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Model of quadrupolar glass of mixed alkali cyanide crystals

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A model of the transition from the orientationally disordered to the quadrupolar-glass (QG) phase of mixed alkali halide cyanide crystals is proposed. Starting from the semimicroscopic Hamiltonian constructed by Vollmayr, Kree, and Zippelius the effective Hamiltonian containing random long-ranged orientational interactions between CN^- ions and their orientational coupling to the random local strain field has been obtained. The CN^- ion is treated as a quadrupolar molecule and no restriction has been made to a finite number of spatial orientations of it. With the Sherrington-Kirkpatrick approach the formula for the free energy has been derived. In the framework of the replica-symmetric theory the Landau expansion of the free energy up to third order in the QG Edwards-Anderson parameter has been performed in the absence of the random local strain field. This predicts a continuous QG transition. However, it is smeared out due to the influence of the random local strains, which in fact have a nonzero value. The elastic compliance has been calculated and it has been shown, that T_{2g} orientational modes govern the softening of the elastic constant C_{44} on approaching the QG transition point, whereas E_{2g} modes are responsible for the much less pronounced temperature dependence of C_{11} and C_{12}. This is in agreement with experimental data.

I. INTRODUCTION

Mixed alkali cyanide crystals such as, e.g., $K(CN)_xBr_{1-x}$, $Na(CN)_xCl_{1-x}$, etc., have attracted considerable interest recently especially in view of a possible orientational (or quadrupolar) glass state in a certain concentration range of x (cf. review article by Binder and Reger[1]). These systems generally show a cubic structure, where the sites of anions are randomly occupied by halide ions and dumbbell-shaped CN^- ions. At high CN^- ion concentrations $x > x_c$ the system undergoes a structural ferroelastic phase transition.[2,3] At lower concentration of CN^- no long-range order has been observed and the global symmetry of the system remains cubic to lowest temperatures.[2,3] However, in this case below some temperature $T_g(x)$ one observes a cooperative freezing of the CN^- ions into random directions and the system forms a quadrupolar-glass (QG) phase reminescent in some aspects of the spin-glass state in disordered magnetic materials.[4] Because of the coupling between rotational and translational degrees of freedom[5] the random freezing of CN^- ions gives rise to local static lattice deformations, but on average the cubic symmetry remains unchanged. Thus, the QG phase of the systems under consideration also has features of a structural glass.

Various experimental investigations provide evidence for the existence of orientational glass. Phenomena such as the temperature dependence of the central line of the quasielastic neutron scattering[6–8] and of the widths of the distributions of the elastic field gradient tensors at the sites of the ^{23}Na nuclei detected by NMR (Ref. 9) are attributed to the appearance of a QG state with frozen-in random CN^- orientations and lattice strains. An important feature of the QG transition is the considerable softening and successive hardening of the shear modulus C_{44}. This effect has been observed by using different experimental methods.[10–13]

An analogy between the glassy state of $(KBr)_x(KCN)_{1-x}$ and spin glasses was stressed by Michel and Rowe.[14] In Ref. 14 they proposed a microscopic model of QG in which the interaction between randomly distributed CN^- ions originates from linear coupling of translational and rotational degrees of freedom. In this model no restriction has been made to a finite number of orientational positions of CN^- ions. In Ref. 15 to the previous model[14] have been included random strain fields as a consequence of the substitutional disorder. The coupling of the random strain fields to translational and rotational dynamic modes can lead to a nonergodic instability.[16]

An alternative model has been formulated by Vollmayr, Kree, and Zippelius.[17,18] They start from coarse-graining averaged interactions, which leads to treating the system as an elastic medium, in which defects (CN^- ions) in the given orientational state cause the local stress. In addition, there are the local anisotropy and long-ranged interaction between defects. A crucial assumption of this model is that due to the strong anisotropy potential CN^- molecular ions have a limited number of orientational states according to cubic symmetry.[18] This allows one to reduce the problem to the p-state Potts model with a random long-ranged interaction and "Potts spins" coupled to the local strains field.

The aim of the present paper is to propose a model. We start from the interactions at a semimicroscopic level derived in Ref. 18, but no restriction is made to a finite number of orientational positions of CN^- ions. It will be shown that due to bilinear coupling between local strains and orientations of defects it is possible to integrate out

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over the displacement field. As a consequence the effective Hamiltonian containing only rotational degrees of freedom of the defects will be obtained. This Hamiltonian can be treated by the methods used in the theory of spin glasses.[4] Because we are mainly interested in the QG phase a possible mechanism leading to a ferroelastic transition will not be considered.

The paper is organized as follows. In Sec. II starting from the semimicroscopic Hamiltonian[18] we calculate the effective orientational Hamiltonian. In Sec. III using the method similar to the Sherrington-Kirkpatrick[4] approach in the theory of spin glasses we perform an averaging over the quenched disorder obtaining the QG Hamiltonian. In this section we also define the Edwards-Anderson QG parameter and calculate the orientational free energy within the replica-symmetric theory. Subsequently we show that our model implies a sharp continuous QG transition in the absence of a random local strain field. Section IV is devoted to an analysis of the effect of random freezing of CN$^-$ ions on elastic constants. Finally in Sec. V some conclusions are drawn.

II. EFFECTIVE ORIENTATIONAL HAMILTONIAN

The coarse-graining procedure leads to the semimicroscopic Hamiltonian[18]

$$H = \sum_{\mathbf{x}} \left[\frac{1}{2}\epsilon_\mu(\mathbf{x}) C^0_{\mu\nu}\epsilon_\nu(\mathbf{x}) + \sigma_\mu(\mathbf{d}(\mathbf{x}),\mathbf{x})\epsilon_\mu(\mathbf{x}) + v(\mathbf{d}(\mathbf{x}),\mathbf{x}) \right] - \frac{1}{2}\sum_{\mathbf{x}\neq\mathbf{y}} J_{\mathbf{x},\mathbf{y}}(\mathbf{d}(\mathbf{x}),\mathbf{d}(\mathbf{y})), \tag{1}$$

where $\epsilon_\mu(\mathbf{x})$ is the (coarse-grained) local strain tensor, $\mathbf{d}(\mathbf{x})$ stands for a unit vector characterizing an orientation of the defect (linear CN$^-$ ion) located at the site $\mathbf{x}$ of a coarse-grained lattice, $\sigma_\mu(\mathbf{d}(\mathbf{x}),\mathbf{x})$ is the local stress arising from a defect in the orientational state $\mathbf{d}(\mathbf{x})$, $C^0_{\mu\nu}$ are the bare elastic constants on the mesoscopic coarse-grained scale, $v(\mathbf{d}(\mathbf{x}),\mathbf{x})$ denotes the local anisotropy, and $J_{\mathbf{x},\mathbf{y}}(\mathbf{d}(\mathbf{x}),\mathbf{d}(\mathbf{y}))$ is the coupling between defects. A summation convention with the respect to the indices $\mu,\nu = 1\ldots 6$ is implied, where $\mu,\nu = (ij),(i'j')$ and i,j,i',j' denote Cartesian indices (x,y,z). The relations between $\mu,(\nu)$ and $(ij)[(i'j')]$ are $\mu = 1 \leftrightarrow (xx)$, $\mu = 2 \leftrightarrow (y,y)$, $\mu = 3 \leftrightarrow (zz)$, $\mu = 4 \leftrightarrow (yz)$, $\mu = 5 \leftrightarrow (xz)$, and $\mu = 6 \leftrightarrow (xy)$.[19] The reasons for using a semimicroscopic model are discussed in detail in Ref. 18. It has been assumed there that $H(1)$ is the simplest effective Hamiltonian, which in accordance with the theory of critical phenomena can describe ordering or the random freezing of orientable defects and is compatible with a microscopic interaction.[18] The quenched random positions of the defects, which replace the halogen atoms, lead to random variables $\sigma_\mu(\mathbf{d}(\mathbf{x}),\mathbf{x})$, $v(\mathbf{d}(\mathbf{x}),\mathbf{x})$, and $J_{\mathbf{x},\mathbf{y}}(\mathbf{d}(\mathbf{x}),\mathbf{d}(\mathbf{y}))$. The coupling $J_{\mathbf{x},\mathbf{y}}(\mathbf{d}(\mathbf{x}),\mathbf{d}(\mathbf{y}))$ contains contributions from direct electrical multipole interactions and indirect interactions via lattice distortions exisiting on the microscopic scale.[18] Because $J_{\mathbf{x},\mathbf{y}}(\mathbf{d}(\mathbf{x}),\mathbf{d}(\mathbf{y}))$ decreases rather slowly with a power-law decay for large distances it cannot be considered as short ranged.[18]

In Eq. (1) the $\mathbf{x},\mathbf{y}$ summation runs over the points of the coarse-grained lattice with cubic point-group symmetry.[18] Alternatively it can be written as an integral,[18]

$$\sum_{\mathbf{x}} \cdots \to \xi_0^{-3}\int d^3x \cdots, \tag{2}$$

where ξ_0 ($a \ll \xi_0 \ll \xi$) is the mesoscopic coarse-graining length. Here a and ξ denote, respectively, the constant of microscopic lattice and correlation length.

Now, we subtract the effect of the substituted CN$^-$ ions in a spherical approximation.[15] This leads to the replacement

$$\sigma_\mu(\mathbf{d}(\mathbf{x}),\mathbf{x}) - \sigma_\mu(\mathbf{x}) \to \sigma_\mu(\mathbf{d}(\mathbf{x}),\mathbf{x}), \tag{3}$$

where

$$\sigma_\mu(\mathbf{x}) = \frac{1}{4\pi}\int d\Omega_{\mathbf{x}}\sigma_\mu(\mathbf{d}(\mathbf{x}),\mathbf{x}) \tag{4}$$

and $\Omega_{\mathbf{x}} = (\theta_{\mathbf{x}},\varphi_{\mathbf{x}})$ specifies the orientation of the defect to the cubic crystal axis.

The replacement (3) is compensated by an appropriate shift

$$\epsilon_\mu(\mathbf{x}) \to \epsilon_\mu(\mathbf{x}) + (C^0)^{-1}_{\mu\nu}\sigma_\nu(\mathbf{x}), \tag{5}$$

where $\| (C^0)^{-1}_{\mu\nu} \|$ is the bare compliance matrix (inverse of $\| C^0_{\mu\nu} \|$). In the following we will neglect the quenched random fluctuation of $\sigma_\mu(\mathbf{x})$ putting

$$\sigma_\mu(\mathbf{x}) \to [\sigma_\mu(\mathbf{x})]_{\mathrm{av}} = \sigma^{(0)}\delta_{ij}, \tag{6}$$

where $[\cdots]_{\mathrm{av}}$ denotes an average over quenched disorder. We assume that the quantities averaged over the quenched disorder still have a cubic symmetry. After the transformations (3)–(6) the Hamiltonian (1) (with an accuracy to some innesential constant term) has the same form, with new $\sigma_\mu(\mathbf{x})$'s and $\epsilon_\mu(\mathbf{x})$'s given, respectively, by Eqs. (3) and (5) with $\sigma_\nu(\mathbf{x}) \to \sigma^{(0)}\delta_{ij}$, while $v(\mathbf{d}(\mathbf{x}),\mathbf{x})$ is replaced by

$$v(\mathbf{d}(\mathbf{x}),\mathbf{x}) - \sigma^{(0)}\sigma_\mu(\mathbf{d}(\mathbf{x}),\mathbf{x})\sum_{\nu}^{3}(C^0)^{-1}_{\mu\nu}.$$

Quenched averages of thermal observables are obtained from the free energy F defined as

$$F = -\beta^{-1}[\ln Z]_{\mathrm{av}}, \tag{7}$$

with

$$Z = \int d^6\bar{\epsilon} \int \prod_{\mathbf{x}} d^3\mathbf{u}(\mathbf{x}) \mathrm{Tr} \exp(-\beta H), \tag{8}$$

where Z is the partition function and Tr denotes the integration over orientations of the defects. In Eq. (8) we have decomposed the strain tensor

$$\epsilon_\mu(\mathbf{x}) = \bar{\epsilon}_\mu + \tilde{\epsilon}_\mu(\mathbf{x}) \tag{9}$$

into a homogenous part $\bar{\epsilon}_\mu$ and inhomogenous part[18]

$$\tilde{\epsilon}_\mu(\mathbf{x}) = \frac{1}{2}\left[\frac{\partial u_j(\mathbf{x})}{\partial x_i} + \frac{\partial u_i(\mathbf{x})}{\partial x_j}\right], \tag{10}$$

where $\mu = (ij)$ and $\mathbf{u}(\mathbf{x})$ denotes the coarse-grainined displacement field. It is assumed that $\mathbf{u}(\mathbf{x})$ obeys a natural boundary condition[18]

$$\mathbf{u}(\mathbf{x}) \to \mathbf{0} \text{ for } |\mathbf{x}| \to \infty. \tag{11}$$

After substitution to Eq. (1) the decomposition (9) and replacing the $\mathbf{x}$ summation by the appropriate integral [cf. Eq. (2)] we obtain $H(1)$ in the form

$$H = \sum_{\mathbf{x}}\left[\frac{1}{2}\bar{\epsilon}_\mu C^0_{\mu\nu}\bar{\epsilon}_\nu + \sigma_\mu(\mathbf{d}(\mathbf{x}),\mathbf{x})\bar{\epsilon}_\mu\right] + \sum_{\mathbf{x}}\left[\frac{1}{2}u_i(\mathbf{x})F_{ij}(\nabla)u_j(\mathbf{x}) - \mathbf{u}_i(\mathbf{x})\frac{\partial\sigma_{ij}(\mathbf{d}(\mathbf{x}),\mathbf{x})}{\partial x_j} + v(\mathbf{d}(\mathbf{x}),\mathbf{x})\right] - \frac{1}{2}\sum_{\mathbf{x}\neq\mathbf{y}} J_{\mathbf{x},\mathbf{y}}(\mathbf{d}(\mathbf{x}),\mathbf{d}(\mathbf{y})), \tag{12}$$

where

$$F_{ij}(\nabla) = -C^0_{ik,lj}\frac{\partial^2}{\partial x_k \partial x_l}. \tag{13}$$

Here and in the following a summation convention with the respect to the Cartesian indices i, j, k, l is assumed. In the derivation of Eq. (12) the following relations were helpful:

$$\sum_{\mathbf{x}} \tilde{\epsilon}_{ij}(\mathbf{x}) \to \frac{\xi_0^{-3}}{2}\int d^3\mathbf{x}\left[\frac{\partial u_j(\mathbf{x})}{\partial x_i} + \frac{\partial u_i(\mathbf{x})}{\partial x_j}\right] = \frac{\xi_0^{-3}}{2}\oint\left[u_j(\mathbf{x})dS_i + u_i(\mathbf{x})dS_j\right] = 0 \tag{14}$$

and

$$\sum_{\mathbf{x}} \tilde{\epsilon}_\mu(\mathbf{x})C^0_{\mu\nu}\tilde{\epsilon}_\nu(\mathbf{x}) \to \xi_0^{-3}\int d^3\mathbf{x} C^0_{ijkl}\frac{\partial u_j(\mathbf{x})}{\partial x_i}\frac{\partial u_l(\mathbf{x})}{\partial x_k}$$
$$= \xi_0^{-3}\oint C^0_{ijkl}u_j(\mathbf{x})\frac{\partial u_l(\mathbf{x})}{\partial x_k}dS_i - \xi_0^{-3}\int d^3\mathbf{x} C^0_{ijkl}u_j(\mathbf{x})\frac{\partial^2}{\partial x_i \partial x_k}u_l(\mathbf{x}) \to \sum_{\mathbf{x}} u_i(\mathbf{x})F_{ij}(\nabla)u_j(\mathbf{x}). \tag{15}$$

Owing to the boundary condition (11) the integrals $\oint dS_i \cdots$ over the surface of the system vanish. Now it is easy to perform in the partition function (8) the Gaussian integrations over the $\bar{\epsilon}_\mu$'s and displacement field $\mathbf{u}(\mathbf{x})$. As a result the free energy (7) can be written in the form

$$F = -\beta^{-1}\left[\ln \mathrm{Tr} \exp(-\beta H_{\mathrm{orient}})\right]_{\mathrm{av}}, \tag{16}$$

where H_{orient} contains only the orientational degrees of freedom of the defects and reads

$$H_{\mathrm{orient}} = -\frac{1}{2}\sum_{\mathbf{x}\neq\mathbf{y}} U(\mathbf{x},\mathbf{y};\mathbf{d}(\mathbf{x}),\mathbf{d}(\mathbf{y})) - \sum_{\mathbf{x}} v(\mathbf{d}(\mathbf{x}),\mathbf{x}), \tag{17}$$

where

$$U(\mathbf{x},\mathbf{y};\mathbf{d}(\mathbf{x}),\mathbf{d}(\mathbf{y})) = \left[\frac{1}{N}(C^0)^{-1}_{\mu\nu} - v_{\mu\nu}(\mathbf{x}-\mathbf{y})\right]\sigma_\mu(\mathbf{d}(\mathbf{x}),\mathbf{x})\sigma_\nu(\mathbf{d}(\mathbf{y}),\mathbf{y}) + J_{\mathbf{x},\mathbf{y}}(\mathbf{d}(\mathbf{x}),\mathbf{d}(\mathbf{y})), \tag{18}$$

with N denoting the number of sites of the coarse-grained lattice and

$$v_{\mu\nu}(\mathbf{x}-\mathbf{y}) = \frac{\partial^2 G_{ik}(\mathbf{x}-\mathbf{y})}{\partial x_j \partial y_l}. \tag{19}$$

In Eq. (19), $\mu = (ij)$, $\nu = (kl)$ and $G_{ik}(\mathbf{x}-\mathbf{y})$ denotes the lattice Green function defined as the inverse of the differential operator $F_{ij}(\nabla)$ [Eq. (13)].

III. EFFECTIVE QUADRUPOLAR GLASS HAMILTONIAN, ORDER PARAMETER, AND FREE ENERGY

The CN$^-$ ions have a small dipolar momentum, but the dipolar orientational freezing effects are less pronounced than quadrupolar ones.[15] Therefore, we will neglect the dipolar momentum of the CN$^-$ ion treating it as a linear molecule without an asymetry between C and N.[14]

In order to obtain multipole interactions we expand the orientational coupling (18) and random anisotropy potential $v(\mathbf{d}(\mathbf{x}),\mathbf{x})$ into the terms of spherical harmonics $Y_{l,\lambda}(\Omega_{\mathbf{x}})$ retaining only the terms with $l = 2$ because they are related to the components of the quadrupolar momentum of the CN$^-$ ion. However, in systems with the cubic symmetry often the symmetry-adapted spherical harmonics $Y_\lambda(\Omega_{\mathbf{x}})$, where ($\lambda = 1\ldots5$), are used instead of the functions $Y_{2,l}(\Omega_{\mathbf{x}})$.[14] For $\lambda = 1,2$ they have E_g symmetry and are defined as

$$Y_1 = Y_{2,0}, \tag{20}$$

$$Y_2 = \frac{1}{\sqrt{2}}(Y_{2,2} + Y_{2,-2}). \tag{21}$$

Note that, in Ref. 14, Y_2 is defined with a factor $1/\sqrt{6}$ instead of $1/\sqrt{2}$ as in Eq. (21). However, this difference is inessential.

For $\lambda = 3,4,5$ the Y_λ's have T_{2g} symmetry and the form

$$Y_3 = \frac{-i}{\sqrt{2}}(Y_{2,2} - Y_{2,-2}), \tag{22}$$

$$Y_4 = \frac{i}{\sqrt{2}}(Y_{2,1} + Y_{2,-1}), \tag{23}$$

$$Y_5 = \frac{-1}{\sqrt{2}}(Y_{2,1} - Y_{2,-1}). \tag{24}$$

The functions Y_λ (20)–(24) satisfy the relation

$$\int d\Omega Y_\lambda(\Omega) Y_{\lambda'}(\Omega) = \delta_{\lambda\lambda'}. \tag{25}$$

Thus, H_{orient} (17) reads

$$H_{\text{orient}} = -\sum_{\mathbf{x}}\sum_{\lambda=1}^{5} h_\lambda(\mathbf{x}) Y_\lambda(\Omega_{\mathbf{x}}) -\frac{1}{2}\sum_{\mathbf{x}\neq\mathbf{y}}\sum_{\lambda,\lambda'=1}^{5} u^{\lambda\lambda'}(\mathbf{x},\mathbf{y}) Y_\lambda(\Omega_{\mathbf{x}}) Y_{\lambda'}(\Omega_{\mathbf{y}}), \tag{26}$$

where $h_\lambda(\mathbf{x})$ and $u^{\lambda\lambda'}(\mathbf{x},\mathbf{y})$ denote, respectively, the random strain fields and orientational coupling. The inessential terms, which do not depend on the orientations of the CN$^-$ ions, have been omited. In H_{orient} [Eq. (26)] there is no interaction of the quadrupolar momenta of the defects with the constant (nonrandom) anisotropy potential because in the cubic structure it couples to the higher multipoles.

Michel and Rowe[14,15] guided by the experiments, consider only three orientational modes (22)–(24) of T_{2g} symmetry. In our model we will not eliminate the E_g orientational modes (20) and (21). However, E_g and T_{2g} modes do not enter the theory on the same footing. As will be seen in Sec. IV the T_{2g} modes are responsible for softening of the elastic constant C_{44}.

In order to calculate the free energy (7) we use the well-known replica procedure[4]

$$F = -\beta^{-1}\lim_{n\to 0}\frac{1}{n}\ln Z_n, \tag{27}$$

with

$$Z_n = \left[\operatorname{Tr}\exp\left(-\beta\sum_{\alpha=1}^{n} H_{\text{orient}}^{(\alpha)}\right)\right]_{\text{av}}, \tag{28}$$

where $H_{\text{orient}}^{(\alpha)}$ is the αth replica of the orientational Hamiltonian (26). Using the cumulant expansion to the right-hand side of Eq. (28) one obtains

$$\begin{aligned} Z_n &= \operatorname{Tr}\exp\left(-\beta\sum_{\alpha=1}^{n}\left[H_{\text{orient}}^{(\alpha)}\right]_{\text{av}} + \frac{\beta^2}{2}\sum_{\alpha,\alpha'}^{n}\left(\left[H_{\text{orient}}^{(\alpha)}H_{\text{orient}}^{(\alpha')}\right]_{\text{av}} - \left[H_{\text{orient}}^{(\alpha)}\right]_{\text{av}}\left[H_{\text{orient}}^{(\alpha')}\right]_{\text{av}}\right) + \cdots\right) \\ &= \operatorname{Tr}\exp(-\beta H_{\text{QG}}), \end{aligned} \tag{29}$$

where

$$H_{\text{QG}} = \sum_{\alpha=1}^{n}\left[H_{\text{orient}}^{(\alpha)}\right]_{\text{av}} - \frac{\beta}{2}\sum_{\alpha,\alpha'}\left(\left[H_{\text{orient}}^{(\alpha)}H_{\text{orient}}^{(\alpha')}\right]_{\text{av}} - \left[H_{\text{orient}}^{(\alpha)}\right]_{\text{av}}\left[H_{\text{orient}}^{(\alpha')}\right]_{\text{av}}\right). \tag{30}$$

In general, the couplings $u^{\lambda\lambda'}(\mathbf{x},\mathbf{y})$ averaged over quenched disorder can be different from zero and in a certain range of values of $\left[u^{\lambda\lambda'}(\mathbf{x},\mathbf{y})\right]_{\text{av}}$ the ferroelastic phase arises.[18] Because we are interested in the pure QG state we neglect the means of orientational couplings putting $\left[u^{\lambda,\lambda'}(\mathbf{x},\mathbf{y})\right]_{\text{av}} = 0$. Furthermore, due to the global cubic symmetry $\left[h_\lambda(\mathbf{x})\right]_{\text{av}} = 0$. Therefore $\left[H_{\text{orient}}^{(\alpha)}\right]_{\text{av}}$ vanishes and H_{QG} takes the form

$$H_{\text{QG}} = -\frac{\beta}{2}\sum_{\alpha,\alpha'=1}^{n}\left[H_{\text{orient}}^{(\alpha)}H_{\text{orient}}^{(\alpha')}\right]_{\text{av}}. \tag{31}$$

We assume that $u^{\lambda\lambda'}(\mathbf{x},\mathbf{y})$'s and $h_\lambda(\mathbf{x})$'s are independent random variables with the following variances:

$$\left[u^{\lambda\lambda'}(\mathbf{x},\mathbf{y})u^{\rho\rho'}(\mathbf{x}',\mathbf{y}')\right]_{\text{av}} = \frac{J^2}{N}\left(\delta_{\mathbf{x},\mathbf{x}'}\delta_{\mathbf{y},\mathbf{y}'}\delta_{\lambda\rho}\delta_{\lambda'\rho'} + \delta_{\mathbf{x},\mathbf{y}'}\delta_{\mathbf{y}\mathbf{x}'}\delta_{\lambda,\rho'}\delta_{\lambda'\rho}\right) \tag{32}$$

and

$$[h_\lambda(\mathbf{x})h_{\lambda'}(\mathbf{x}')]_{\text{av}} = \Delta^2\delta_{\mathbf{x},\mathbf{x}'}\delta_{\lambda\lambda'}. \tag{33}$$

The parameters Δ and J are constants of a coarse-grained model and are treated as adjustable parameters (cf. Ref. 18). From the physical point of view such a form of variances (32) and (33) is a result of the approximation in which one ignores the correlations between random average orientations of CN$^-$ ions and their spatial distribution. An analogous approximation has been used in the theory of the QG phase of solid hydrogen and has been discussed in Refs. 20 and 21.

With the help of Eqs. (32) and (33) we obtain H_{QG} in the form

$$\begin{aligned} H_{\text{QG}} = &-\frac{\beta J^2}{4N}\sum_{\mathbf{x}\neq\mathbf{y}}\sum_{\alpha,\alpha'=1}^{n}\hat{q}_{\alpha\alpha'}(\mathbf{x})\hat{q}_{\alpha\alpha'}(\mathbf{y}) \\ &-\frac{\beta\Delta^2}{2}\sum_{\mathbf{x}}\sum_{\alpha,\alpha'=1}^{n}\hat{q}_{\alpha\alpha'}(\mathbf{x}) + \text{const}, \end{aligned} \tag{34}$$

where

$$\hat{q}_{\alpha\alpha'}(\mathbf{x}) = (1-\delta_{\alpha\alpha'})\sum_{\lambda=1}^{5}Y_\lambda(\Omega_{\mathbf{x}}^{\alpha})Y_\lambda(\Omega_{\mathbf{x}}^{\alpha'}). \tag{35}$$

Owing to the relation

$$\sum_{\lambda=1}^{5}[Y_\lambda(\Omega_{\mathbf{x}}^{\alpha})]^2 = \frac{5}{4\pi}, \tag{36}$$

the terms diagonal in replica indices give a contribution to the inessential constant in Eq. (34).

After a Gauss transformation similar to that used in the Sherrington-Kirkpatrick method[4] one obtains Z_n [Eq. (29)] in the form

$$Z_n = \int d(q)\exp(-N\mathcal{H}[q]), \tag{37}$$

where $d(q) = \prod_{\alpha,\alpha'} dq_{\alpha\alpha'}$, with

$$\mathcal{H}[q] = \frac{1}{4\overline{T}^2}\sum_{\alpha,\alpha'=1}^{n}q^2_{\alpha\alpha'} - \ln\left\langle \exp\left[\frac{1}{2\overline{T}^2}\sum_{\alpha,\alpha'=1}^{n}(q_{\alpha\alpha'}+\overline{\Delta}^2)\hat{q}_{\alpha\alpha'}\right]\right\rangle_0 + n\,\text{const}, \tag{38}$$

where

$$\langle\cdots\rangle_0 = \frac{1}{4\pi}\int d\Omega\cdots\ . \tag{39}$$

$q_{\alpha\alpha'}$ denotes the QG order parameter field, $\hat{q}_{\alpha\alpha'}$ is $\hat{q}_{\alpha\alpha'}(\mathbf{x})$ at an arbitrary site $\mathbf{x}$, and $\overline{T}$ and $\overline{\Delta}$ are, respectively, the temperature and Δ scaled by the parameter J.

In the thermodynamic limit when $N\to\infty$ all integrations in (37) can be done by the saddle-point method. The free energy (27) per one site of the coarse-grained lattice takes the form

$$\frac{F}{N} = \beta^{-1}\lim_{n\to 0}\frac{1}{n}\mathcal{H}[q], \tag{40}$$

where $q_{\alpha\alpha'}$ satisfies the equation

$$q_{\alpha\alpha'} = \langle\hat{q}_{\alpha\alpha'}\rangle, \tag{41}$$

where

$$\langle\cdots\rangle = \frac{\operatorname{Tr}\exp\left[\frac{1}{2\overline{T}^2}\sum_{\alpha,\alpha'=1}^{n}(q_{\alpha\alpha'}+\overline{\Delta}^2)\hat{q}_{\alpha\alpha'}\right]\cdots}{\operatorname{Tr}\exp\left[\frac{1}{2\overline{T}^2}\sum_{\alpha,\alpha'=1}^{n}(q_{\alpha\alpha'}+\overline{\Delta}^2)\hat{q}_{\alpha\alpha'}\right]}. \tag{42}$$

The QG Edwards-Anderson parameter q_{EA} for our system is defined as follows[9] (cf. also Ref. 22 for the definition of q_{EA} for a QG phase of solid hydrogen):

$$q_{\text{EA}} = \sum_{\lambda}[\langle Y_\lambda(\Omega_{\mathbf{x}})\rangle_T^2]_{\text{av}}, \tag{43}$$

where $\langle\cdots\rangle_T$ denotes the thermal average. It is easy to show that q_{EA} [Eq. (43)] is equal to

$$\lim_{n\to 0}\frac{1}{n(n-1)}\sum_{\alpha,\alpha'=1}^{n}q_{\alpha\alpha'},$$

with $q_{\alpha\alpha'}$ satisfying Eq. (41).

It is seen that the effective QG Hamiltonian (34) and q_{EA} (43) have spherical symmetry. This is a direct consequence of the assumption that the variances of $u^{\lambda\lambda'}(\mathbf{x},\mathbf{y})$ and $h_\lambda(\mathbf{x})$ have the form given by Eqs (32) and (33), respectively. Obviously, more appropriate would be the cubic symmetry of H_{QG} and q_{EA}. This could be realized by demanding that $\hat{q}_{\alpha\alpha'}(\mathbf{x})$ entering H_{QG} be invariants of the cubic-point symmetry group. However, even in that case the general form of H_{QG} (34) will be unchanged. Therefore, the use of the isotropic H_{QG} and q_{EA} instead of the cubic ones seems to be not too essential a problem.

In the replica-symmetric theory we put $q_{\alpha\alpha'} = q_{\text{EA}}$ obtaining the free energy (40) in the form

$$\frac{F}{NJ} = -\frac{1}{4\overline{T}}q_{\text{EA}}^2 + \overline{T}\lim_{n\to 0}\frac{1}{n}\ln\left\langle\exp\left[\frac{1}{2\overline{T}^2}(q_{\text{EA}}+\overline{\Delta}^2)\sum_{\alpha,\alpha'=1}^{n}\hat{q}_{\alpha\alpha'}\right]\right\rangle_0 + \text{const}. \tag{44}$$

We wish first to investigate the QG transition in the absence of the fields $h_\lambda(\mathbf{x})$. Expecting that this transition is continuous we expand $F/(NJ)$ [Eq. (44)] with $\overline{\Delta} = 0$ up to third order with the respect to q_{EA}. This yields

$$\frac{F}{NJ} = \frac{1}{\overline{T}}\left(\frac{\overline{T}_g^2}{\overline{T}^2} - 1\right) q_{\mathrm{EA}}^2 - \frac{w_0}{\overline{T}^5} q_{\mathrm{EA}}^3 + \mathcal{O}(q_{\mathrm{EA}}^4), \tag{45}$$

where $\overline{T}_g = \sqrt{5}/(4\pi)$ is the QG transition temperature scaled by J and

$$w_0 = \sum_{\lambda_1,\ldots,\lambda_3} \left[\frac{1}{3}\langle Y_{\lambda_1} Y_{\lambda_2}\rangle_0 \langle Y_{\lambda_2} Y_{\lambda_3}\rangle_0 \langle Y_{\lambda_3} Y_{\lambda_1}\rangle_0 - \frac{1}{12}\langle Y_{\lambda_1} Y_{\lambda_2} Y_{\lambda_3}\rangle_0^2\right] = \frac{15}{896\pi^3} > 0. \tag{46}$$

Because $w_0 > 0$ the QG transition is continuous with the following asymptotic behavior of q_{EA} for $\overline{T} \to \overline{T}_g^-$:

$$q_{\mathrm{EA}} = \frac{4\overline{T}_g^3}{3w_0}(\overline{T}_g - \overline{T}), \tag{47}$$

which is typical of a glassy transition. In the presence of the random strain fields with a variance Δ the sharp phase transition is smeared out and $q_{\mathrm{EA}} \neq 0$ for a finite temperature.[9]

IV. ELASTIC CONSTANTS

Now we will discuss the modification of the elastic properties due to the random freezing of the quadrupoles. Proceeding similarly as in Ref. 18 we obtain the relation between elastic constants and orientation correlations in the form

$$S_{\mu\nu} = (C^0)^{-1}_{\mu\nu} + \frac{\beta}{N}\sum_{\mathbf{x},\mathbf{y}} (C^0)^{-1}_{\mu\mu'} (C^0)^{-1}_{\nu\nu'} \left[\langle \sigma_{\mu'}(\mathbf{d}(\mathbf{x}),\mathbf{x}) \sigma_{\nu'}(\mathbf{d}(\mathbf{y}),\mathbf{y})\rangle_T^c\right]_{\mathrm{av}}, \tag{48}$$

where $\langle\cdots\rangle_T^c$ denotes a cumulant thermal average. Now we expand $\sigma_\mu(\mathbf{d}(\mathbf{x}),\mathbf{x})$ into the terms of symmetry-adapted spherical harmonics (20)–(24):

$$\sigma_\mu(\mathbf{d}(\mathbf{x}),\mathbf{x}) = \sum_{\lambda=1}^{5} \sigma_\mu^\lambda(\mathbf{x}) Y_\lambda(\Omega_{\mathbf{x}}) + \cdots. \tag{49}$$

After this Eq. (48) takes the form

$$S_{\mu\nu} = (C^0)^{-1}_{\mu\nu} + \frac{\beta}{N}\sum_{\mathbf{x},\mathbf{y}} \sum_{\lambda,\lambda'=1}^{5} (C^0)^{-1}_{\mu\mu'} (C^0)_{\nu\nu'} \left[\sigma_{\mu'}^\lambda(\mathbf{x}) \sigma_{\nu'}^{\lambda'}(\mathbf{y}) \langle Y_\lambda(\Omega_{\mathbf{x}}) Y_{\lambda'}(\Omega_{\mathbf{y}})\rangle_T^c\right]_{\mathrm{av}}. \tag{50}$$

We neglect the quenched random fluctuations of $\sigma_\mu^\lambda(\mathbf{x})$'s, replacing them as follows:

$$\sigma_\mu^\lambda(\mathbf{x}) \to \left[\sigma_\mu^\lambda(\mathbf{x})\right]_{\mathrm{av}} = \sigma_\mu^\lambda. \tag{51}$$

This yields

$$S_{\mu\nu} = (C^0)^{-1}_{\mu\nu} + \frac{\beta}{N}\sum_{\mathbf{x},\mathbf{y}} \sum_{\lambda,\lambda'=1}^{5} (C^0)^{-1}_{\mu\mu'} (C^0)^{-1}_{\nu\nu'} \sigma_{\mu'}^\lambda \sigma_{\nu'}^{\lambda'} \left[\langle Y_\lambda(\Omega_{\mathbf{x}}) Y_{\lambda'}(\Omega_{\mathbf{y}})\rangle_T^c\right]_{\mathrm{av}}. \tag{52}$$

In the theory of spin glasses it is known that the replica-symmetric solution of the Sherrington-Kirkpatrick model is related to the fact that the thermal average $\langle\cdots\rangle_T$ is not the standard Boltzmann-Gibbs average, but is performed within a pure state.[23] In this case the so-called clustering property holds, which means that the spatial correlations between spins at different sites vanish in the thermodynamic limit.[4,20] A similar clustering property should be fulfilled for our long-ranged model. Therefore, for $N \to \infty$ we have

$$\left[\langle Y_\lambda(\Omega_{\mathbf{x}}) Y_{\lambda'}(\Omega_{\mathbf{y}})\rangle_T^c\right]_{\mathrm{av}} = \delta_{\mathbf{x},\mathbf{y}}\Big(\left[\langle Y_\lambda(\Omega_{\mathbf{x}}) Y_{\lambda'}(\Omega_{\mathbf{x}})\rangle_T\right]_{\mathrm{av}} - \left[\langle Y_\lambda(\Omega_{\mathbf{x}})\rangle_T \langle Y_{\lambda'}(\Omega_{\mathbf{x}})\rangle_T\right]_{\mathrm{av}}\Big). \tag{53}$$

Because our QG model averaged over the quenched disorder has a spherical symmetry we write

$$\begin{aligned}\left[Y_\lambda(\Omega_{\mathbf{x}}) Y_{\lambda'}(\Omega_{\mathbf{x}})_T\right]_{\mathrm{av}} &= \frac{1}{5}\delta_{\lambda\lambda'} \sum_{\lambda=1}^{5} \left[\langle Y_\lambda^2(\Omega_{\mathbf{x}})\rangle_T\right]_{\mathrm{av}} \\ &= \frac{1}{4\pi}\delta_{\lambda\lambda'}\end{aligned} \tag{54}$$

and

$$\left[\langle Y_\lambda(\Omega_{\mathbf{x}})\rangle_T \langle Y_{\lambda'}(\Omega_{\mathbf{x}})\rangle_T\right]_{\rm av} = \frac{q_{\rm EA}}{5}\delta_{\lambda\lambda'}. \qquad (55)$$

Finally, with the help of (53), (54), and (55) we transform Eq. (52) to the form

$$S_{\mu\nu} = (C^0)^{-1}_{\mu\nu} + \frac{\beta}{4\pi}(C^0)^{-1}_{\mu\mu'}(C^0)^{-1}_{\nu\nu'} \times \left(\sum_{\lambda=1}^{5}\sigma^\lambda_{\mu'}\sigma^\lambda_{\nu'}\right)\left(1 - \frac{4\pi}{5}q_{\rm EA}\right). \qquad (56)$$

The coefficients σ^λ_μ have cubic symmetry and can be written as (cf. Ref. 14)

$$\begin{aligned} \bar{\sigma}^1 &= A(1,1,-2,0,0,0), \\ \bar{\sigma}^2 &= \sqrt{3}A(-1,1,0,0,0,0), \\ \bar{\sigma}^3 &= B(0,0,0,0,0,1), \\ \bar{\sigma}^4 &= B(0,0,0,1,0,0), \\ \bar{\sigma}^5 &= B(0,0,0,0,1,0). \end{aligned} \qquad (57)$$

The matrix $S_{\mu\nu}$ is the inverse of the matrix of renormalized elastic constants $C_{\mu\nu}$. According to the global cubic symmetry of the system there are three independent $C_{\mu\nu}$, namely, C_{11}, C_{12}, and C_{44}. With the help of Eqs. (56) and (57) we find

$$C_{44} = \frac{C^0_{44}}{1 + \frac{B^2}{20\pi T C^0_{44}}\left(1 - \frac{4\pi}{5}q_{\rm EA}\right)}, \qquad (58)$$

$$C_{11} = \frac{1}{3}(C^0_{11} + 2C^0_{12}) + \frac{2}{3}\frac{(C^0_{11} - C^0_{12})}{1 + \frac{6A^2}{20\pi T(C^0_{11} - C^0_{12})}\left(1 - \frac{4\pi}{5}q_{\rm EA}\right)}, \qquad (59)$$

and

$$C_{12} = \frac{1}{3}(C^0_{11} + 2C^0_{12}) - \frac{1}{3}\frac{(C^0_{11} - C^0_{12})}{1 + \frac{6A^2}{20\pi T(C^0_{11} - C^0_{12})}\left(1 - \frac{4\pi}{5}q_{\rm EA}\right)}, \qquad (60)$$

where C^0_{44}, C^0_{11}, and C^0_{12} are the bare elastic constants. From Eqs. (58)–(60) it is seen that the T_{2g} orientational modes govern the softening of C_{44} on approaching the QG transition point, whereas the orientational modes of E_g symmetry are responsible for a change of C_{11} and C_{12}. Because the temperature dependence of C_{44} is much more pronounced[11–13] than that of other ones, it can be concluded that T_{2g} modes should play a dominant role in the orientational coupling. This is in an agreement with the viewpoint presented in Refs. 14 and 15.

V. DISCUSSION OF THE RESULTS

The starting point of our model is the semimicroscopic Hamiltonian given in Ref. 18. It has been shown that the homogeneous elastic constants $\bar{\epsilon}_\mu$ and displacement fields can be eliminated by a Gaussian integration over them in the partition function (8). Hence the orientational freezing of CN$^-$ ions can be considered without their explicit presence, using an effective orientational Hamiltonian (17). Similarly as in Ref. 14 we have treated a dumbbell-shaped CN$^-$ ion as a quadrupole, the components of which are related to the symmetry-adapted spherical harmonics. No limitations about the spatial orientation of CN$^-$ ions have been made. In Ref. 18 it has been assumed that due to the strong crystal field the CN$^-$ ions can only occupy a limited numbers of orientations. According to Ref. 18 three different anisotropy potentials that have been considered with absolute minima in the following directions.[18]

(A) The three fourfold axes which are parallel to the cubic axes.

(B) The four threefold axes which are parallel to the body diagonals of the cube.

(C) The six twofold axes parallel to the face diagonal of the cube.

A difference between the consequences of our approach and that proposed in Ref. 18 is most apparent in the calculation of the renormalized elastic constant for a glassy state. It has been shown in Ref. 18 that the random freezing of quadrupoles affects C_{12} for the symmetry (B), C_{11} and C_{44} for the symmetry (A), and C_{11}, C_{12}, and C_{44} for the symmetry (C). In our model the three elastic constants are affected in any case. However, only the softening of C_{44} is more important because it is much more pronounced than changes of C_{11} and C_{12}. Obviously, the model presented in Ref. 18 has a wider scope of application, because it takes into account the glassy phase as well as the ferroelastic phase with long-range orientational order, while in the present paper we are interested only in the QG phase. Nevertheless we hope that some modifications of our approach can be made in order to also describe the ferroelastic transition. Currently calculations of the temperature dependence of the Edwards-Anderson QG parameter $q_{\rm EA}$ and C_{44} without and in the presence of the local strain fields are in progress.

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