and

$$W^R(\{\sigma\})=V^R-C^s\sum_{\mathbf{r},\alpha}\sigma(\mathbf{r})Y_\alpha^2(\mathbf{r}) . \tag{A10}$$

$\underline{L}(\mathbf{k})$ is given by Eq. (5.2) and C^s by Eq. (4.8a),

$$\mathbf{B}(\mathbf{k})=\gamma(\mathbf{k})-\boldsymbol{\lambda}^\dagger(k)\underline{M}^{-1}(\mathbf{k})\underline{v}(\mathbf{k}) . \tag{A11}$$

The occurence of the random field $\mathbf{h}$ in Eq. (A9) is due to the term V^{SR} in Eq. (4.1).

The remaining problem consists in the evaluation of the orientational free energy $F_R(\mathbf{B},\mathbf{h})$. In order to perform a molecular field approximation, we separate the orientational mode into two parts

$$\mathbf{Y}(\mathbf{k})=\mathbf{Y}^e(\mathbf{k})-\boldsymbol{\Delta}(\mathbf{k}) . \tag{A12}$$

Here $\boldsymbol{\Delta}(\mathbf{k})$ accounts for fluctuations, with

$$\langle\boldsymbol{\Delta}(\mathbf{k})\rangle=\mathrm{Tr}[\rho\boldsymbol{\Delta}(\mathbf{k})]=0 . \tag{A13}$$

On the other hand, with the density matrix $\rho_W(\{\sigma\})$ defined by means of the potential (A10), $W(\{\sigma\})$, one has

$$\langle Y(\mathbf{k})\rangle_{W(\{\sigma\})}\equiv \mathrm{Tr}[\rho_W(\{\sigma\})Y(\mathbf{k})]=0 \ . \qquad \text{(A14)}$$

Substituting Eq. (A12) into Eq. (A8) and neglecting second order terms in Δ (mean-field approximation), we obtain

$$F_R^{\mathrm{MF}}(\mathbf{B},\mathbf{h})=\sum_{\mathbf{k}}[\tfrac{1}{2}\mathbf{Y}^{e\dagger}(\mathbf{k})\underline{L}(\mathbf{k})\mathbf{Y}^e(\mathbf{k}) - B^\dagger(\mathbf{k})\mathbf{Y}^e(\mathbf{k})]+F_R^W+F_R^\Delta \ . \qquad \text{(A15)}$$

Here F_R^W is the single particle rotational free energy

$$F_R^W=-T\ln \mathrm{Tr}[\exp(-\beta W^R)] \ . \qquad \text{(A16)}$$

F_R^Δ is given by

$$F_R^\Delta=-T\ln\left\langle \exp\left[-\beta\sum_{\mathbf{k}}[\mathbf{a}^\dagger(k)+\mathbf{h}^\dagger(\mathbf{k})]\Delta(\mathbf{k})\right]\right\rangle_{W(\{\sigma\})} \qquad \text{(A17)}$$

with

$$\mathbf{a}(\mathbf{k})=-\mathbf{Y}^e(\mathbf{k})\underline{L}(\mathbf{k})+\mathbf{B}(\mathbf{k}) \ . \qquad \text{(A18)}$$

Expression (A17) shows that the random field $\mathbf{h}$ occurs as an additional, symmetry breaking external field. Since the thermal average $\langle \ \rangle_W$ implies cubic symmetry, we expect that the lowest-order contributions in the random field are quadratic. We next perform a cumulant expansion of F_R^Δ and retain contributions up to second order in h and in Y^e. Subsequently we take the configurational average by using Eqs. (3.8a) and (3.8b). The final result reads

$$\bar{F}_R^\Delta=\sum_{\mathbf{k}}[\overline{\mathbf{a}^\dagger}(\mathbf{k})\overline{\mathbf{Y}^e}(\mathbf{k})-\tfrac{1}{2}\underline{\chi}^0\overline{\mathbf{a}^\dagger}(\mathbf{k})\bar{\mathbf{a}}(\mathbf{k})] \ , \qquad \text{(A19)}$$

where $\underline{\chi}^0$ is given by Eq. (4.9). In obtaining this expression, we have taken into account

$$\overline{\langle Y_\alpha^\dagger(\mathbf{k})Y_\beta(\mathbf{k})\rangle_{W(\{\sigma\})}}=\delta_{\alpha\beta_x}\langle Y_\alpha^2\rangle_W \ , \qquad \text{(A20a)}$$

and

$$\begin{aligned}\langle Y_{\alpha_1}(\mathbf{n}_1)Y_{\alpha_2}(\mathbf{n}_2)Y_{\alpha_3}(\mathbf{n}_3)Y_{\alpha_4}(\mathbf{n}_4)\rangle_W &= \delta_{\mathbf{n}_1\mathbf{n}_2}\delta_{\mathbf{n}_2\mathbf{n}_3}\delta_{\mathbf{n}_3\mathbf{n}_4}[\delta_{\alpha_1\alpha_2}\delta_{\alpha_2\alpha_3}\delta_{\alpha_3\alpha_4}\langle Y_\alpha^4\rangle_W+\delta_{\alpha_1\alpha_2}\delta_{\alpha_3\alpha_4}\langle Y_{\alpha_1}^2Y_{\alpha_3}^2\rangle_W(1-\delta_{\alpha_1\alpha_3})+\text{perm.}]\\ &\quad +[\delta_{\mathbf{n}_1\mathbf{n}_2}\delta_{\mathbf{n}_3\mathbf{n}_4}\delta_{\alpha_1\alpha_2}\delta_{\alpha_3\alpha_4}\langle Y_{\alpha_1}^2\rangle_W\langle Y_{\alpha_3}^2\rangle_W(1-\delta_{\mathbf{n}_1\mathbf{n}_3})+\text{perm.}] \ . \qquad \text{(A20b)}\end{aligned}$$

The subscript W denotes a thermal average calculated with the potential W^R, Eq. (4.7b). The Lagrange parameter γ [see Eqs. (A5), (A11), and (A18)] is obtained from $\partial\bar{F}_R^\Delta/\partial\gamma(\mathbf{k})=0$, or equivalently

$$\bar{\mathbf{a}}(\mathbf{k})=(\underline{\chi}^0)^{-1}\overline{\mathbf{Y}}^e(\mathbf{k}) \ . \qquad \text{(A21)}$$

Substituting this result into Eq. (A19), taking into account Eqs. (A5)—(A7), (A15), (A16) and (A19) we arrive at the result (4.6).

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[1] H. Suga, T. Matsuo, and S. Seki, Bull. Chem. Soc. Jpn. **38**, 1115 (1965).

[2] D. Durand and F. Lüty, Ferroelectrics **16**, 205 (1977); M. Julian and F. Lüty, Ferroelectrics **16**, 201 (1977).

[3] F. Lüty, in *Defects in Insulating Crystals*, edited by V. M. Turkevich and K. K. Shvarts (Springer-Verlag, Berlin, New York, 1981), p. 69.

[4] J. M. Rowe, J. J. Rush, N. Y. Chesser, D. L. Hinks, and S. Susman, J. Chem. Phys. **68**, 4320 (1978).

[5] S. K. Satija and C. H. Wang, Solid State Commun. **28**, 617 (1978).

[6] A. Loidl, R. Feile, K. Knorr, B. Renker, J. Daubert, D. Durand, and J. B. Suck, Z. Phys. B **38**, 253 (1980).

[7] S. Haussühl, Solid State Commun. **13**, 147 (1973).

[8] J. M. Rowe, J. J. Rush, D. G. Hinks, and S. Susman, Phys. Rev. Lett. **43**, 1158 (1979).

[9] A. Loidl, R. Feile, K. Knorr, and J. K. Kjems, Phys. Rev. B **29**, 6052 (1984); A. Loidl, K. Knorr, R. Feile, and J. K. Kjems, Phys. Rev. Lett. **51**, 1054 (1983).

[10] A. Loidl, M. Müllner, G. F. McIntyre, K. Knorr, and H. Jex, Solid State Commun. **54**, 367 (1985).

[11] B. W. Fisher and M. W. Klein, Phys. Rev. Lett. **43**, 289 (1979).

[12] K. H. Michel and J. M. Rowe, Phys. Rev. B **22**, 1417 (1980).

[13] J. J. De Yoreo, M. Meissner, R. O. Pohl, J. M. Rowe, J. J. Rush, and S. Susman, Phys. Rev. Lett. **51**, 1050 (1983).

[14] D. Moy, J. N. Dobbs, and A. C. Anderson, Phys, Rev. B **29**, 2160 (1984).

[15] P. M. Goldbart and D. Sherrington, J. Phys. C **18**, 1923 (1985).

[16] D. J. Gross, I. Kanter, and H. Sompolinsky, Phys. Rev. Lett. **55**, 304 (1985).

[17] C. W. Garland, J. Z. Kwiecien, and J. C. Damien, Phys. Rev. B **25**, 5818 (1982).

[18] J. Z. Kwiecien, R. C. Leung, and C. W. Garland, Phys. Rev. B **23**, 4419 (1981).

[19] M. A. Krivoglass, *Théorie de la Diffusion des Rayons X et des Neutrons Thermiques par les Cristaux Rèels* (Masson et Cie, Paris 1969).

[20] K. H. Michel and J. Naudts, Phys. Rev. Lett. **39**, 212 (1977); J. Chem. Phys. **67**, 547 (1977).

[21] K. H. Michel and J. M. Rowe, Phys. Rev. B **32**, 5818 (1985); **32**, 5827 (1985).

[22] K. Knorr and A. Loidl, Phys. Rev. B **31**, 5387 (1985).

[23] S. Elschner, K. Knorr, and A. Loidl, Z. Phys. B **61**, 209 (1985).

[24] S. Elschner and J. Petersson, J. Phys. C **19**, 3373 (1986); S. Elschner, Proceedings of the XXII Congress Ampère, edited by K. A. Müller, R. Kind, and J. Roos (Publisher, Zürich, 1984), p. 86.

[25] T. Schneider and E. Pytte, Phys. Rev. B **15**, 1519 (1977).

[26] A. Aharony, Phys. Rev. B **18**, 3318 (1978).

[27] K. Knorr and A. Loidl, Z. Phys. B **46**, 219 (1982).

[28] F. Lüty and J. Ortiz-Lopez, Phys. Rev. Lett. **50**, 1289 (1983).

[29] S. Bhattacharya, S. R. Nagel, L. Fleishman, and S. Susman, Phys. Rev. Lett. **48**, 1263 (1982); W. O. Birge, Y. H. Jeong, S. R. Nagel, S. Bhattacharya, and S. Susman, Phys. Rev. B **30**, 2306 (1984).

[30] U. G. Volkmann, R. Böhmer, A. Loidl, K. Knorr, U. T. Höchli, and S. Haussühl, Phys. Rev. Lett. **56**, 1716 (1986).

[31] J. P. Sethna, S. R. Nagel, and T. V. Ramakrishnan, Phys. Rev. Lett. **53**, 2489 (1984).

[32] D. Durand and F. Lüty, Phys. Status Solidi B **81**, 443 (1977).

[33] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1958).

[34] B. De Raedt, K. Binder, and K. H. Michel, J. Chem. Phys. **75**, 2977 (1981).

[35] T. Theuns and K. H. Michel (umpublished).

[36] M. L. Klein and I. R. McDonald, J. Chem. Phys. **79**, 2333 (1983).

[37] D. Sahu and S. Mahanti, Phys. Rev. B **26**, 2981 (1982).

[38] M. L. Klein, I. R. McDonald, and Y. Ozaki, J. Chem. Phys. **79**, 5579 (1983).

[39] N. S. Sullivan, M. Devoret, B. P. Cowan, and C. Urbina, Phys. Rev. B **17**, 5011 (1978).

[40] W. Press, B. Janik, and H. Grimm, Z. Phys. B **49**, 9 (1982).

[41] E. Courtens, J. Phys. Lett. **43**, L199 (1982); Phys. Rev. Lett. **52** 69 (1984).

[42] A. Loidl, T. Schräder, R. Böhmer, K. Knorr, J. J. Kjems, and R. Born, Phys. Rev. B **34**, 1238 (1986).

[43] J. Feder and E. Pytte, Phys. Rev. B **8**, 3978 (1973).

[44] K. H. Michel and E. Courtens, Phys. Rev. B **23**, 513 (1981); K. H. Michel and K. Parlinski, *ibid.* **31**, 1823 (1985).