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Quadrupolar random-field model for orientational glasses

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We give a microscopic description of the local potential felt by an orientable molecule whose neighboring atoms are randomly substituted. Since the potential can be interpreted in terms of ferromagnetic or antiferromagnetic quadrupolar fields, we propose a random-field model for crystals with substitutional disorder. In the mean–field limit our model shows different types of planar ordering and discontinuous flops from <100> to <111> uniaxial order. Apart from the case of purely ferromagnetic fields, long-ranged order is stabilized even if the random fields are large. We also discuss a coupling between orientational and elastic degrees of freedom. Depending on the values of the model parameters, we find low-temperature phases with tetragonal, rhombohedral, orthorhombic, or monoclinic symmetry.

In the last decade much experimental[1] and theoretical[2] work has been devoted to the understanding of crystalline systems with orientable molecules and substitutional disorder. At high temperature these crystals exhibit a plastic-crystal phase with the molecules rotating more or less freely, whereas their low-temperature behavior depends significantly on the degree of randomness in the chemical constitution: For small defect concentrations one usually finds a transition to a long-ranged orientationally ordered phase, but in a broad concentration range a glassy state is observed, in which the molecular orientations are frozen into random directions. Due to a coupling between the orientational and elastic degrees of freedom, orientational ordering leads to macroscopic lattice distortions, while in the glassy phase the global symmetry of the crystal remains unchanged. Usually the phase transition is accompanied by a pronounced softening of the elastic constants and the appearance of a central peak in inelastic neutron-scattering experiments.

It is essential to distinguish between two types of substitutional disorder: If the sublattice of orientable molecules is diluted with spherical atoms (typical experimental realizations are $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ or mixtures of ortho-H_2 and para-H_2), the situation is quite similar to magnetic spin glasses.[3] The effective interaction between two CN^- ions, for example, depends on the distance and the orientation of the quadrupoles relative to their connecting bond[4] so that in a diluted system *random interactions* should play an important role. If, on the other hand, the sublattice of orientable molecules remains unchanged, but their surrounding spherical ions are randomly substituted by ions of different size [as is the case in $(\mathrm{NaCN})_{1-x}(\mathrm{KCN})_x$], then the physical properties of the system are expected to be dominated by *random (strain) fields.* Moreover, experiments with pure cyanides[5] and alkali halides with CN^- defects[6] indicate that additional *stochastic anisotropies* should be present in the mixed crystals.

Several publications[7–9] have been concerned with random interactions in quadrupolar glasses, whereas Michel and co-workers[10] have proposed a microscopic random strain model for mixed alkali halide–alkali cyanide crystals. Our model building is based on a detailed investigation of the *local potential* of a single quadrupole, which is surrounded by cations of different sizes, as for example the CN^- molecule in $(\mathrm{NaCN})_{1-x}(\mathrm{KCN})_x$. We find that the effect of substitutional disorder in these crystals can be described in terms of random fields either favoring (*ferromagnetic* fields) or disfavoring (*antiferromagnetic* fields) a certain axis at each site. Therefore we concentrate in this paper on the influence of random fields on orientational ordering. Possible random contributions to the quadrupole-quadrupole interaction are assumed to be small, and a uniform ferromagnetic interaction is considered.

In Sec. I we analyze the local orientational potential of a single qudrupole in a substitutionally disordered crystal. Our random-field model is proposed in Sec. II. Discussing its mean-field theory in the following section, we find that stochastic fields can lead to new types of orientational order: We observe planar ordering and a spin-flop behavior similar to the findings in anisotropic Heisenberg models with uniaxial random fields.[11] Strong ferromagnetic random fields can suppress the phase transition, whereas antiferromagnetic fields stabilize long-ranged ordered ground states. Following the lines of Ref. 9, Sec. IV briefly investigates the consequences of a bilinear coupling between orientational and elastic degrees of freedom. In particular, our model predicts a variety of lattice symmetries in the low-temperature phases. In the last section we give a summary and discussion of our main results.

I. ORIENTATIONAL POTENTIAL OF A SINGLE QUADRUPOLE

In the following we consider a substitutionally disordered crystal such as $(\mathrm{NaCN})_{1-x}(\mathrm{KCN})_x$ in its cubic high-temperature phase. The linear CN^- ions occupy the sites of a fcc sublattice and are surrounded by octahedral cages of cations. The exact nature of the crystal field felt by the CN^- molecule in the center depends not only on the number of Na^+ and K^+ ions in the cage, but also on the

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symmetry of the cation configuration. (See Table I for a complete classification.) Following Ref. 12, we idealize the CN$^-$ quadrupole as a dumbbell, whose ends interact with the surrounding alkali ions. In the center-of-mass system of the dumbbell, its ends are located at $\pm\mathbf{d}$, and the positions of the cations will be denoted by

$$\begin{aligned} \mathbf{a}_i &= a\mathbf{e}_i, \quad i = 1,2,3 \ , \\ \mathbf{a}_{i+3} &= -\mathbf{a}_i \ , \end{aligned} \tag{1}$$

where the $\mathbf{e}_i$ are Cartesian unit vectors. We assume a Born-Mayer-type interaction (attractive or repulsive) between the cations and the ends of the dumbbell,

$$V_i^{(2)}(\mathbf{d}) = \sum_{\sigma=\pm 1} \alpha_i e^{-\beta_i |\mathbf{a}_i + \sigma \mathbf{d}|} \ , \tag{2}$$

but our main results are valid for any other interaction, which depends only on the distance of the atoms. Experiments[5,6] and computer simulations[13] on $(\mathrm{NaCN})_{1-x}(\mathrm{KCN})_x$ give evidence that the Na$^+$ and K$^+$ ions act as attractive and repulsive centers, respectively. Hence, we expect

$$\alpha_K, \beta_K, \beta_{Na} > 0 \ , \quad \text{but} \quad \alpha_{Na} < 0 \ . \tag{3}$$

Expanding $V_i^{(2)}(\mathbf{d})$ to fourth order and neglecting constant terms, one has

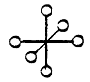
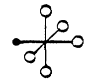
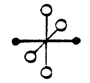
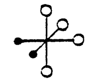
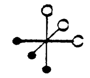
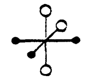
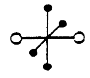
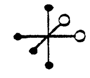
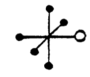
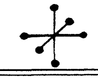
$$\begin{aligned} V_i^{(2)}(\mathbf{d}) = \alpha_i e^{-\beta_i a} \Big\{ & A(\beta_i)\,(\mathbf{a}_i \cdot \mathbf{d})^2 + B(\beta_i)\,(\mathbf{a}_i \cdot \mathbf{d})^4 \\ & + O((d/a)^6) \Big\} \end{aligned} \tag{4}$$

with $A(\beta_i), B(\beta_i) > 0$ in leading order. The resulting orientational potential for a given cation configuration

$$V(\mathbf{d}) = \sum_{i=1}^{6} V_i^{(2)}(\mathbf{d}) \tag{5}$$

is shown in Table I, where we have introduced the constants

TABLE I. Possible cation cages in $(\mathrm{NaCN})_{1-x}(\mathrm{KCN})_x$ and the resulting orientational potentials felt by the CN$^-$ ion in the center. Open circles denote K$^+$and solid circles Na$^+$ ions, respectively. All other configurations can be obtained by cubic-symmetry transformations.

Na:K	Configuration	Multiplicity	Orientational potential $V(\vec{d}) = \ldots$	
0:6		1	0	$+\ E_4(d_1^4 + d_2^4 + d_3^4)$
1:5		6	$-(C_2 + D_2)(\vec{e}_1 \cdot \vec{d})^2$	$+\ D_4 d_1^4 + E_4(d_2^4 + d_3^4)$
2:4a		3	$-2(C_2 + D_2)(\vec{e}_1 \cdot \vec{d})^2$	$-\ C_4 d_1^4 + E_4(d_2^4 + d_3^4)$
2:4b		12	$(C_2 + D_2)(\vec{e}_3 \cdot \vec{d})^2$	$+\ D_4(d_1^4 + d_2^4) + E_4 d_3^4$
3:3a		8	0	$+\ D_4(d_1^4 + d_2^4 + d_3^4)$
3:3b		12	$-2C_2 d_1^2 + (D_2 - C_2) d_2^2 + 2D_2 d_3^2$	$-\ C_4 d_1^4 + D_4 d_2^4 + E_4 d_3^4$
4:2a		3	$2(C_2 + D_2)(\vec{e}_1 \cdot \vec{d})^2$	$+\ E_4 d_1^4 - C_4(d_2^4 + d_3^4)$
4:2b		12	$-(C_2 + D_2)(\vec{e}_3 \cdot \vec{d})^2$	$+\ D_4(d_1^4 + d_2^4) - C_4 d_3^4$
5:1		6	$(C_2 + D_2)(\vec{e}_1 \cdot \vec{d})^2$	$+\ D_4 d_1^4 - C_4(d_2^4 + d_3^4)$
6:0		1	0	$-\ C_4(d_1^4 + d_2^4 + d_3^4)$

$$\begin{aligned}
C_2 &:= -\alpha_{Na} e^{-\beta_{Na} a} A(\beta_{Na}) a^2 \ , \\
D_2 &:= \alpha_K e^{-\beta_K a} A(\beta_K) a^2 \ , \\
C_4 &:= -\alpha_{Na} e^{-\beta_{Na} a} 2B(\beta_{Na}) a^4 \ , \\
D_4 &:= \left\{ \alpha_{Na} e^{-\beta_{Na} a} B(\beta_{Na}) + \alpha_K e^{-\beta_K a} B(\beta_K) \right\} a^4 \ , \\
E_4 &:= \alpha_K e^{-\beta_K a} 2B(\beta_K) a^4 \ .
\end{aligned} \tag{6}$$

It should be stressed that terms proportional to $(\mathbf{e}_i \cdot \mathbf{d})^2$ have to be interpreted as local *quadrupolar fields*, since they can be rewritten in the form $H f_{\mu\nu}(\mathbf{e}_i) f_{\mu\nu}(\mathbf{s})$ (cf. next section). Using the terminology of magnetic systems we call fields with negative H *ferromagnetic* and those with positive H *antiferromagnetic*. Fourth-order terms in the expansion of $V(\mathbf{d})$ represent *stochastic anisotropies* for the quadrupoles: The quartic potential

$$v(\mathbf{d}) = c_1 d_1^4 + c_2 d_2^4 + c_3 d_3^4$$

has its minimum along a $\langle 100 \rangle$ axis, if at least one coefficient c_i is negative. If all coefficients are equal and positive, all $\langle 111 \rangle$ axes are favored equally.

II. MODEL BUILDING

Using the results of the preceding section we now construct a model Hamiltonian for crystals with substitutional disorder. Consider a fcc lattice of uniaxial quadrupoles

$$f_{\mu\nu}(x) \equiv f_{\mu\nu}(\mathbf{s}(x)) = s_\mu s_\nu - \frac{1}{3}\delta_{\mu\nu} \ , \tag{7}$$

where $\mathbf{s}(x) = \mathbf{d}(x)/d$ is a three-dimensional unit vector denoting the orientation of a CN^- molecule at site x. In a realistic description, substitutional disorder will give random contributions to the quadrupole-quadrupole interaction, even if the sublattice of orientable molecules is undiluted. However, these are small effects as compared to the deformation of the local orientational potential described above. (Other possible sources of frustration are discussed in the last section.) Therefore we consider a bilinear ferromagnetic interaction between the quadrupoles:

$$\mathcal{H}^{\text{int}} = -\frac{1}{2N} \sum_{\langle x, x' \rangle} f_{\mu\nu}(x) J_{\mu\nu\rho\sigma} f_{\rho\sigma}(x') \ . \tag{8}$$

Demanding cubic symmetry for the coupling tensor and using the important property

$$f_{\mu\mu} = 0 \ , \tag{9}$$

we obtain

$$\mathcal{H}^{\text{int}} = -\frac{1}{2N} \sum_{\langle x, x' \rangle} f_{\mu\nu}(x) J_{\mu\nu} f_{\mu\nu}(x') \tag{10}$$

as the interaction part of the Hamiltonian, where

$$J_{\mu\nu} = \widetilde{J}\delta_{\mu\nu} + J(1 - \delta_{\mu\nu}) \ , \qquad \widetilde{J}, J \geq 0 \ . \tag{11}$$

The case $\widetilde{J} = J$ corresponds to a fully isotropic interaction, whereas for $\widetilde{J} > J$ $\langle 100 \rangle$ ordering and for $J > \widetilde{J}$ $\langle 111 \rangle$ ordering is favored. If the atoms are substituted independently at each site, every cation configuration in Table I will have a finite probability. We expect the quadratic terms in $V(\mathbf{d})$ to play the dominant role and approximate the results of Sec. I by

$$\begin{aligned}
\mathcal{H} &= \mathcal{H}^{\text{int}} + \mathcal{H}^{\text{rf}} \\
&= -\frac{1}{2N} \sum_{\langle x, x' \rangle} f_{\mu\nu}(x) J_{\mu\nu} f_{\mu\nu}(x') \\
&\quad -D \sum_x \xi(x) \left[\mathbf{s}(x) \cdot \mathbf{n}(x) \right]^2 \ .
\end{aligned} \tag{12}$$

Here $D > 0$ is an averaged field strength, and both $\xi(x)$ and the unit vector $\mathbf{n}(x)$ are independent and identically distributed random variables with $\xi(x)$ taking on only the values $1, 0, -1$ and

$$p(\mathbf{n}) = \frac{1}{3} \sum_{i=1}^{3} \delta(\mathbf{n} - \mathbf{e}_i) \ . \tag{13}$$

Sites with $\xi(x) = -1$ correspond to 2:4b, 4:2a, and 5:1 configurations, whereas $\xi(x) = 0$ and $\xi(x) = +1$ can be identified with 0:6, 3:3a, 6:0 and 1:5, 2:4a, 4:2b, 3:3b cages, respectively. At this point we have approximated the quadratic potential of the 3:3b configurations (see Table I) by a ferromagnetic term of the form $-2(C_2 + D_2)(\mathbf{e}_1 \cdot \mathbf{d})^2$. Since our main concern is the effect of random fields on orientational ordering, we neglect sites with $\xi(x) = 0$ in the following and instead consider a probability density

$$p(\xi) = q\delta(\xi - 1) + (1 - q)\delta(\xi + 1) \ , \tag{14}$$

where q has to be determined from the proportion between real lattice sites with negative and with positive quadratic potential. Certainly this simplification is justified only at intermediate defect concentrations. Since the probability of a given cation cage to consist of m $Na^+$and $(6 - m)$ K^+ ions is simply $\binom{6}{m}(1 - x)^m x^{6-m}$, our model parameters are connected with the real KCN concentration x via

$$D(x) = 2d^2(C_2 + D_2) \frac{x - 2x^2 + 2x^3 - x^4}{2x - 5x^2 + 4x^3 + 3x^4 - 6x^5 + 2x^6} \ , \tag{15}$$

$$q(x) = \frac{4x^2 - 12x^3 + 13x^4 - 4x^5 - x^6}{2x - 5x^2 + 4x^3 + 3x^4 - 6x^5 + 2x^6} \tag{16}$$

(see Fig. 1 for a plot). It should be noted that there is a certain asymmetry, well known, e.g., from the isotropic quadrupolar glass,[7] in our Hamiltonian: At sites with ferromagnetic local fields only the axis $\pm\mathbf{n}(x)$ is preferred, whereas antiferromagnetic fields favor an entire plane, thus giving rise to more complex forms of orientational ordering.

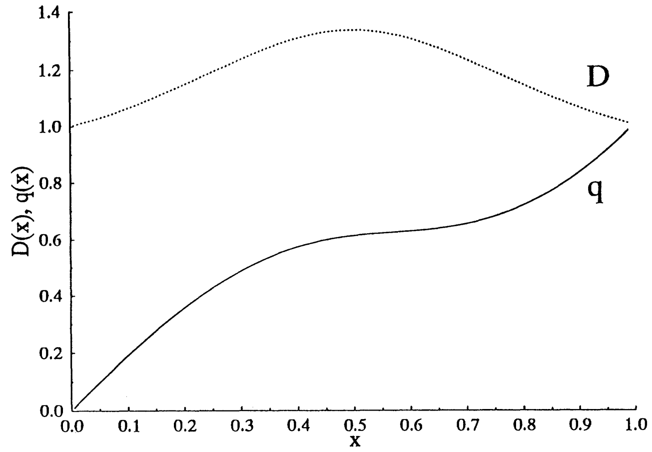


FIG. 1. The model parameters D and q as functions of the KCN concentration x. D is measured in units of $2d^2(C_2+D_2)$.

III. MODEL WITH INFINITE-RANGED INTERACTIONS

A. Ground states

We now consider the Hamiltonian defined by (12) in the limit of infinite interaction range. As a first step, an investigation of the system at $T = 0$ can elucidate how orientational ordering is affected by the quadrupolar fields. Since the random-field axes are chosen from a *discrete* set of vectors, calculating the ground states is simply a minimization problem in a 12-dimensional configuration space: Due to the infinite-ranged interaction, all quadrupoles with the same values of the local random variables are subject to the same molecular field and, consequently, behave identically. We thus divide the quadrupoles into six groups:

$$\begin{aligned} \mathbf{s}(x) &= \mathbf{s}^a(\varphi_a,\theta_a) \text{ for all } x \text{ with } \mathbf{n}(x) = \mathbf{n}^a, \\ \xi(x) &= (-1)^a \quad (a = 1,\ldots,6)\ , \end{aligned} \tag{17}$$

where $\mathbf{n}^1 = \mathbf{n}^2 = \mathbf{e}_1$, $\mathbf{n}^3 = \mathbf{n}^4 = \mathbf{e}_2$, etc., and φ_a, θ_a denote azimuthal and polar angles, respectively. Setting $J \equiv 1$ as a reference energy and defining

$$\begin{aligned} G_{ab} &= \begin{cases} q^2 & a \text{ and } b \text{ even} \\ (1-q)^2 & a \text{ and } b \text{ odd} \\ q(1-q) & \text{else}\ , \end{cases} \\ g_a &= \begin{cases} q & a \text{ even} \\ q-1 & a \text{ odd}\ , \end{cases} \end{aligned} \tag{18}$$

we obtain the total energy per site

$$\begin{aligned} E/N = &-\frac{1}{18}\sum_{a,b=1}^{6} G_{ab}\left\{\left(\mathbf{s}^a\cdot\mathbf{s}^b\right)^2 + \left(\tilde{J}-1\right)\left(s^a_\mu\right)^2\left(s^b_\mu\right)^2\right\} \\ &-\frac{D}{3}\sum_a g_a\left(\mathbf{s}^a\cdot\mathbf{n}^a\right)^2\ , \end{aligned} \tag{19}$$

which has to be minimized numerically with respect to $\{\varphi_a, \theta_a\}$.

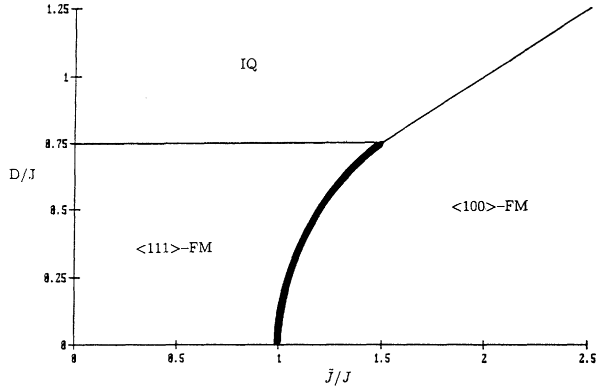


FIG. 2. Ground states of the continuous model for $q = 1$. The quadrupole-flop line is drawn thick.

We now concentrate on two limiting cases: the model with purely ferromagnetic ($q = 1$) and purely antiferromagnetic ($q = 0$) fields. Although both cases are *not* realized in $(\mathrm{NaCN})_{1-x}(\mathrm{KCN})_x$, they clarify the different effects of either type of disorder.

Figure 2 presents the ground-state diagram in the case of purely *ferromagnetic* quadrupolar fields. In this instance the orientational ordering conserves uniaxial symmetry, that is

$$[f_{\mu\nu}(\mathbf{s})] = M f_{\mu\nu}(\mathbf{e}_M)\ , \tag{20}$$

where $[\cdots]$ denotes the configurational average and $\mathbf{e}_M$ is a unit vector characterizing the symmetry axis. As can be seen from the case of a totally isotropic interaction ($\tilde{J} = 1$), the random fields give rise to a hidden anisotropy in the system: Even small fields break the rotational invariance of the interaction and favor $\langle 111\rangle$ ordering (with $\mathbf{e}_M$ being a body diagonal). Finally, at a critical value $D = D_c$ long-ranged order is suppressed and an *independent quadrupole* (IQ) phase becomes globally stable. In this phase all quadrupoles align along their local preferential axes and the macroscopic quadrupole moment vanishes. For $\tilde{J} > 1$, however, the quadrupolar interaction favors $\langle 100\rangle$ ordering, and the competing influence of the random fields can lead to a "quadrupole-flop" at $D = D^* < D_c$ from axial to bodydiagonal order (thick line in Fig. 2). This behavior is quite similar to the "spin flops" from longitudinal to transversal order observed in disordered anisotropic Heisenberg models.[11]

In contrast, the situation becomes more complex if one sets $q = 0$ (purely *antiferromagnetic* fields). The corresponding phase diagram (see Fig. 3) can be considered as the continuation of Fig. 2 to negative D. Now the local axes $\mathbf{n}(x)$ are disfavored and even in the limit of large D a long-ranged ordered ground state is preserved. We find different types of *planar* ordering with the quadrupolar orientation restricted to one plane, for example the x-y plane, such that

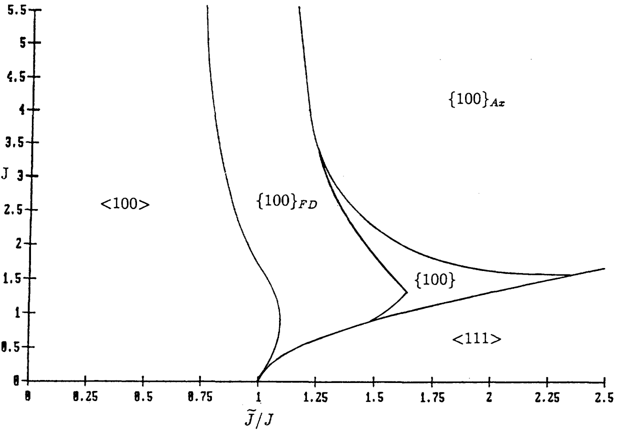


FIG. 3. Ground states of the continuous model for $q = 0$. The phase diagram can be interpreted as the continuation of Fig. 2 to negative D.

$$s_3^a \equiv 0 \ , \qquad a = 1,3,5 \ . \tag{21}$$

(Since $q = 0$, other $\mathbf{s}^a$ are irrelevant.) We distinguish between the following three planar phases:

(a) $\{100\}_{FD}$ ordering, where a face diagonal is a symmetry axis:

$$\mathbf{s}^1 = \begin{pmatrix} \sin\alpha \\ \cos\alpha \\ 0 \end{pmatrix} , \quad \mathbf{s}^3 = \begin{pmatrix} \cos\alpha \\ \sin\alpha \\ 0 \end{pmatrix} ,$$
$$\mathbf{s}^5 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} . \tag{22}$$

Due to the competition between quadrupolar interaction and local fields, $\mathbf{s}^1$ and $\mathbf{s}^3$ take an intermediate position between the face diagonal and their local preferential plane. For large D, however, the random-field contribution dominates and one has $\alpha \to 0$.

(b) $\{100\}_{Ax}$ ordering with axial symmetry:

$$\mathbf{s}^1 = \mathbf{s}^5 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} , \quad \vec{s}^3 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} , \tag{23}$$

where all quadrupoles minimize their local orientational potential.

(c) The general $\{100\}$ phase with lower symmetry, where only (21) holds and thus the averaged quadrupole moment is of the form

$$[\mathbf{f}] = \begin{pmatrix} A & B & 0 \\ B & \frac{1}{3} - A & 0 \\ 0 & 0 & -\frac{1}{3} \end{pmatrix} . \tag{24}$$

For the special cases of a $\{100\}_{Ax}$ and a $\{100\}_{FD}$ phase one has $A = B = 0$ and $A = \frac{1}{6}$, $B = \frac{1}{6} + \frac{\sin 2\alpha}{3}$, respectively.

So far we have focused on the cases $q = 1$ and 0. As pointed out in Sec. II, the parameter range of experimental interest would be $q \approx 0.5$. In the framework of mean-field theory, however, this case is essentially a superposition of the two systems discussed above. Consequently, at least a fraction of the quadrupoles orders ferromagnetically at $T = 0$. The relevance of these results for short-ranged models will be discussed in the last section.

B. $T \neq 0$

Now we are going to discuss the properties of the model defined by (12) at $T \neq 0$. Introducing the tensor $m_{\mu\nu}$ of Gaussian integration variables and performing a saddle-point integration, we obtain as free energy per site in the thermodynamic limit

$$\begin{aligned} f/N &= \min_{\mathbf{m}} \left\{ \frac{1}{2} m_{\mu\nu} J_{\mu\nu} m_{\mu\nu} - T \left[\ln z_0(\mathbf{n}, \xi) \right] \right\} \\ &\equiv \min_{\mathbf{m}} \left\{ \frac{1}{2} m_{\mu\nu} J_{\mu\nu} m_{\mu\nu} - T \left[\ln \int d\mathbf{s} \; e^{\beta m_{\mu\nu} J_{\mu\nu} f_{\mu\nu}(\mathbf{s}) + \beta \xi D (\mathbf{s}\cdot\mathbf{n})^2} \right] \right\} , \end{aligned} \tag{25}$$

where $\beta = \frac{1}{T}$ is the inverse temperature and the $\mathbf{s}$ integration has to be taken over the unit sphere. Since the disorder is local in the site index x, we have used the law of large numbers ($[\cdots]$ denotes configurational averaging), thus proving the self-averaging property of the free energy (see, e.g., Ref. 14). The self-consistency equation for $\mathbf{m}$ at the saddle point shows that the order-parameter matrix can be identified with the average quadrupole moment

$$m_{\mu\nu} = \left[\langle f_{\mu\nu}(\mathbf{s}) \rangle_{z_0} \right] = \left[\langle f_{\mu\nu}(\mathbf{s}) \rangle \right] , \tag{26}$$

where $\langle \cdots \rangle_{z_0}$ stands for an average taken with the single-site partition function in (25), and $\langle \cdots \rangle$, as usual, denotes thermal averaging.

In order to analyze the flop transition from $\langle 100 \rangle$ to $\langle 111 \rangle$ order in the case of purely ferromagnetic fields, we write

$$m_{\mu\nu} = M_z f_{\mu\nu}(\mathbf{e}_3) + M_d f_{\mu\nu}(\mathbf{e}_d) \ , \quad \mathbf{e}_d = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} . \tag{27}$$

Using this ansatz in (25) yields

$$\begin{aligned} f/N = \min_{M_z, M_d} \Bigg\{ & \frac{\tilde{J}}{3} (M_z^2 + M_z) + \frac{1}{3} (M_d^2 + M_d) \\ & -T \left[\ln \int d\mathbf{s} \; \exp\left\{ \beta \tilde{J} M_z (\mathbf{s}\cdot\mathbf{e}_3)^2 \right. \right. \\ & \left. \left. + \beta M_d (\mathbf{s}\cdot\mathbf{e}_d)^2 + \beta D (\mathbf{s}\cdot\mathbf{n})^2 \right\} \right] \Bigg\} . \end{aligned} \tag{28}$$

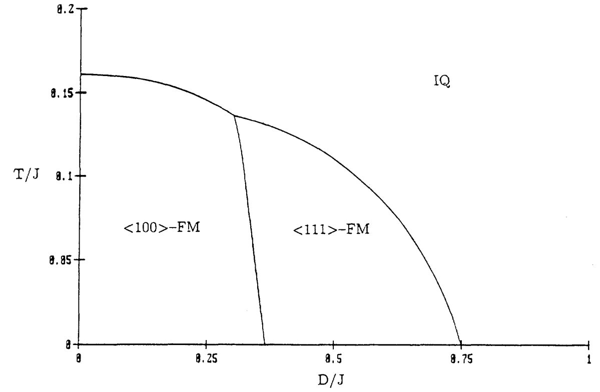


FIG. 4. Phase diagram of the continuous model with $q=1$ and $\tilde{J}/J=1.1$.

Figure 4 shows a typical phase diagram resulting from a numerical investigation of the free-energy landscape. Again, in a certain parameter range quadrupole flopping is possible, but in contrast to Ref. 11 *all* transitions are first order. Furthermore, it should be noted that there is no intermediate mixed phase with M_z and $M_d \neq 0$.

IV. ELASTIC PROPERTIES OF THE MODEL

We now briefly discuss the coupling between orientational and elastic degrees of freedom in our model. Each quadrupole acts as a local stress center, which couples bilinearly to the strain field of the crystal. Here we concentrate on homogeneous deformations of the lattice, i.e., $\epsilon_{\mu\nu}(x)=\epsilon_{\mu\nu}$, but strain fluctuations could be treated in a self-consistent cumulant expansion.[9] If we again assume cubic symmetry and consider the elastic energy in the harmonic approximation the complete Hamiltonian for the six elastic and N orientational variables reads

$$\begin{aligned}\mathcal{H} &= \mathcal{H}^{\text{orient}}[\{f_{\mu\nu}(x)\}] \\ &\quad + \frac{N}{2}\,\epsilon_{\mu\nu}C^{0}_{\mu\nu\rho\sigma}\epsilon_{\rho\sigma} - \epsilon_{\mu\nu}\lambda_{\mu\nu}\sum_{x} f_{\mu\nu}(x) \qquad (29)\\ \lambda_{\mu\nu} &= \lambda_1\delta_{\mu\nu} + \lambda_2(1-\delta_{\mu\nu})\end{aligned}$$

Here $\mathcal{H}^{\text{orient}}$ denotes the Hamiltonian (12), $\mathbf{C}^0$ is the tensor of the bare elastic constants, and λ_1, λ_2 are coupling constants.

The thermodynamic properties of the infinite-ranged models can be calculated by saddle-point integrations yielding exact relations between elastic and orientational variables. These read

$$\begin{aligned}[\langle\epsilon_{\mu\nu}\rangle] &= S^{0}_{\mu\nu\rho\sigma}\lambda_{\rho\sigma}\,[\langle f_{\rho\sigma}(\mathbf{s})\rangle] \\ &= S^{0}_{\mu\nu\rho\sigma}\lambda_{\rho\sigma}m_{\rho\sigma} \\ &= \{(S^0_{11}-S^0_{12})\lambda_1\delta_{\mu\nu} + 2S^0_{44}\lambda_2(1-\delta_{\mu\nu})\}\,m_{\mu\nu}\ , \qquad (30)\end{aligned}$$

where $\mathbf{S}^0$ is the bare elastic compliance tensor. Thus $\langle 100\rangle$, $\langle 111\rangle$, and $\{100\}$ ordering leads to long-ranged lattice deformations with *tetragonal, rhombohedral*, and *monoclinic* symmetry, respectively, whereas the $\{100\}_{FD}$ and $\{100\}_{Ax}$ phases have *orthorhombic* symmetry. With the help of Eq. (30) the elastic degrees of freedom can be eliminated, and one only has to calculate thermodynamic averages of a model without coupling to the elastic degrees of freedom, but with a renormalized quadrupolar interaction:

$$\begin{aligned}\tilde{J}^{\text{eff}} &= \tilde{J} + \lambda_1^2(S^0_{11}-S^0_{12})\ ,\\ J^{\text{eff}} &= J + 2\lambda_2^2 S^0_{44}\ .\end{aligned} \qquad (31)$$

The temperature dependence of the elastic constants can be obtained by the following exact relations:[9]

$$S_{\mu\nu\rho\sigma} = S^0_{\mu\nu\rho\sigma} + S^0_{\mu\nu\alpha\beta}\lambda_{\alpha\beta}\chi_{\alpha\beta\gamma\delta}\lambda_{\gamma\delta}S^0_{\gamma\delta\rho\sigma}\ , \qquad (32)$$

so that in the weak-coupling limit the elastic constants are given by

$$C_{\mu\nu\rho\sigma} = C^0_{\mu\nu\rho\sigma} - \lambda_{\mu\nu}\lambda_{\rho\sigma}\chi_{\mu\nu\rho\sigma}\ . \qquad (33)$$

χ is the uniform susceptibility defined as the response of the system to a uniform quadrupolar field $\mathbf{H}$:

$$\chi_{\mu\nu\rho\sigma} = \left.\frac{\partial m_{\mu\nu}}{\partial H_{\rho\sigma}}\right|_{\mathbf{H}=0}\ . \qquad (34)$$

Because of the symmetries of χ (see below) one has the invariants

$$\begin{aligned}\sum_{j=1}^{3} C_{ij} &= C^0_{11} + 2C^0_{12} \quad \text{for } i = 1,\ldots,3\\ \sum_{j=1}^{3} C_{ij} &= 0 \qquad\qquad\quad\ \ \text{for } i = 4,\ldots,6\ .\end{aligned} \qquad (35)$$

χ can easily be calculated by means of the local susceptibility

$$\chi^{\text{loc}}_{\mu\nu\rho\sigma} = \beta\Big[\langle f_{\mu\nu}(\mathbf{s})f_{\rho\sigma}(\mathbf{s})\rangle_{z_0} - \langle f_{\mu\nu}(\mathbf{s})\rangle_{z_0}\langle f_{\rho\sigma}(\mathbf{s})\rangle_{z_0}\Big] \qquad (36)$$

and the relation

$$\chi_{\mu\nu\rho\sigma} = \chi^{\text{loc}}_{\mu\nu\alpha\beta}J_{\alpha\beta}\chi_{\alpha\beta\rho\sigma} + \chi^{\text{loc}}_{\mu\nu\rho\sigma}\ . \qquad (37)$$

In the $\langle 100\rangle$ and $\langle 111\rangle$ phases, for example, the fourth-rank tensor χ has tetragonal and rhombohedral symmetry, respectively. Because of property (9) the number of independent components can be reduced further:

$$\chi_{\mu\nu\rho\rho} = \chi_{\rho\rho\mu\nu} = 0\ . \qquad (38)$$

Thus, Eq. (37) has to be solved for at most four components. We numerically find a Curie-Weiss behavior at high temperatures, but the divergencies at T_c are cut off by the discontinuous transition. Consequently, the elastic constants exhibit a minimum with a discontinuity at the critical temperature. If, however, the system remains at all temperatures in the disorder dominated IQ phase (see Fig. 4), **C** has only a rather weak T dependence.

V. CONCLUSIONS

Based on a microscopic investigation of the orientational potential felt by a quadrupole in a random cage of cations, we have proposed a model Hamiltonian for crystals with substitutional disorder. Considering only second-order terms in the expansion of the potential, we arrive at a random-field model with ferromagnetic and antiferromagnetic local fields. In the limit of infinite interaction range we find various long-ranged ordered phases in the model, including planar ordering and flops between the $\langle 100\rangle$ and the $\langle 111\rangle$ phase, reminiscent of the disordered uniaxial Heisenberg model. In the case of purely ferromagnetic fields, large field strength leads to a disordered ground state with the quadrupoles freezing parallel to their local preferential axes (IQ phase). For purely antiferromagnetic fields and the mixed case, long-ranged order is stabilized even if the random fields are large. Experiments on $(\mathrm{NaCN})_{1-x}(\mathrm{KCN})_x$ (Refs. 15 and 16) indicate that at intermediate K^+ concentrations these systems remain in an IQ-like phase at all *accessible* temperatures. However, exceedingly long-time scales possibly prevent the experimentalist from observing partially ordered states at very low temperatures.

Another important question is whether or not the ground states predicted by mean-field theory survive in models with short-ranged interactions. Domain-wall arguments of the Imry-Ma type[17] can also be applied to the case of antiferromagnetic random fields yielding a lower critical dimension $d_l = 4$ for arbitrary q [cf. Eq. (14)]. In real systems the elastic interaction of the quadrupoles may lead to additional global anisotropies that restrict the possible molecular orientations to a *discrete* set of axes.[9,18] In this case ferromagnetic ordering would be stable in three dimensions.

There is another mechanism to destroy ferromagnetic order in the short-ranged model:[18] Consider, for example, a $\{100\}_{Ax}$ ground state in the limit of large field strength. In the infinite-ranged model the qN quadrupoles with $\xi(x) = 1$ will order along their local preferential axes, $\frac{2}{3}(1-q)N$ molecules will freeze in the same, say $\mathbf{e}_3$, axis, and $\frac{1}{3}(1-q)N$ quadrupoles will freeze in the $\mathbf{e}_1$ axis. Altogether we have $\mathbf{e}_3$ alignment at $\frac{1}{3}(2-q)N$ sites. In a short-ranged model this ground state can only be established if there is a connecting cluster of such sites, which means $\frac{1}{3}(2-q) > p_c$, the percolation threshold of the lattice. For a $2d$ square lattice ($p_c = 0.593$) and for a triangular lattice ($p_c = 0.5$) this condition can be violated, while for a fcc lattice the percolation threshold is too small ($p_c = 0.198$). Thus, in three dimensions a long-ranged ordered ground state is not ruled out by this argument.

Furthermore, we have given a discussion of the coupling between orientational and elastic degrees of freedom in the crystal. Since this coupling is linear, the phase diagram of the pure system remains valid (apart from a renormalization of the quadrupolar interaction), and exact relations between averaged orientational and elastic quantities can be derived: Long-ranged orientational ordering gives rise to macroscopic lattice deformations, the magnitude of which is determined by the averaged quadrupolar moment of the orientational degrees of freedom. We find a variety of lattice symmetries in the low-temperature phases including a *monoclinic* phase as observed in $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$. This indicates that antiferromagnetic random fields may also play an important role in mixed alkali halide–alkali cyanides. The temperature dependence of the elastic constants can be obtained from another exact relation, which connects the orientational susceptibility with the elastic compliance tensor.

In summary, we have analyzed in detail the *random fields* and *stochastic anisotropies* that appear in a certain class of mixed cyanides. As a next step towards understanding the phase diagrams and elastic properties of these systems we would like to combine the local effects of substitutional disorder with a more realistic description of the quadrupole-quadrupole interaction. Being mediated by lattice strains, it falls off like r^{-3} in three dimensions,[19] so it is an open question whether or not a long-ranged model is adequate. Furthermore, the interaction is known to depend not only on the relative orientation of the quadrupoles, but also on the distance vector joining them. As a result, the bonds are frustrated and may give rise to glassy states even in *uniform* systems.[20] Finally, the quadrupolar interaction may also have a randomly fluctuating component, which is, however, expected to be much smaller than in mixed crystals with randomly distributed orientable defects.

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