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# Structural phase transitions and polymorphism in mixed crystals $M(\mathrm{CN})_xX_{1-x}$ ($M$=Na, K, Rb; $X$=Cl, Br, I)

K. H. Michel and T. Theuns*

*Department of Physics, Universitaire Instelling Antwerpen, B-2610 Wilrijk, Belgium*

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A microscopic model, which takes into account quadratic and cubic interactions between translational and orientational degrees of freedom, for mixed alkali-cyanide–alkali-halide crystals is proposed. The resulting free energy allows us to clarify the mechanisms which lead to the orthorhombic, monoclinic, and rhombohedral phases. The influence of external parameters such as temperature, CN concentration, and pressure is discussed.

## I. INTRODUCTION

The alkali cyanides $M$CN,[1–6] where $M$ stands for an alkali-metal atom (Na,K,Rb), and the mixed alkali-cyanide–alkali-halides $M(\mathrm{CN})_xX_{1-x}$,[7–9] where $X$ is a halogen atom (Cl,Br,I), exhibit a large variety of crystalline phases. Transitions among these phases are characterized by interesting anomalies in elastic,[10,11] optical,[12] and dielectric properties.[13,14] The phase transitions are influenced by experimental parameters such as pressure,[15,16] temperature, and composition.[13,17,7]

In the present paper we study the polymorphism of these crystals as a function of external parameters. The problem is of considerable interest. Recently it has been suggested[18] that KCN at the ferroelastic transition is close to a triple point where cubic, orthorhombic, and monoclinic phases coexist. In mixed crystals, the substitutional impurities cause random strain fields.[19,20] The random strain fields are essential for the formation of the orientational glass state.[21] It has also been proposed,[22] as an extension of these concepts, that dynamic random strain fields in molecular crystals can be generated by molecules in an excited rotational state.

Previously, the occurrence of the ferroelastic phase transition in the alkali cyanides has been described by a theory based on bilinear translation-rotation coupling.[23] Comparison with group-theoretical arguments[24] shows that this microscopic model is incomplete. It does not lead to a negative fourth-order term in the free energy. If one considers an order parameter of $T_{2g}$ symmetry only, the existence of such a term is required in order to obtain a first-order phase transition to the orthorhombic structure. On the basis of experimental results,[8,9] we will restrict ourselves here to $T_{2g}$ symmetry.

On the other hand, if one allows for a coupling of one component of $E_g$ symmetry with a square of $T_{2g}$ symmetry, it is possible to obtain a first-order transition, too. This coupling was introduced by Sahu and Mahanti,[25] who have derived a Landau free energy with third- and fourth-order terms, including coupling terms of $E_g$ and $T_{2g}$ symmetry.

In the next section we will extend the model by making the electric quadrupole interaction displacement dependent. Such a generalization of the compressible Ising model[26] leads to a negative fourth-order term in the free energy. In Sec. III, we calculate the free energy by starting from the microscopic model. The calculation is based on molecular-field theory, but takes into account random strain fields in mixed crystals. Next (Sec. IV) we discuss the physical consequences, in particular the polymorphism as a function of experimental parameters. We shall show that the present model leads in a consistent way to transitions from the cubic to the orthorhombic, monoclinic and rhombohedral phases. In particular, we find that the monoclinic structure is due to cubic coupling between a Brillouin-zone–center mode and two zone-boundary modes. Concluding remarks are given in Sec. V

## II. THE MODEL

We consider a mixed crystal $M(\mathrm{CN})_xX_{1-x}$ in the high-temperature cubic phase. The lattice structure has $Fm3m$ space-group symmetry. The CN ions have dynamic orientational disorder (plastic phase). Starting from $M$CN, the mixed crystal is obtained by random substitution of CN ions by halogens ($X$). The total interaction potential is given by

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

The first four terms on the right-hand side have been considered previously.[19] The harmonic acoustic-phonon potential is given by

$$V^{TT}=\tfrac{1}{2}\sum_{\mathbf{q}}M_{ij}(\mathbf{q})s_i^{\dagger}(\mathbf{q})s_j(\mathbf{q}) , \qquad (2.2)$$

$M(k)$ stands for the corresponding bare dynamical matrix in absence of $T$-$R$ coupling. $s_i(\mathbf{q})$ denotes the Fourier transform of the $i$th Cartesian component of the acoustic lattice displacements of wave vector $\mathbf{q}$. The contribution $V^{TR}$ in Eq. (2.1) represents the bilinear translation ($T$) -rotation ($R$) coupling[23]

$$V^{TR}=\sum_{\mathbf{q}}\hat{v}_{\alpha i}(\mathbf{q})Y_{\alpha}^{\dagger}(\mathbf{q})s_i(\mathbf{q}) . \qquad (2.3a)$$

Here $Y_\alpha(\mathbf{q})$ is the Fourier transform of the three symmetry-adapted functions $Y_\alpha$ of $T_{2g}$ symmetry and angular momentum quantum number $l=2$. $Y_\alpha$ are proportional to $\hat{x}\,\hat{y}$, $\hat{y}\,\hat{z}$, and $\hat{z}\,\hat{x}$ for $\alpha=1$, 2, and 3, respectively. The matrix $\hat{v}(\mathbf{q})$ is given by[23,27]

$$\hat{v}(\mathbf{q})=-\frac{i2B}{\sqrt{m}}\begin{bmatrix}\sin(q_y a) & \sin(q_x a) & 0\\ 0 & \sin(q_z a) & \sin(q_y a)\\ \sin(q_z a) & 0 & \sin(q_x a)\end{bmatrix}\;, \tag{2.3b}$$

$B$ is a constant, and $m$ is the average total mass per unit cell.

Substitutional disorder is taken into account by the occupation variable $\sigma(\mathbf{n})$ with value $+1$ in presence of a CN ion and value 0 in presence of an $X$ ion at lattice site $\mathbf{n}$. We therefore write

$$Y_\alpha(\mathbf{q})=\frac{1}{\sqrt{N}}\sigma(\mathbf{n})Y_\alpha(\mathbf{n})e^{-i\mathbf{q}\cdot\mathbf{X}(\mathbf{n})}\;, \tag{2.4}$$

where $N$ is the number of unit cells, and where $\mathbf{X}(\mathbf{n})$ denotes the rigid-lattice position. The term $V^R$ in Eq. (2.1) refers to a sum of single-particle crystal-field potentials[27] of symmetry $A_{1g}$. The electrical quadrupole-quadrupole interaction among neighboring CN ions[28,29] is given by

$$V^{RR}=\tfrac{1}{2}\sum_{\mathbf{q}}J_{\alpha\beta}(\mathbf{q})Y_\alpha^\dagger(\mathbf{q})Y_\beta(\mathbf{q})\;. \tag{2.5}$$

The matrix $J(\mathbf{q})$ is quoted in Appendix A. In the case of a compressible lattice, the quadrupole interaction has to be expanded in terms of lattice displacements. Additional details of the calculation are given in Appendix A. Here we quote the result

$$V^{RRT}=\frac{1}{2\sqrt{N}}\sum_{\mathbf{p},\mathbf{q}}J'_{\alpha\beta i}(\mathbf{p},\mathbf{q})Y_\alpha^\dagger(\mathbf{p}+\mathbf{q})Y_\beta(\mathbf{p})s_i(\mathbf{q})\;. \tag{2.6}$$

The term $V^{SR}$ in Eq. (2.1) accounts for the interaction of the residual CN ions with the static random strain fields which are generated by the substitutional halogen ions,[19]

$$V^{SR}=\sum_{\mathbf{q}}Y_\alpha(\mathbf{q})h_\alpha(-\mathbf{q},\{\sigma\})\;. \tag{2.7}$$

Here

$$h_\alpha(\mathbf{q},\{\sigma\})=\frac{1}{\sqrt{N}}\sum_{\mathbf{n}}h_\alpha(\mathbf{n},\{\sigma\})e^{-i\mathbf{q}\cdot\mathbf{X}(\mathbf{n})} \tag{2.8}$$

is a static random field for which we assume a Gaussian distribution. We have $\bar{h}_\alpha=0$ and

$$\overline{h_\alpha h_\beta}=x(1-x)h^2\delta_{\alpha\beta}\equiv H\delta_{\alpha\beta}\;, \tag{2.9}$$

where the overbar denotes a configurational average. The quantity $h^2$ has been calculated in Ref. 19.

## III. FREE ENERGY

In the preceding section we derived the model potential $V$, Eq. (2.1), for a system of interacting molecules on a compressible lattice and in the presence of static random-strain fields. The positional disorder is quenched. Here we will calculate the free energy for that model. We will use the same procedure as in Ref. 19. This means that we take the virtual-crystal approximation in treating the effective orientational interaction. In contradistinction with spin-glass theory,[30] we neglect the random-bond aspects of the molecular interaction. This seems to be reasonable because in the present system the elastic interactions are strong and vary on a length scale much larger than the average distance between CN molecular ions. On the other hand, we treat the effect of the halogen impurities as a static random field which couples to the orientational order parameter. As has been shown[31] for an Ising spin system, the random-field problem can be treated within molecular-field theory. We will adopt here the same point of view. We first calculate the free energy for a given configuration $\{\sigma\}$ of substitutional halogen impurities. At the end of the calculation, we take the configurational averages.

We start with the free energy

$$F=\mathrm{Tr}(\rho V+T\rho\ln\rho)\;. \tag{3.1}$$

Here Tr denotes the trace and $T=\beta^{-1}$ denotes the temperature (with units in which $k_B=1$). The density matrix $\rho$ and the instantaneous expectation values $s^e$ and $Y^e$ satisfy the relations

$$\mathrm{Tr}\rho=1\;, \tag{3.2a}$$

$$s_i^e(\mathbf{q})=\mathrm{Tr}[\rho s_i(\mathbf{q})]\;, \tag{3.2b}$$

$$Y_\alpha^e(\mathbf{q})=\mathrm{Tr}[\rho Y_\alpha(\mathbf{q})]\;. \tag{3.2c}$$

We have used the method of Lagrange multipliers, which was applied before to a spin-phonon coupled system[32] and to molecular crystals.[33] Details of the calculation will be published separately. The final result for the free energy reads

$$\begin{aligned}F=F_{\mathrm{ph}}+F_R+\sum\Bigg[&\tfrac{1}{2}M_{ij}(\mathbf{q})s_i^{e\dagger}(\mathbf{q})s_j^e(\mathbf{q})+\hat{v}_{\alpha i}(\mathbf{q})Y_\alpha^{e\dagger}(\mathbf{q})s_i^e(\mathbf{q})+\tfrac{1}{2}\left[J(\mathbf{q})+\underline{1}C^s+\underline{1}\frac{T}{x\alpha_1}X(2)\right]_{\alpha\beta}Y_\alpha^{e\dagger}(\mathbf{q})Y_\beta^e(\mathbf{q})\\&+\frac{1}{2\sqrt{N}}J'_{\alpha\beta i}(\mathbf{p},\mathbf{q})Y_\alpha^{e\dagger}(\mathbf{p}+\mathbf{q})Y_\beta^e(\mathbf{p})s_i^e(\mathbf{q})\Bigg]+F_S^{(3)}+F_S^{(4)}+F_S^{(6)}\;.\end{aligned} \tag{3.3}$$

Here $\underline{1}$ stands for the unit matrix and summation $\sum$ is understood to be over the wave vector $\mathbf{q},\mathbf{p}$ and over repeated indices $i,\alpha,\ldots$. The first five terms on the right-hand side have been derived previously.[19] The contributions $F_S^{(n)}$, $n=3,4,6$, are due to entropy. Explicitly we have

$$F_S^{(3)}=-\frac{\alpha_2 T}{3!\underline{x}^2\alpha_1^3}X(3,1)\frac{1}{\sqrt{N}}\sum Y_\alpha^e(\mathbf{p})Y_\beta^e(\mathbf{q})\times Y_\gamma^{e\dagger}(\mathbf{p}+\mathbf{q})\varepsilon_{\alpha\beta\gamma}\;, \tag{3.4a}$$

where $\varepsilon_{\alpha\beta\gamma}=1$ if $\alpha$, $\beta$, and $\gamma$ are different, and $\varepsilon_{\alpha\beta\gamma}=0$ otherwise. Furthermore, we have

$$F_S^{(4)}=\frac{T}{4!x^3\alpha_1^5}\frac{1}{N}\sum\{[6\alpha_2^2X(3,2)-3\alpha_1 a_1 X(4,1)+3\alpha_1 a_2 X^2(2)](1-\delta_{\alpha\beta})$$
$$+[6\alpha_2^2X(3,2)+3\alpha_1 a_2 X^2(2)-\alpha_1 a_2 X(4,2)]\delta_{\alpha\beta}\}\,Y_\alpha(\mathbf{p})Y_\alpha(\mathbf{q})Y_\beta(\mathbf{k})Y_\beta^\dagger(\mathbf{p}+\mathbf{q}+\mathbf{k})\ . \tag{3.4b}$$

Here we have introduced the definitions

$$X(2)=\langle Y^2\rangle_0^{-1}\ , \tag{3.5a}$$
$$X(3,1)=\langle YYY\rangle_0 X^3(2)\ , \tag{3.5b}$$
$$X(4,1)=\langle Y^2Y^2\rangle_0 X^4(2)\ , \tag{3.5c}$$
$$X(4,2)=\langle Y^4\rangle_0 X^4(2)\ , \tag{3.5d}$$
$$X(3,2)=X^2(3,1)\langle Y^2\rangle_0, \tag{3.5e}$$

and

$$\alpha_1=1-B_1H/T^2,\quad \alpha_2=1+C_1H/T^2\ , \tag{3.6a}$$
$$a_1=1-D_1H/T^2,\quad a_2=1-D_2H/T^2\ . \tag{3.6b}$$

The coefficients $B_1, C_1$ and $D_1, D_2$ are given in Appendix B; the quantity $H$ has been defined in Eq. (2.9). The thermal averages $\langle\ \rangle_0$ are evaluated with the single-particle density matrix

$$\rho_W=\exp(-\beta W^R)/\mathrm{Tr}[\exp(-\beta W^R)]\ , \tag{3.7}$$

where $W^R$ is the sum of the crystal-field potential and the self-interaction.[27] We have not calculated explicitly the sixth-order term. We only assume that $F_S^{(6)}\geq 0$. For a given configuration of orientations $\{Y_\alpha^e\}$, we determine the displacements $\{s_i^e\}$ by minimizing $F$ with respect to $s_i^e(\mathbf{q})$ and obtain

$$s_i^e(\mathbf{q})=-M_{ij}^{-1}(\mathbf{q})\left[v_{\alpha j}^{\tau}(-\mathbf{q})Y_\alpha^e(\mathbf{q})+\frac{1}{2\sqrt{N}}\sum_{\mathbf{p}}J'_{\alpha\beta j}(\mathbf{p},-\mathbf{q})Y_\alpha^{e\dagger}(\mathbf{p}-\mathbf{q})Y_\beta^e(\mathbf{p})\right]\ . \tag{3.8}$$

We then eliminate $s^e$ and obtain $F$ as a Landau expansion in $Y^e$,

$$F=F_{\mathrm{ph}}+F_R+F_I+F_S\ . \tag{3.9}$$

Here $F_I$ is the contribution due to interaction,

$$F_I=\sum\left[\tfrac{1}{2}L_{\alpha\beta}(\mathbf{q})Y_\alpha^{e\dagger}(\mathbf{q})Y_\beta^e(\mathbf{q})-\frac{1}{8N}I_{\alpha\beta\gamma\delta}(\mathbf{p},\mathbf{k};\mathbf{q})Y_\alpha^{e\dagger}(\mathbf{p}+\mathbf{q})Y_\beta^e(\mathbf{p})Y_\gamma^{e\dagger}(\mathbf{k}-\mathbf{q})Y_\delta^e(\mathbf{k})\right.$$
$$\left.-\frac{1}{2\sqrt{N}}K_{\alpha\beta\gamma}(\mathbf{p},\mathbf{q})Y_\alpha^{e\dagger}(\mathbf{p}+\mathbf{q})Y_\beta^e(\mathbf{p})Y_\gamma^e(\mathbf{q})\right]\ , \tag{3.10}$$

where

$$L_{\alpha\beta}(\mathbf{q})=J_{\alpha\beta}(\mathbf{q})-C_{\alpha\beta}(\mathbf{q})+\delta_{\alpha\beta}C^s\ , \tag{3.11a}$$
$$I_{\alpha\beta\gamma\delta}(\mathbf{p},\mathbf{k};\mathbf{q})=J'_{\alpha\beta i}(\mathbf{p},\mathbf{q})M_{ij}^{-1}(\mathbf{q})J'_{\gamma\delta j}(\mathbf{k},-\mathbf{q})\ , \tag{3.11b}$$
$$K_{\alpha\beta\gamma}(\mathbf{p},\mathbf{q})=J'_{\alpha\beta i}(\mathbf{p},\mathbf{q})M_{ij}^{-1}(\mathbf{q})v_{\gamma j}^{\tau}(-\mathbf{q})\ , \tag{3.11c}$$
$$C_{\alpha\beta}(\mathbf{q})=\hat{v}_{\alpha i}(\mathbf{q})M_{ij}^{-1}(\mathbf{q})\hat{v}_{\beta j}^{\tau}(-\mathbf{q})\ , \tag{3.11d}$$
$$C^s=\frac{1}{N}\sum_{\mathbf{q}}C_{\alpha\alpha}(\mathbf{q})\ ; \tag{3.11e}$$

the index $\tau$ stands for transposed. The entropy contribution $F_S$ is given by

$$F_S=\sum_n F_S^{(n)},\quad n=2,3,4,6\ . \tag{3.12}$$

We have already specified $F_S^{(3)}$ and $F_S^{(4)}$, and we quote

$$F_S^{(2)}=\frac{1}{2}\frac{T}{y}\sum Y_\alpha^{e\dagger}(\mathbf{q})Y_\alpha^e(\mathbf{q})\ , \tag{3.13}$$

where

$$y=x\alpha_1X^{-1}(2)\ . \tag{3.14}$$

## IV. DISCUSSION

Expression (3.9) of the free energy describes the state of the mixed crystal $M(\mathrm{CN})_xX_{1-x}$ in the orientationally disordered phase. The coefficients of the series expansion in powers of the orientational order parameter $Y_\alpha$ depend on temperature, CN concentration $x$, and lattice constant $2a$. The dependence on these external parameters is different for the interaction contribution $F_I$ and the entropy $F_S$, respectively. The competition between internal energy and entropy is essential in determining the crystalline structure. *A priori,* there exists a wide range of possibilities for the low-$T$ phases. Our present knowledge of the atomistic constants, in particular of the electric quadrupole moment of the $\mathrm{CN}^-$ ion in a crystalline structure,[34] is not sufficient to allow for a quantitative calculation for the free energy. We therefore restrict ourselves to a more qualitative discussion, using group theory and experiment as guidelines.

### A. Orthorhombic phases

We first consider the ferroelastic transition $Fm3m\rightarrow Immm$ in KCN and NaCN. One component of

$T_{2g}$ symmetry condenses with wave vector $\mathbf{q}$ at the Brillouin-zone center.[24] We consider $\mathbf{q}_0=(q_x,0,0)$, with $q_x \to 0$. The order parameter is $Y_l^e(\mathbf{q})=\sqrt{N}\,\eta$, with $Y_\alpha^e=0$, $\alpha=2,3$. The free-energy term $F_I$, Eq. (3.10), reads

$$(1/N)F_I=A_I\eta^2+C_I\eta^4 \ , \tag{4.1}$$

with

$$A_I=\tfrac{1}{2}L_{11}(\mathbf{q}_0) \ , \tag{4.2a}$$

$$C_I=-\tfrac{1}{8}J'_{11x}(0,\mathbf{q}_0)M_{xx}^{-1}(\mathbf{q}_0)J'^{*}_{11x}(0,\mathbf{q}_0) \ . \tag{4.2b}$$

From Eq. (3.12) we get

$$(1/N)F_S=A_S\eta^2+C_S\eta^4+D_S\eta^6 \ , \tag{4.3}$$

with

$$A_S=\tfrac{1}{2}Ty^{-1} \ , \tag{4.4a}$$

$$C_S=\frac{T}{4!x^3\alpha_1^4}[3a_2X^2(2)-a_1X(4,2)] \ . \tag{4.4b}$$

We have not explicitly calculated $D_S$. All we need in the following is the assumption that $D_S$ is positive. For an Ising model, $D_S=T/30$.

Applying Landau theory[35] to $F=F_I+F_S$, we find a first-order or a second-order phase transition, depending on whether the fourth-order term in the expansion is negative or positive. Consequently, the transition to the orthorhombic phase is of first order if

$$|C_I|>C_S \ . \tag{4.5}$$

We observe that in all cases which we have studied numerically, $C_S$ was found to be positive. For an Ising model, $C_S=T/12$. Condition (4.5) apparently holds for $x \approx 1$ in $M(\mathrm{CN})_xX_{1-x}$ for $M$ given by Na or K. The first-order transition occurs at a temperature

$$T_1=T_c+\frac{C^2}{4A'D_S} \ , \tag{4.6}$$

where $C=-|C_I|+C_S$ and

$$T_c=y|L_{11}(\mathbf{q}_0)| \ . \tag{4.7a}$$

Defining $A'$ by $A=A'(T-T_c)$ with $A=A_I+A_S$, we have

$$A'=A_ST^{-1} \ . \tag{4.7b}$$

The discontinuity of the order parameter is given by

$$\Delta\eta=\left[\frac{-C}{2D_S}\right]^{1/2} \ . \tag{4.8}$$

By applying hydrostatic pressure, one finds that $T_1$ increases and that the first-order character of the transition becomes more pronounced.[15,16] An increase of pressure leads to a decrease of the lattice constant $a$. From Eqs. (A8c) and (4.2b) it then follows that $|J'|$ and $|C_I|$ increase. On the other hand, quantities such as $T_C$, $M$, $C_S$, and $D_S$, which depend on attractive and repulsive forces, are practically unaffected by pressure. We conclude that the orthorhombic phase is stabilized by hydrostatic pressure since the negative fourth-order term $\propto -|C_I|\eta^4$ in the free energy becomes dominant. Recalling that $\eta \propto \hat{x}\,\hat{y}$, we see that this term also favors an alignment of the CN quadrupoles along [110] directions of the original cubic phase. In Eq. (4.8), $\Delta\eta$ increases with $|C_I|$.

From Eqs. (4.2b) and (4.4b) we notice that $C_I \propto x^0$ and $C_S \propto x^{-3}$, $x$ being the CN concentration. If $C_S$ and $C_I$ are of the same order of magnitude, it follows that the inequality (4.5) can be reversed with decreasing $x$. In $\mathrm{K(CN)}_x\mathrm{Br}_{1-x}$, the orthorhombic phase already becomes unstable for $x \approx 0.95$,[9] while in $\mathrm{Na(CN)}_x\mathrm{Cl}_{1-x}$ the orthorhombic phase extends to $x \approx 0.90$.[36]

The first-order nature of the ferroelastic transition to the orthorhombic structure is more pronounced in NaCN than in KCN, while RbCN exhibits a transition to an antiferroelastic monoclinic structure.[37] We recall that $a=2.95$, 3.25, and 3.42 Å for these three compounds, respectively. Since $C_I \propto a^{-10}$, we are led to the conclusion that, in NaCN, $|C_I|>C_S$, while, in RbCN, $|C_I|<C_S$. In KCN, $|C_I| \approx C_S$, and thermal cycling experiments show that KCN acts as a "bistable borderline case."[18] The ferroelastic phase obtained in the first cycle consists of orthorhombic domains. By returning to higher $T$, scars of these domains remain as imperfections in the cubic phase. These imperfections are sources of random strain fields (similar to random strain fields caused by substitutional halogens). The strain fields affect the free energy through the factors $\alpha_1$ [see Eqs. (3.6a) and (4.4b)]. In Eq. (3.6a) for $\alpha_1$, the random field $H$ is now caused by the scars. An increase of $C_S \propto \alpha_1^{-4}$ leads to a destabilization of the orthorhombic structure to the advantage of the antiferroelastic monoclinic phase.

### B. Monoclinic phases

The monoclinic structure has been found in KCN subjected to thermal cycling,[38,18] in RbCN,[37] and in compounds $M(\mathrm{CN})_xX_{1-x}$ (Refs. 8, 9, 39, and 40) for certain ranges of concentrations. The structure contains two formula units per primitive unit cell,[39] the $\mathrm{CN}^-$ ions are arranged in skewed directions.[37] In addition to shear deformations with respect to the cubic structure, reflections have been detected at the $L$ point of the original cubic Brillouin zone.[8] On the other hand, the transition to the "antiferroelastic"[18] monoclinic structure is also preceded by a softening of the elastic constants $c_{44}$ in the cubic phase.[41] We attribute the interplay of these phenomena to a coupling of type (2.6) between two orientational modes at the $L$ point of the Brillouin zone and a shear mode at the zone center. See Eqs. (A10a) and (A10b).

Following Parlinski,[24] we consider the reduction of the physical representation of orientations to the point group of the wave vector $\mathbf{p}_L=(\pi/2a)(1,1,1)$. We consider the irreducible representation $\hat{\tau}^5$ with basis spanned by the symmetry adapted function $Y_{l=2}^{1s} \propto \hat{y}\,\hat{z}$ and $Y_{l=2}^{1-c} \propto -\hat{z}\,\hat{x}$. They correspond to our functions $\pm Y_\alpha$, $\alpha=2,3$, respectively. Following Ref. 24, we take the amplitude $\rho$ of the two components equal but with an opposite sign:

$$Y_\alpha(\mathbf{n})=\pm(\rho/\sqrt{N})\cos[\mathbf{p}_I\cdot\mathbf{X}(\mathbf{n})]\ , \tag{4.9}$$

where we retain the + sign for $\alpha=2$ and − sign for $\alpha=3$. At the $L$ point, the electrical quadrupole interaction (A2) is nondiagonal in the components $\alpha$, and we find from Eq. (2.5)

$$V^{RR}=-\xi\rho^2\ , \tag{4.10}$$

where $\xi=\sqrt{2}\pi Q^2/a^5$. This interaction corresponds to a staggered (antiferroelastic[18]) arrangement of the CN quadrupoles in space. If there were no coupling to the elastic degrees of freedom, the corresponding transition temperature would be given by

$$T_Q=\xi y\ . \tag{4.11}$$

With $x=1$, $\alpha_1=1$, $X^{-1}(2)\approx 0.08$, and $\xi=939$ K, we would obtain $T_Q=75$ K for KCN, while the ferroelastic transition, with the same parameters,[27] occurs at 191 K. For RbCN, we estimate $T_Q=58$ K, while the experimental result is 132 K,[14] close to a value to be expected from a ferroelastic transition.

We consider the free energy (3.3) and separate shear modes, which are related to the Brillouin-zone center $\mathbf{q}_0=(0,0,q_z)$ with $q_z\to 0$, from zone-boundary ($L$ point) modes:

$$F(\mathbf{p}_L,q_z)=\tfrac{1}{2}M_{ii}(q_z)s_i^{e\dagger}(q_z)s_i(q_z)+\hat{v}_{\alpha i}(q_z)Y_\alpha^{e\dagger}(q_z)s_i^e(q_z)+\frac{1}{2}\left[J(q_z)+C^s+\frac{T}{y}\right]_{\alpha\alpha}Y_\alpha^{e\dagger}(q_z)Y_\alpha^e(q_z)$$
$$+\frac{N}{y}(T-T_Q)\rho^2+\frac{ic\sqrt{N}q_z}{\sqrt{m}}[s_y(q_z)+s_x(q_z)]\rho^2+NC_S'\rho^4+ND_S'\rho^6\ , \tag{4.12}$$

where $c=5\pi Q^2/[a^5(\sqrt{2})^3]$, and

$$C_S'=\frac{2T}{4!x^3\alpha_1^5}[12\alpha_2^2X(3,2)+6\alpha_1a_2X^2(2)$$
$$-3\alpha_1a_1X(4,1)-\alpha_1a_1X(4,2)]\ . \tag{4.13}$$

Both $C_S'$ and $D_S'$ are positive. We assume that fourth- and higher-order terms in $Y^e(q_z)$ are negligible. Furthermore, we neglect the longitudinal modes $s_z(q_z)$ and also the orientational modes $Y_l(q_z)$. These modes are stiff in comparison to the soft transverse modes.[23] We therefore consider Eq. (4.12) for the indices $\alpha=2$ and 3, and $i=x$, and $y$. For a given configuration of $\rho$ and $s_i(q_z)$, we minimize $F$ with respect to $Y_2^{e\dagger}(q_z)$ and obtain

$$Y_2(q_z)=-[J_{22}(0)+C^s+(T/y)]^{-1}\hat{v}_{2y}(q_z)s_y(q_z)\ . \tag{4.14}$$

A similar expression is obtained for $Y_3(q_z)$ with $\hat{v}_{2y}$ replaced by $\hat{v}_{3x}$ and $s_y$ by $s_x$. We notice that $J_{22}=J_{33}\equiv J$. Eliminating $Y_2(q_z)$ and $Y_3(q_z)$, we obtain for the free energy (4.12)

$$F(\mathbf{p}_L,q_z)=\tfrac{1}{2}D_{ii}(q_z)s_i^{e\dagger}(q_z)s_i^e(q_z)$$
$$+\frac{ic\sqrt{N}}{\sqrt{m}}q_z1_{ii}s_i^e(q_z)\rho^2$$
$$+\frac{N}{y}(T-T_Q)\rho^2+NC_S'\rho^4+ND_S'\rho^6\ , \tag{4.15}$$

where $D_{xx}=D_{yy}$, with[27]

$$D_{xx}(q_z)=\frac{2a^3}{m}q_z^2c_{44}^0\left[\frac{T-T_c}{T+(C^s+J)y}\right]\ . \tag{4.16}$$

The ferroelastic transition temperature $T_c$ is given by Eq. (4.7a). Due to the coupling $c$ in Eq. (4.15) between shear modes and staggered quadrupoles, the real transition occurs at a temperature $T_1>T_c$. We now determine $T_1$. Minimizing Eq. (4.15) with respect to $s_i$ for $\rho$ fixed, we get

$$s_i(q_z)=i\frac{c\sqrt{N}}{\sqrt{m}}q_zD_{ii}^{-1}(q_z)\rho^2\ . \tag{4.17}$$

Elimination of $s_i$ yields

$$(1/N)F(\mathbf{p}_L,q_z)=(1/y)(T-T_Q)\rho^2+C'\rho^4+D_S'\rho^6\ , \tag{4.18a}$$

$$C'=C_S'-(c^2/2m)q_z^2D_{11}^{-1}(q_z)\ . \tag{4.18b}$$

If $C'$ is negative, we obtain a first-order transition at a temperature $T_1$ which follows from the solution of

$$y(T_1)[C'(T_1)]^2-4(T_1-T_Q)D_S'(T_1)=0\ . \tag{4.19}$$

We recall that $T_Q$ is of the order of $0.5T_c$. Furthermore, $y$, $C_S$, and $D_S'$ are smooth functions of $T$. The dominant $T$ dependence arises from the last term on the right-hand side of Eq. (4.18b) if $T$ approaches $T_c$. Taking for the smooth functions their value at $T_c$, we obtain the transition temperature

$$T_1=T_C+\frac{\alpha'}{C_S'\pm 2[(T_c-T_Q)D_S'y^{-1}]^{1/2}}\ . \tag{4.20}$$

The + sign has to be taken if $C_S'<[(T_c-T_Q)D_S'y^{-1}]^{1/2}$. We have defined

$$\alpha'=\frac{c^2}{4a^3c_{44}^0}[T_c+(C^s+J)y]\ . \tag{4.21}$$

The discontinuity of $\rho$ at $T_1$ is given by

$$\Delta\rho=\left[\frac{-C'}{2D'}\right]^{1/2}=\left[\frac{T_1-T_Q}{yD_S'}\right]^{1/4}\ . \tag{4.22}$$

Since $D_S'\propto x^{-5}$, we get $\Delta\rho\propto x^{5/4}$ and consequently $\Delta\rho$ decreases with decreasing $x$. This result is in agreement with the decrease of the intensity of $L$-point reflections[8] with decreasing concentration of CN. Defining the shear mode $\varepsilon_{zi}$ by

$$iq_z s_i^e(q_z) = \sqrt{mN}\,\varepsilon_{zi} \ , \tag{4.23}$$

$i = x,y$, we obtain from Eq. (4.17) that a discontinuity in $\rho$ implies a discontinuity in $\varepsilon$. Since $D_{xx}(q_z) = D_{yy}(q_z)$, we have $\varepsilon_{zx} = \varepsilon_{zy}$, which is characteristic for the monoclinic phase. A coupling linear in zone-center shear modes and quadratic in zone-boundary optical modes has been previously considered in order to describe the structural transitions in perovskites.[42] There the optical displacements at the zone boundary drive the antiferrodistortive transition. Our model here is more complicated since in the cyanides we include, in addition, the interaction between zone-center modes.

### C. Rhombohedral phase

A rhombohedral phase which is characterized by three equal shears has been found for certain ranges of $T$ and $x$ in $\mathrm{K(CN)}_x\mathrm{Br}_{1-x}$ (Refs. 8, 43, and 44) and $\mathrm{Na(CN)}_x\mathrm{Cl}_{1-x}$.[36] The transition from the cubic phase is close to second order in the first compound and first order in the second. The three equal shear strains lead to a shortening of the cubic lattice cell along the diagonal [111], in the first case, and to a stretching along [111], in the second. These situations correspond, respectively, to an orientation of the CN ions in a (111) plane and to an alignment along the [111] direction.

In order to account for the rhombohedral symmetry, we must have

$$Y_\alpha^e(\mathbf{q}=0) \equiv \sqrt{N}\,\eta_\alpha = \sqrt{N}\,\eta, \quad \alpha = 1,2,3 \ . \tag{4.24}$$

Here $\eta$ is the amplitude. Retaining only terms linear in $\eta$ we obtain from Eq. (3.8) in the long-wavelength limit for $\mathbf{q} = (q_x,0,0)$

$$iq_x s_y^e = iq_x s_z^e = \beta\eta \ . \tag{4.25a}$$

Similarly we have for $\mathbf{q} = (0,q_y,0)$

$$iq_y s_x^e = iq_y s_z^e = \beta\eta \ , \tag{4.25b}$$

and for $\mathbf{q} = (0,0,q_z)$

$$iq_z s_x^e = iq_z s_y^e = \beta\eta \ , \tag{4.25c}$$

where $\beta = B(mN)^{1/2}/a^2c_{44}^0$. Defining

$$\varepsilon_{ij} = \tfrac{1}{2} i (q_i s_j^e + q_j s_i^e)/(mN)^{1/2} = \beta'\eta \ , \tag{4.26}$$

we obtain

$$\varepsilon_{xy} = \varepsilon_{yz} = \varepsilon_{zx} = \beta'\eta \ , \tag{4.27}$$

with

$$\beta' = B/a^2c_{44}^0 \ .$$

In the case of $\mathrm{K(CN)}_x\mathrm{Br}_{1-x}$, the functions $Y_1, Y_2, Y_3$ correspond, respectively, to an alignment along $[1\bar{1}0]$, $[01\bar{1}]$, and $[\bar{1}01]$. Since, then, $\hat{x}\,\hat{y}$, $\hat{y}\,\hat{z}$, and $\hat{z}\,\hat{x}$ are negative, we write $\eta = -|\eta|$. Since $B$ is positive,[45] we see that an alignment of the CN ions in a (111) plane leads to negative shear components or equivalently to a contraction of the cubic lattice (squeeze) along the diagonal [111].

On the other hand, in the case of $\mathrm{Na(CN)}_x\mathrm{Cl}_{1-x}$ the functions $Y_1, Y_2, Y_3$ correspond to components along [110],[011],[101] and $\hat{x}\,\hat{y}$, $\hat{y}\,\hat{z}$, and $\hat{z}\,\hat{x}$ are positive. We then write $\eta = +|\eta|$. The shears are positive and lead to a stretching of the cubic lattice cell along [111].

The third-order terms in the free energy are different from zero. From Eq. (3.4a) we obtain in the long-wavelength limit

$$F_S^{(3)} = -C_S^{(3)} N\eta^3 \ , \tag{4.28a}$$

where

$$C_S^{(3)} = \frac{\alpha_2 T}{x^2\alpha_1^3} X(3,1) > 0 \ . \tag{4.28b}$$

The last term on the right-hand side of Eq. (3.10) yields

$$F_I^{(3)} = C_I^{(3)} N\eta^3 \ , \tag{4.29a}$$

with

$$C_I^{(3)} = \frac{12cB}{c_{44}^0 a^2} > 0 \ . \tag{4.29b}$$

Under the assumption that the coefficient of the fourth-order term in the free energy is positive, we know that the nature of the phase transition is determined by the sign and magnitude of the coefficient

$$C^{(3)} \equiv C_I^{(3)} - C_S^{(3)} \tag{4.30}$$

of the third-order term.[35] If $C^{(3)} = 0$, the transition is second order; otherwise it is of first order. If $C^{(3)} > 0$, the stable solution in the ordered phase corresponds to $\eta < 0$, while if $C^{(3)} < 0$ one has $\eta > 0$. The first case seems to be realized in $\mathrm{K(CN)}_x\mathrm{Br}_{1-x}$ with $x$ close to 0.73, while the second case seems to hold in $\mathrm{Na(CN)}_x\mathrm{Cl}_{1-x}$.[36] We have made numerical calculations, starting from microscopic potential parameters. We find that, for $\mathrm{K(CN)}_x\mathrm{Br}_{1-x}$, $C^{(3)}$ is indeed positive for $x > x_c$ with $x_c = 0.86$. Experimentally one finds[44] that the transition from the cubic to the rhombohedral phase is already continuous at $x_c = 0.73$. Given the uncertainties in the microscopic parameters, we consider our value for $x_c$ to be a fair result. For details of the calculation, we refer to Appendix C.

## V. CONCLUDING REMARKS

On the basis of a microscopic model, we have given a theory of the polymorphism of mixed crystals $M(\mathrm{CN})_x X_{1-x}$, where $M$ is an alkali-metal ion and $X$ a halogen ion. As an extension of previous work, where only bilinear interactions between displacive acoustic and orientational degrees of freedom had been considered, we have also taken into account cubic interactions. They are due to the dependence of the electric quadrupole interaction on lattice displacements. In calculating the free energy, we obtain negative fourth-order terms in the orientational order parameter. The negative terms due to interaction compete with positive fourth-order terms due to entropy. This competition is influenced by experimental parameters such as $T$, $x$, and $P$ (pressure).

The ferroelastic orthorhombic phase is obtained from the condensation of a single orientational mode $Y_1^e(\mathbf{q}_0)=\sqrt{N}\,\eta$ at the Brillouin-zone center $\mathbf{q}_0=(q_x,0,0)$, as $q_x \to 0$. The concomitantly condensing shear mode is obtained from Eq. (3.8) with the result

$$\varepsilon_{xy}=iq_x s_y/(mN)^{1/2}=B\eta/a^2c_{44}^0 \ . \tag{5.1}$$

The cubic interaction (A9b) corresponding to a coupling of a stretching mode $\varepsilon_{xx}$, and is in this respect analogous to the compressible Ising model.

The situation which leads to the monoclinic structure is more complicated. A cubic coupling between a shear mode at the zone center and two different orientational components at the $L$ point is essential in driving the transition from the cubic to the monoclinic phase. The two orientational modes have the same amplitude $\rho$ but opposite sign. Two shear modes $\varepsilon_{zx}=\varepsilon_{zy}$ become different. The present theory accounts for two main characteristics of the antiferroelastic monoclinic structure: a staggered arrangement of the CN quadrupoles and the equality of two shear modes. Due to the coupling between zone-boundary and zone-center modes, the transition is still preceded by a softening of $c_{44}$ in the cubic phase.

The transition to the orthorhombic and to the monoclinic phases are of first order. The first-order character decreases with decreasing $\mathrm{CN}^-$ concentration, since there is in the free energy a competition between fourth-order terms with different signs.

We have finally discussed a mechanism which leads to the rhombohedral phases. The existence of three coherent and equal shears $\varepsilon_{xy}=\varepsilon_{yz}=\varepsilon_{zx}$ follows from the equality of the three $T_{2g}$ orientational components. The sign of the orientational amplitude $\eta$ determines the sign of the shears and possibly accounts for the difference between $\mathrm{K(CN)}_x\mathrm{Br}_{1-x}$ and $\mathrm{Na(CN)}_x\mathrm{Cl}_{1-x}$. The first- versus second-order character of the phase transition is now governed by the competition of entropy and interaction contributions to the third-order term in the free energy.

All the previous results have been obtained from a Landau expression of the free energy. The free energy has been calculated on the basis of the microscopic model. The concentration dependence has been taken into account by performing configurational averages within mean-field theory. We have also included in our model static random strain fields which are due to the substitutional halogens. The inclusion of random strain fields allows us to give a consistent interpretation of thermal cycling experiments.

The present approach of discussing the phase transitions on the basis of the molecular-field theory may appear primitive from the point of view of critical phenomena. The critical behavior of an Ising model on a compressible cubic lattice has been studied by renormalization-group methods.[46] It has been found that at constant pressure, the anisotropic cubic solid has a first-order transition.

The purpose of our work has been the proposal of a new microscopic model which exhibits the polymorphism of mixed crystals with orientational disorder. In a first approach, a discussion of the phase transition based on Landau-type theory is, therefore, legitimate. As an extension for further studies, we mention the inclusion of surface effects which have been found to be relevant in metal-hydrogen systems.[47]

Beyond the problem of polymorphism, our results are relevant for the understanding of the mechanism which leads to the orientational glass state[48,44] in $M(\mathrm{CN})_xX_{1-x}$ and related compounds. It has been suggested[49] that, in addition to a smooth $T$-dependent freezing, a nonergodic instability can occur as a characteristic feature of the orientational glass. The threshold condition for such an instability is realized close to a virtual second-order phase transition. Since dilution of CN concentration favors the second-order character of the structural transition, it is conceivable that a nonergodic instability occurs only below a critical concentration $x_c$.

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## APPENDIX A

The Fourier transform of the quadrupole-quadrupole interaction reads

$$J_{\alpha\beta}(\mathbf{k})=\sum_{\mathbf{h}} J_{\alpha\beta}(\mathbf{X}(\mathbf{h}))e^{-i\mathbf{k}\cdot\mathbf{X}(\mathbf{h})} \ . \tag{A1}$$

Here $\mathbf{X}(\mathbf{h})$ is the position vector of one of the 12 nearest-neighbor $\mathrm{CN}^-$ ions which surround a given $\mathrm{CN}^-$ at the origin $\mathbf{X}(0)=0$ in the fcc structure. The calculation of $J_{\alpha\beta}(\mathbf{k})$ has been outlined in Ref. 29. Here we quote the full matrix $J(\mathbf{k})$, since we will need the result in the following. We obtain

$$\begin{aligned} J(\mathbf{k})=\frac{Q^2\pi}{a^5\sqrt{2}}\{&\cos[(k_z+k_y)a]J^{+(yz)}+\cos[(k_z-k_y)a]J^{-(yz)} \\ &+\cos[(k_z+k_x)a]J^{+(zx)}+\cos[(k_z-k_x)a]J^{-(zx)}+\cos[(k_y+k_x)a]J^{+(xy)}+\cos[(k_y-k_x)a]J^{-(xy)}\} \ , \end{aligned} \tag{A2}$$

with

$$J^{\pm(yz)}=\begin{bmatrix} -\frac{3}{5} & 0 & \mp 1 \\ 0 & \frac{19}{10} & 0 \\ \mp 1 & 0 & -\frac{3}{5} \end{bmatrix} . \tag{A3}$$

The matrices $J^{\pm(xz)}$ and $J^{\pm(xy)}$ follow from Eq. (A3) by cyclic permutation of elements. $Q$ stands for the quadrupole moment of the CN ion. In order to calculate the interaction on a compressible lattice, we start from

$$V^{RR}=\frac{1}{2}\sum_{\mathbf{n}}\sum_{\mathbf{h}}J(\mathbf{R}(\mathbf{n}+\mathbf{h})-\mathbf{R}(\mathbf{n}))$$

$$\times\sigma(\mathbf{n}+\mathbf{h})Y_\alpha(\mathbf{n}+\mathbf{h})\sigma(\mathbf{n})Y_\beta(\mathbf{n}) , \tag{A4}$$

where

$$\mathbf{R}(\mathbf{n})=\mathbf{X}(\mathbf{n})+\mathbf{u}(\mathbf{n}) , \tag{A5}$$

$\mathbf{u}(\mathbf{n})$ being the lattice displacement. We expand the potential (A4) in powers of $\mathbf{u}$, take Fourier transforms according to Eq. (2.4), and use

$$\mathbf{u}(\mathbf{n})=\frac{1}{(m_{\mathrm{CN}})^{1/2}N^{1/2}}\sum_{\mathbf{q}}\mathbf{u}(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{X}(\mathbf{n})} . \tag{A6}$$

Finally, we transform to acoustic coordinates. The result corresponds to a zeroth-order term in $\mathbf{u}$ which is given by Eq. (2.5) and a first-order correction, given by Eq. (2.6). Retaining only the coupling to long-wavelength acoustic phonons, we find

$$J'_{\alpha\beta i}(\mathbf{p},\mathbf{q})=J'^{(xy)}_{\alpha\beta i}(\mathbf{p},\mathbf{q})+J'^{(yz)}_{\alpha\beta i}(\mathbf{p},\mathbf{q})+J'^{(zx)}_{\alpha\beta i}(\mathbf{p},\mathbf{q}) . \tag{A7}$$

Here

$$J'^{(xy)}_{\alpha\beta z}(\mathbf{p},\mathbf{q})=0 , \tag{A8a}$$

$$J'^{(xy)}_{\alpha\beta x}(\mathbf{p},\mathbf{q})=\frac{-i5\pi Q^2}{\sqrt{m}\,a^5(\sqrt{2})^3}\{(q_y+q_x)J^{+(xy)}_{\alpha\beta}\cos[(p_x+p_y)a]+(q_x-q_y)J^{-(xy)}_{\alpha\beta}\cos[(p_x-p_y)a]\} , \tag{A8b}$$

$$J'^{(xy)}_{\alpha\beta y}(\mathbf{p},\mathbf{q})=-\frac{i5\pi Q^2}{\sqrt{m}\,a^5(\sqrt{2})^3}\{(q_x+q_y)J^{+(xy)}_{\alpha\beta}\cos[(p_x+p_y)a]+(q_y-q_x)J^{-(xy)}_{\alpha\beta}\cos(p_y-p_x)a]\} . \tag{A8c}$$

The expressions for $J'^{(yz)}_{\alpha\beta i}(\mathbf{p},\mathbf{q})$ and $J'^{(zx)}_{\alpha\beta i}(\mathbf{p},\mathbf{q})$ follow by permutation of indices from Eqs. (A8a)–(A8c). In Eq. (A8b), $m=m_{\mathrm{CN}}+m_{\mathrm{K}}$ denotes the total mass per unit cell.

Having the explicit form of the interaction $J'$, we find that in the limit $\mathbf{p}=0$ and $\mathbf{q}\rightarrow 0$, the terms $\alpha=\beta$ in Eq. (2.6) correspond to a coupling or orientational interactions to stretching, while the terms $\alpha\neq\beta$ correspond to a coupling to lattice shears. Defining

$$c=5\pi Q^2/[a^5(\sqrt{2})^3] , \tag{A9a}$$

we find, for instance,

$$J'_{\alpha\beta x}(0,\mathbf{q})s_x(\mathbf{q})=-\frac{-2ic}{\sqrt{m}}[q_x(J^{+(xy)}_{\alpha\beta}+J^{+(xz)}_{\alpha\beta})\delta_{\alpha\beta}$$

$$+q_y(J^{+(xy)}_{\alpha\beta}+J^{+(xz)}_{\alpha\beta})$$

$$\times(1-\delta_{\alpha\beta})]s_x(\mathbf{q}) . \tag{A9b}$$

Taking $\mathbf{q}=(q_x,0,0)$, we see that $J'_{11x}(0,q_x)$ in Eq. (4.2b) corresponds to a coupling of two pairs of $Y_1$ functions, which is mediated by compressional lattice waves.

With $\mathbf{p}=\mathbf{p}_L$ (Sec. IV), we obtain a coupling to shear modes from $J'_{\alpha\alpha i}(\mathbf{q},\mathbf{p}_L)$. In particular, with $\mathbf{q}=(0,0,q_z)$, we get

$$J'_{\alpha\alpha y}(q_z,\mathbf{p}_L)s_y(q_z)=\frac{2ic}{\sqrt{m}}J^{+(yz)}_{\alpha\alpha}q_zs_y(q_z) , \tag{A10a}$$

$$J'_{\alpha\alpha x}(q_z,\mathbf{p}_L)s_x(q_z)=\frac{2ic}{\sqrt{m}}J^{+(xz)}_{\alpha\alpha}q_zs_x(q_z) , \tag{A10b}$$

which corresponds to a coupling of zone-boundary orientational modes $Y_\alpha$ to shear waves. The interaction (2.6) then reduces to

$$V^{RRT}(\mathbf{p}_L,q_z)=i\frac{c}{\sqrt{Nm}}\tfrac{13}{10}q_z[s_y(q_z)+s_x(q_z)]\rho^2 . \tag{A11}$$

## APPENDIX B

We quote explicit expressions for the coefficients $B_1$, $C_1$, $D_1$, and $D_2$ which have been introduced in Sec. III:

$$B_1=\frac{5\langle Y^2\rangle_0^2-2\langle Y^2Y^2\rangle_0-\langle Y_4\rangle_0}{2\langle Y^2\rangle_0} , \tag{B1}$$

$$C_1=\frac{3}{2}\left[\frac{\langle Y^3YY\rangle_0}{\langle YYY\rangle_0}-\langle Y^2\rangle_0\right] , \tag{B2}$$

$$D_1=-\frac{1}{2y_1}[\langle Y^6\rangle_0-4\langle Y^4Y^2\rangle_0-18\langle(YYY)^2\rangle_0$$

$$+12\langle YYY\rangle_0^2-11\langle Y^2\rangle_0y_1] , \tag{B3a}$$

with

$$y_1 = \langle Y^4 \rangle_0 - 3\langle Y^2 Y^2 \rangle_0 \,, \tag{B3b}$$

$$D_2 = \frac{1}{6\langle Y^2 \rangle_0^2} \Bigg\{ (3/y_1)[-\langle Y^2Y^2 \rangle_0 \langle Y^6 \rangle_0 + 2(y_1 + 2\langle Y^2Y^2 \rangle_0)\langle Y^4Y^2 \rangle_0 + 6(y_1 + 3\langle Y^2Y^2 \rangle_0)\langle (YYY)^2 \rangle_0] \\ -6\left[ 2\left[ 1 + 3\frac{\langle Y^2Y^2 \rangle_0}{y_1} \right] \langle YYY \rangle_0^2 - (\langle Y^4Y^2 \rangle_0 + 2\langle Y^2Y^2 \rangle_0)\langle Y^2 \rangle_0 + 7\langle Y^2 \rangle_0^3 \right] \Bigg\} \,. \tag{B4}$$

## APPENDIX C

We have calculated for $K(CN)_xBr_{1-x}$ the critical concentration $x_c$ where the transition from the cubic to the rhombohedral phase becomes second order. We start from the same microscopic parameters for the Born-Mayer, Coulomb and van der Waals potentials, which have been used in the second paper of Ref. 27 for the calculation of $T_c$ in KCN. With a quadrupole moment $Q = 0.72Q_0$, where $Q_0 = -4.64 \times 10^{-10}$ esu Å$^2$, we have obtained[27] $T_c(x=1) = 191$ K and $B = 1461$ K/Å. We then find from Eq. (4.29a)

$$C_I^{(3)} = 5916 \text{ K} \,, \tag{C1}$$

where we have used $c_{44}^0 = 0.48 \times 10^{11}$ dyn/cm$^2$ and $a = 3.25$ Å.

In order to calculate the single-particle susceptibilities which enter Eq. (4.28b) for $C_S^{(3)}$, we need to know the single-particle potential $W^R(\Omega)$. Here $\Omega = (\theta, \varphi)$ denotes the polar angles for the CN orientation. Expansion in cubic harmonics $K(\Omega)$ yields

$$W^R(\Omega) = \alpha_{41}K_{41}(\Omega) + \alpha_{61}K_{61}(\Omega) \,, \tag{C2}$$

where the coefficients $\alpha_{14} = 23.8$ K and $\alpha_{61} = -88.5$ K have been calculated in Ref. 27 by including self-energy effects. The corresponding single-particle susceptibilities are then evaluated:

$$\langle Y_{xy} Y_{yz} Y_{xz} \rangle_0 = 0.0147 \,, \tag{C3a}$$

$$\langle Y_{xy}^2 \rangle_0 = 0.082 \,, \tag{C3b}$$

for $T = 150$ K. With $\alpha_2 \approx 1$, $\alpha_1 \approx 1$, and observing that $T_c(x) = xT_c(x=1)$, we get

$$C_S^{(3)} = \frac{xT_c(x=1) \times 26.66}{x^2} \,. \tag{C4}$$

Comparing with Eq. (C1), we find that $C_I^{(3)} \geq C_S^{(3)}$ for $x \geq 0.86$. Experimentally[44] one finds $x_c \approx 0.73$. From Eq. (4.28b) we see that $C_S^{(3)}$ is very sensitive to the value of $\langle Y_{xy}^2 \rangle_0$. Uncertainties in the values of $\alpha_{41}$ and $\alpha_{61}$, due to uncertainties about the value of the quadrupole moment $Q$ (see Refs. 29 and 27), and due to uncertainties in the values of the Born-Mayer potentials, cause uncertainties in the value of $\langle Y_{xy}^2 \rangle_0$.

We have performed similar calculations for the case of $Na(CN)_xCl_{1-x}$. For $x = 0.7$ and $T = 200$ K, we obtain $C_S^{(3)} > C_I^{(3)}$, with $C_S^{(3)} = 13\,643$ K and $C_I^{(3)} = 12\,654.6$ K. Here we have used the values $T_c(x=1) = 286$ K, $\alpha_{41} = -200$, $\alpha_{61} = -120$, $\langle Y_{xy}^2 \rangle_0 = 0.068$, $\langle Y_{xy} Y_{yz} Y_{zx} \rangle_0 = 0.0105$ at $T = 200$ K, $B = 2478$ K/Å, $c_{44}^0 = 0.75 \times 10^{11}$ dyn/cm$^2$, and $a = 2.95$ Å.

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*Present address: Rijksuniversitair Centrum, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium.

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