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Calculation of the order parameter of solid hydrogen in the quadrupolar-glass phase

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The calculation of the temperature and concentration dependence of the quadrupolar-glass (QG) order parameter of solid hydrogen is presented. Starting from the microscopic Hamiltonian describing the electric quadrupole-quadrupole interaction, the effective Hamiltonian containing only commuting operators related to the components of the tensor of molecular quadrupolar momentum has been obtained. By means of this Hamiltonian the equation for the average QG order parameter has been formulated within the replica theory. The calculated temperature and concentration dependence of the order parameter is compared with the experimental data obtained by Meyer and Washburn.

I. INTRODUCTION

In the past 15 years there has been considerable experimental[1–10] and theoretical[11–22] work, including Monte Carlo simulations,[23,24] on the orientational ordering of randomly distributed quadrupole-bearing molecules of orthohydrogen (o-H_2) in a matrix of spherical parahydrogen species (p-H_2), for concentrations X of o-H_2 molecules smaller than 0.55. The NMR line-shape measurements,[1,4,8,10] as well as the damping of spin echoes and the nuclear spin-lattice relaxation[2,3,5,7] show that, for such concentrations, no long-range order exists, and it is now believed that solid ortho-para hydrogen mixtures for $X < 0.55$ form a quadrupolar glass (QG), in which the local average orientation of the o-H_2 molecules vary randomly from site to site without any long-range spatial correlation. The suggestion of the possibility of the existence of a QG was given by Sullivan *et al.*[1] and was a great stimulus to further investigation, both experimental and theoretical, into the orientational nature of such systems (see, e.g., the review by Binder and Reger[25]). The qualitative description of a QG is similar to that of the short-ranged spin glass such as $Eu_xSr_{1-x}S$.[1,12] In both systems frustration and disorder are ingredients leading to formation of a glassy state. However, the mechanism for formation of a QG is more subtle and more complex. In spin glasses the frustration is a result of competing ferromagnetic and antiferromagnetic interactions, which are randomly distributed in a mixed system. In a crystal of solid hydrogen the frustration exists even in pure orthohydrogen. This is connected with the topological incompatibility between the configuration of lowest energy of an isolated pair of quadrupolar molecules (a mutually perpendicular arrangement called a "tee" configuration) and the crystal-lattice structure (one cannot arrange all molecules with a "tee" configuration for nearest neighbors on any three-dimensional lattice except for the simple cubic one). At a high concentration of the o-H_2 component, below a certain temperature T_c the system exists in an orientationally ordered phase (the crystal lattice is fcc and space group $Pa3$) and the interaction energy of the nearest neighbors is only 0.53 that of the "tee" configuration. A further dilution, when o-H_2 molecules are replaced by spherically symmetric p-H_2 species leads to a rearrangement of the enviroments of o-H_2 molecules, which below the critical concentration $X_c \approx 0.55$ becomes so substantial that long-range order is lost and only the local ordering characteristic of a glassy state is preserved (see the excellent discusion by Sullivan *et al.*[15]). The structure of the crystal lattice remains hcp to the lowest temperatures (see, e.g., Ref. 12). An important feature of solid hydrogen with a reduced concentration of the o-H_2 component ($X < 0.55$) is the lack of a sharp phase transition from the orientationally disordered to the QG state as the temperature is lowered. Numerous experiments (see, e.g., Refs. 4, 7, 8, and 10) show that the QG order parameter has a nonzero value at any temperature and does not exhibit the singularity characteristic of a phase transition. This indicates a gradual freezing of the rotational degree of freedom of o-H_2 molecules. The qualitative theoretical analysis by Harris and Meyer[12] shows that in the hydrogen crystal in the QG state, random local electric-field gradients coupled to the local order parameter exist, which means that a phase transition is excluded. A recent renormalization-group (RG) study[22] leads to a similar conclusion about the absence of a sharp phase transition. In Ref. 22 the free-energy functional in the Landau-Ginzburg-Wilson form was obtained from the microscopic Hamiltonian of the system, and it was shown that the considered model has no stable fixed points. The lack of a stable fixed point indicates a discontinuous phase transition in ideal systems, but in random ones it can lead to a suppression of any sharp phase transition.[26]

The present paper contains calculation of the temperature and concentration dependence of the QG order parameter, starting with the microscopic electric quadrupole-quadrupole (EQQ) interaction between o-H_2 molecules in the crystal. A treatment with the full EQQ Hamiltonian containing five noncommuting operators related to the components of the quadrupolar momentum tensor of each o-H_2 molecule is a complex task and leads

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to a tremendous numerical problem. Therefore we will replace the exact EQQ Hamiltonian by an effective one which only enters the commuting operators. The contribution due to the discarded part of the full EQQ Hamiltonian can be taken into account to some extent by an appropriate renormalization of the coupling constants in the effective Hamiltonian.

The paper is organized as follows. In Sec. II the effective Hamiltonian is derived, starting with the full EQQ Hamiltonian. In Sec. III the equation for the QG order parameter is obtained within replica theory. It is shown there that the assumption about a Gaussian distribution of the EQQ couplings is admissible. This permits one to perform the averaging over disorder in a much simpler manner than with the assumption about isotropically distributed average local orientations of o-H_2 molecules. An analysis of the low-temperature asymptotic behavior of the QG order parameter is performed in Sec. IV. Finally, in Sec. V the temperature and concentration dependence of the QG order parameter is presented and the agreement of our results with the data obtained from NMR experiments is discussed.

II. EFFECTIVE HAMILTONIAN

As Nakamura has shown many years ago,[27] the EQQ interactions are the most important orientational interactions between molecules in solid hydrogen. In the solid state, only the rotational states with the lowest J are populated, and one considers the spherical symmetric p-H_2 species with $J = 0$ and quadrupolar o-H_2 molecules with $J = 1$. Therefore, the components of the molecular quadrupolar momentum tensor can be replaced by their operator equivalents in the manifold $J = 1$.[28] It is convenient to specify the orientations of the o-H_2 molecule at a given site to the local coordinate system chosen so as to coincide with the principal axes of the molecular quadrupolar momentum tensor.[1,8,28] Thus, the Hamiltonian of our system can be written in the form (see, Ref. 22),

$$H = \frac{1}{2}\sum_{i\neq j} \hat{x}_i \hat{x}_j H_{ij} \ , \tag{1}$$

where $\hat{x}_i = 0$ and 1 for p-H_2 and o-H_2, respectively, and the summation in Eq. (1) runs over sites of the hcp lattice,

$$H_{ij} = \sum_{\mu,\nu=-2}^{2} \gamma_{ij}^{\mu\nu} \mathcal{O}_i^{\mu} \mathcal{O}_j^{\nu}, \tag{2}$$

with

$$\mathcal{O}_i^0 = 3(J_i^z)^2 - 2 \ , \tag{3a}$$

$$\mathcal{O}_i^{\pm 1} = J_i^{\pm} J_i^z + J_i^z J_i^{\pm} \ , \tag{3b}$$

$$\mathcal{O}_i^{\pm 2} = (J_i^{\pm})^2 \ , \tag{3c}$$

$$J_i^{\pm} = J_i^x \pm i J_i^y \ , \tag{3d}$$

and the operators J_i^x, J_i^y, and J_i^z denote the components in the local coordinate system of the angular momentum operator $\mathbf{J}_i$ related to the molecule located at the ith site. The couplings $\gamma_{ij}^{\mu\nu}$ which enter Eq. (2) have the form[22,29] (cf. also Ref. 28)

$$\gamma_{ij}^{\mu\nu} = \frac{25}{9}(70\pi)^{1/2}\Gamma\left(\frac{R}{|\mathbf{R}_{ij}|}\right)^5 A_\mu A_\nu \sum_{M,N} C(224|MN) \times Y_{4,M+N}^{*}(\mathbf{\Omega}_{ij}) D_{M\mu}^{2*}(\hat{\chi}_i) D_{N\nu}^{2*}(\hat{\chi}_j) \ , \tag{4}$$

where

$$A_0 = -\frac{1}{5} \ , \tag{5a}$$

$$A_{\pm 1} = \mp\left(\frac{3}{50}\right)^{1/2} \ , \tag{5b}$$

$$A_{\pm 2} = -\left(\frac{3}{50}\right)^{1/2} \ , \tag{5c}$$

$C(224|MN)$ denotes a Clebsh-Gordan coefficient, $Y_{4,M+N}$ is a spherical harmonic, $\mathbf{\Omega}_{ij} = (\theta_{ij}, \varphi_{ij})$ specify the orientation of the intermolecular separation vector $\mathbf{R}_{ij}$, $D_{M\mu}^2$ is a rotation matrix, and $\hat{\chi}_i$ denotes the triad of Euler angles $\alpha_i, \beta_i, \gamma_i$ describing the orientation of the local coordinate system of the ith molecule to the coordinate system fixed in the crystal. In Eq. (4)

$$\Gamma = \frac{6e^2Q^2}{25R^5} \tag{6}$$

is the EQQ coupling constant for a rigid lattice, where eQ is the molecular quadrupolar momentum and R denotes the intermolecular separation between nearest neighbors.

However, in the calculation of Γ the dielectric screening and static and dynamic renormalization due to phonon interactions should be taken into account.[30,31] Therefore, we will assume $\Gamma = 0.82$ K.[30,31] It is convenient to introduce instead of the operators $\mathcal{O}_i^{\mu}$ (3) the operators S_i^{μ} defined as

$$S_i^{+2} = \frac{1}{\sqrt{2}}\left(\mathcal{O}_i^{+2} + \mathcal{O}_i^{-2}\right) \ , \tag{7a}$$

$$S_i^{+1} = \frac{1}{\sqrt{2}}\left(\mathcal{O}_i^{+1} + \mathcal{O}_i^{-2}\right) \ , \tag{7b}$$

$$S_i^{0} = \mathcal{O}_i^{0} \ , \tag{7c}$$

$$S_i^{-1} = \frac{-i}{\sqrt{2}}\left(\mathcal{O}_i^{+1} - \mathcal{O}_i^{-1}\right) \ , \tag{7d}$$

$$S_i^{-2} = \frac{-i}{\sqrt{2}}\left(\mathcal{O}_i^{+2} - \mathcal{O}_i^{-2}\right) \ , \tag{7e}$$

Note that the operators S_i^μ (7) differs from those used in Ref. 16. The Hamiltonian (1) rewritten in terms of S_i^μ takes the form

$$H = -\frac{1}{2}\sum_{i\neq j}\sum_{\mu\nu=-2}^{+2} J_{ij}^{\mu\nu}\hat{x}_i S_i^\mu \hat{x}_j S_j^\nu \ , \tag{8}$$

where the 25 couplings $J_{ij}^{\mu\nu}$ are simple linear combinations of $\gamma_{ij}^{\mu,\nu}$'s (4). We will not write them in an explicit form and only note that the matrices $\parallel J_{ij}^{\mu\nu} \parallel$ and $\parallel \gamma_{ij}^{\mu\nu} \parallel$ are related by the unitary transformation. In addition the $J_{ij}^{\mu\nu}$'s are real and $J_{ij}^{\mu\nu} = J_{ji}^{\nu\mu}$.

In the local coordinate system only two intrinsic quadrupolar parameters remain (cf. Ref. 7), i.e.,

$$\sigma_i = \langle Q_{0,i}\rangle_T \ , \tag{9a}$$

$$\eta_i = \langle Q_{2,i}\rangle_T \ , \tag{9b}$$

where

$$Q_{0,i} = 1 - \frac{3}{2}(J_i^z)^2 = -\frac{1}{2}S_i^0 \ , \tag{10a}$$

$$Q_{2,i} = \frac{\sqrt{3}}{2}[(J_i^x)^2 - (J_i^x)] = \frac{1}{2}\sqrt{\frac{3}{2}}S_i^{+2} \ , \tag{10b}$$

and $\langle\cdots\rangle_T$ denotes a thermal average. Obviously, the operators $Q_{0,i}$ and $Q_{2,i}$ commute and satisfy the condition

$$Q_{0,i}^2 + Q_{2,i}^2 = 1 \ . \tag{11}$$

The local quadrupolar parameters σ_i (9a) and η_i (9b) measure, respectively, the alignment of the orthomolecule along the local z_i axis and its eccentricity.[7]

The problem now is to calculate the effective Hamiltonian containing only the commuting operators $Q_{0,i}$ (10a) and $Q_{2,i}$ (10b). Following Ref. 16 we decompose the Hamiltonian H (8) into two parts: the diagonal part H_0 and the nondiagonal (in the eigenstates of H_0) H_1, defined as

$$H_0 = -\frac{1}{2}\sum_{i\neq j}\sum_{\mu\nu=0,2} J_{ij}^{\mu\nu}\hat{x}_i S_i^\mu \hat{x}_j S_j^\nu \tag{12}$$

and

$$H_1 = H - H_0 \ . \tag{13}$$

The partition function $Z = \exp[-\beta(H_0 + H_1)]$ can be written as the following series (cf. Ref. 32)

$$\begin{aligned} Z &= 1 + \sum_{k=1}^{\infty}(-1)^k \int_0^\beta d\tau_1 \int_0^{\tau_1} d\tau_2 \cdots \int_0^{\tau_{k-1}} d\tau_k \mathrm{Tr}\, e^{-\beta H_0} H_1(\tau_1)H_1(\tau_2)\cdots H_1(\tau_k) \\ &= 1 + \sum_{k=1}^{\infty}(-1)^k \int_0^\beta d\tau_1 \cdots \int_0^{\tau_{k-1}} d\tau_k \sum_{m,m_1,\cdots,m_k} e^{-\beta E_m^0}\langle m|H_1|m_1\rangle\cdots\langle m_{k-1}|H_1|m\rangle e^{\tau_1\left(E_m^0 - E_{m_1}^0\right)}\ldots e^{\tau_k\left(E_{m_{k-1}}^0 - E_m^0\right)} \ , \end{aligned} \tag{14}$$

where E_l^0 and $|l\rangle$ denote, respectively, the eigenenergies and normalized eigenstates of H_0 (12).

We expect that the secular terms in the series (14) are of primary importance. Therefore, taking into account the matrix elements $\langle l|H_1|r\rangle$ with $E_l^0 = E_r^0$ one can perform the integrations over τ parameters, obtaining the following result,

$$Z \approx \sum_m e^{-\beta E_m^0}\langle m|e^{-\beta H_1}|m\rangle \ . \tag{15}$$

Now we write the quantum-mechanical average of $\exp(-\beta H_1)$ with the help of the cumulant expansion

$$\begin{aligned} \langle m|\exp(-\beta H_1)|m\rangle = \exp\Big[&-\beta\langle m|H_1|m\rangle \\ &+\frac{\beta^2}{2}\left(\langle m|H_1^2|m\rangle\right. \\ &\left.-\langle m|H_1|m\rangle^2\right)+\cdots\Big] \ . \end{aligned} \tag{16}$$

Taking into account that $\langle m|H_1|m\rangle = 0$, with the help of Eq. (14) we get the partition function in the form

$$Z \approx \mathrm{Tr}\exp(-\beta H_{\text{eff}}) \ . \tag{17}$$

If we restrict ourselves to the second cumulant, the H_{eff} reads

$$H_{\text{eff}} = H_0 - \frac{\beta}{2}\left(H_1^2\right)_{\text{diag}} \ , \tag{18}$$

where $(\cdots)_{\text{diag}}$ denotes the diagonal part (in the eigenstates of H_0).

Taking into account the properties of the angular momentum operators in the manifold $J = 1$ we obtain the following relation, which is helpful to calculate $\left(H_1^2\right)_{\text{diag}}$:

$$\left(S_i^\mu S_i^{\mu'}\right)_{\text{diag}} = \delta_{\mu\mu'}\left(a_\mu + b_\mu Q_{0,i} + c_\mu Q_{2,i}\right) + d_{\mu\mu'}Q_{2,i} \ , \tag{19}$$

where

$$\begin{aligned} &\frac{3}{2}a_{\pm 1} = \frac{3}{2}a_{\pm 2} = a_0 = 2, \\ &-\frac{3}{2}b_{\pm 2} = 3b_{\pm 1} = b_0 = 2, \\ &c_0 = c_{\pm 2} = 0,\ c_{\pm 1} = \mp\frac{2}{\sqrt{3}}, \end{aligned} \tag{20}$$

and

$$d_{\mu\mu'} = 2\sqrt{\frac{2}{3}}(\delta_{\mu 0}\delta_{\mu' 2} + \delta_{\mu 2}\delta_{\mu' 0}) \ . \tag{21}$$

We expect that the main contribution to $(H_1^2)_{\text{diag}}$ comes from the two-body terms. Discarding the three-body terms one obtains

$$(H_1^2)_{\text{diag}} = -\frac{1}{2}\sum_{i\neq j} \hat{x}_i\hat{x}_j(H_1^2(i,j))_{\text{diag}} \ , \tag{22}$$

where

$$H_1(i,j) = -\sum_{\mu\nu=-2}^{+2} J_{ij}^{\mu\nu} S_i^{\mu} S_j^{\nu} + \sum_{\mu\nu=0,+2} J_{ij}^{\mu\nu} S_i^{\mu} S_j^{\nu} \ . \tag{23}$$

With the help of Eqs. (19), (22), and (23), we have

$$\begin{aligned} H_{\text{eff}} = -\frac{1}{2}\sum_{i\neq j}\sum_{\mu\nu=0,2} \tilde{J}_{ij}^{\mu\nu}\hat{x}_i Q_{\mu,i}\hat{x}_j Q_{\nu,j} \\ -\sum_i \sum_{\mu=0,2} \hat{x}_i V_i^{\mu} Q_{\mu,i} \ , \end{aligned} \tag{24}$$

where

$$\tilde{J}_{ij}^{\mu\nu} = J_{ij}^{\mu\nu} + \Delta J_{ij}^{\mu\nu}, \tag{25}$$

with

$$\Delta J_{ij}^{00} = \frac{\beta}{2}\left[\sum_{\mu\nu=-2}^{+2}(J_{ij}^{\mu\nu})^2 b_\mu b_\nu - \sum_{\mu\nu=0,2}(J_{ij}^{\mu\nu})^2 b_\mu b_\nu\right] , \tag{26a}$$

$$\Delta J_{ij}^{22} = \frac{\beta}{2}\left[\sum_{\mu\nu=-2}^{+2}(J_{ij}^{\mu\nu})^2 c_\mu c_\nu + 8\sqrt{\frac{2}{3}}\sum_{\mu=\pm 1,-2} J_{ij}^{0\mu} J_{ij}^{2\mu} c_\mu\right] , \tag{26b}$$

$$\Delta J_{ij}^{02} = \frac{\beta}{2}\left[\sum_{\mu\nu=-2}^{+2}(J_{ij}^{\mu\nu})^2 b_\mu b_\nu + 4\sqrt{\frac{2}{3}}\sum_{\mu=\pm 1,-2} J_{ij}^{\mu 0} J_{ij}^{\mu 2} b_\mu\right] , \tag{26c}$$

$$V_i^0 = \frac{\beta}{2}\sum_j \hat{x}_j\left[\sum_{\mu\nu=-2}^{+2}(J_{ij}^{\mu\nu})^2 b_\mu a_\nu - \sum_{\mu\nu=0,2}(J_{ij}^{\mu\nu})^2 b_\mu a_\nu\right] , \tag{26d}$$

$$\begin{aligned} V_i^2 = \frac{\beta}{2}\sum_j \hat{x}_j\Bigg[\sum_{\mu\nu=-2}^{+2}(J_{ij}^{\mu\nu})^2 c_\mu a_\nu \\ +4\sqrt{\frac{2}{3}}\sum_{\mu=\pm,-2} J_{ij}^{0\mu} J_{ij}^{2\mu} a_\mu\Bigg], \end{aligned} \tag{26e}$$

and

$$\Delta J_{ij}^{20} = \Delta J_{ji}^{02} \ .$$

In Ref. 16 an effective Hamiltonian similar to ours [Eq. (23)] has been introduced, but the contribution related to $d_{\mu\mu'}$ has not been taken into account.

III. QG ORDER PARAMETER

The orientational free energy of our system is

$$F = -k_B T[\ln Z]_{\text{av}} \ , \tag{27}$$

where $k_B T = \beta^{-1}$ and $[\cdots]_{\text{av}}$ denotes an averaging over disorder. The partition function Z in Eq. (27) will be used in the approximated form (17) with H_{eff} (24). One of the standard methods to calculate the free energy of disordered system is the replica approach (see, e.g., Ref. 33). Applying it, one obtains

$$F = -k_B T \lim_{n\to 0}\frac{1}{n}\ln Z_n \tag{28}$$

with

$$Z_n = \left[\operatorname{Tr}\exp\Big(-\beta\sum_{\alpha=1}^{n} H_{\text{eff}}^{(\alpha)}\Big)\right]_{\text{av}} , \tag{29}$$

where $H_{\text{eff}}^{(\alpha)}$ is the αth replica of the effective Hamiltonian (24).

The problem now is to perform an averaging over disorder in Eq. (29). The disorder is introduced to H_{eff} (24) by the numbers $\hat{x}_i$ and the couplings $\tilde{J}_{ij}^{\mu\nu}$ via the triads of the Euler angles $\hat{\chi}_i$ and $\hat{\chi}_j$ which characterize the random orientations of the local coordinate systems. Since in Ref. 22 it was assumed that orientations of the local axes are isotropically distributed over all solid angles independently of the configurations of the o-H$_2$ molecules,[4,15,16,18,22] the operation $[\cdots]_{\text{av}}$ was decomposed there into a sequence of two stages: first one averages over directions of the local coordinate system (the orientational averaging) and then over configurations of o-H$_2$ species. In fact, $\hat{\chi}_i$ is correlated with the distribution of o-H$_2$ molecules, so that the EQQ coupling $\gamma_{ij}^{\mu\nu}$ (4) (and consequently $J_{ij}^{\mu\nu}$) depends on the set $(\hat{x}_1, \ldots, \hat{x}_k, \ldots)$ with $\hat{x}_i = \hat{x}_j = 1$ which characterize the configuration of o-H$_2$ species. If we assume that each of such random configurations gives an equal (with accuracy to the ± sign) contribution to the value of the EQQ coupling $\gamma_{ij}^{\mu\nu}$ $(J_{ij}^{\mu\nu})$ we obtain a Gaussian distribution for these variables. In theories of spin and quadrupolar glasses the Gaussian distribution of random couplings is widely exploited;[33,25] therefore the above idea seems to be acceptable. An additional advantage of the Gaussian distribution in our problem is that all moments of the EQQ couplings can be calculated in a simple way, whereas the orientational averaging gives complicated formulas for moments higher than the second. Guided by the result of the orientational averaging (cf. Ref. 22) we write

$$\overline{\gamma_{ij}^{\mu\nu}} = 0 \, , \tag{30}$$

and

$$\begin{aligned}\overline{\gamma_{ij}^{\mu\nu}\gamma_{i'j'}^{\mu'\nu'}} = \big(&\delta_{ii'}\delta_{jj'}\delta_{\mu,-\mu'}\delta_{\nu,-\nu'} \\ &+\delta_{ij'}\delta_{i'j}\delta_{\mu,-\nu'}\delta_{\mu',-\nu}\big)A_\mu^2 A_\nu^2 J_{ij}^2 \, ,\end{aligned} \tag{31}$$

where

$$J_{ij} = J\left(\frac{R}{|\mathbf{R}_{ij}|}\right)^5 \tag{32}$$

and $\overline{\cdots}$ denotes the Gaussian averaging with the fixed numbers $\hat{x}_i$ and $\hat{x}_j$. Taking into account that the matrices $\| J_{ij}^{\mu\nu} \|$ and $\| \gamma_{ij}^{\mu\nu} \|$ are related to each other by unitary transformation with the help of Eqs. (30) and (31) one obtains

$$\overline{J_{ij}^{\mu\nu}} = 0 \tag{33}$$

and

$$\overline{J_{ij}^{\mu\nu}J_{i'j'}^{\mu'\mu'}} = \big(\delta_{ii'}\delta_{jj'}\delta_{\mu\mu'}\delta_{\nu\nu'} + \delta_{ij'}\delta_{i'j}\delta_{\mu\nu'}\delta_{\mu'\nu}\big)A_\mu^2 A_\nu^2 J_{ij}^2 \, . \tag{34}$$

The parameter J entering Eq. (32) is related to the variance of the introduced Gaussian distribution and does not necessarily have to be the same as that calculated with the orientational averaging.[22] Unfortunately, we have no possibility to calculate it from first principles in the case of the Gaussian averaging. Therefore we will use here its value calculated in Ref. 22. Thus, taking into account the result of Ref. 22, we have

$$J = \frac{5}{8}\sqrt{\frac{35}{3}}\Gamma \, . \tag{35}$$

With the help of the procedure discussed above one obtains Z_n (29) in the form

$$Z_n = \left[\exp\left\{\frac{\beta^2}{2}\sum_{\alpha\alpha'=1}^{n}\overline{H_{\text{eff}}^{(\alpha)}H_{\text{eff}}^{\alpha'}}\right\}\right]_{\hat{x}} \, , \tag{36}$$

where $[\cdots]_{\hat{x}}$ denotes an averaging over $\hat{x}_i$ numbers. In Eq. (36) the higher moments of $H_{\text{eff}}^{(\alpha)}$ than second have been neglected (cf. the discussion in Ref. 22) and it has been taken into account that $\overline{H_{\text{eff}}^{(\alpha)}} = 0$.

According to the requirement that the $\overline{\cdots}$ averaging of a product of couplings $J_{ij}^{\mu\nu}$ for given sites i, j is performed at the fixed numbers $\hat{x}_i$ and $\hat{x}_j$, a dependence on $\hat{x}_i$'s in the exponent on the right-hand side of Eq. (36) is preserved, and hence the presence of the operation $[\cdots]_{\hat{x}}$ in (36). To calculate Z_n (36) we use the following relations

$$\overline{V_i^\mu V_{i'}^\nu} = \delta_{ii'}\delta_{\mu\nu}D^2, \tag{37}$$

with

$$D^2 = \beta^2\frac{108}{(625)^2}\sum_j J_{ij}^4\hat{x}_j \tag{38}$$

and

$$\overline{\tilde{J}_{ij}^{\mu\nu}\tilde{J}_{ij}^{\mu'\nu'}} = \delta_{\mu\mu'}\delta_{\nu\nu'}\frac{16}{625}J_{ij}^2\left[1+\beta^2 J_{ij}^2\frac{33}{5000}\right] . \tag{39}$$

Finally, Z_n has the form

$$Z_n = [\operatorname{Tr}\exp(-\beta\mathcal{H})]_{\hat{x}}, \tag{40}$$

with

$$\begin{aligned}\mathcal{H} = &-\frac{\beta}{4}\sum_{\alpha\alpha'=1}^{n}\sum_{i\neq j}\tilde{J}_{ij}^2\hat{x}_i\hat{q}_i^{\alpha\alpha'}\hat{x}_j\hat{q}_j^{\alpha\alpha'} \\ &-\frac{\beta}{2}D^2\sum_{\alpha\alpha'=1}^{n}\sum_i\hat{x}_i\hat{q}_i^{\alpha\alpha'} \, ,\end{aligned} \tag{41}$$

where

$$\hat{q}_i^{\alpha\alpha'} = \left(1-\delta_{\alpha\alpha'}\right)\sum_{\mu=0,2}Q_{\alpha i}^\mu Q_{\alpha' i}^\mu \, . \tag{42}$$

Here $Q_{\alpha i}^\mu$ is the αth replica of the operator Q_i^μ [cf. Eqs. (10)].

In Ref. 16 equations similar to (37)–(39) have been obtained, however the term corresponding to $\overline{\left(V_i^2\right)}^2$ has not been taken into account. This is essential because in such a case the terms diagonal in replica indices contain the fields coupled to the molecular quadrupolar momenta, which in turn lead to the nonvanishing global quadrupolar momentum of the system. Such a situation cannot appear for the pure QG state. In the present work this disadvantage is avoided since the contribution due to the terms diagonal in replica indices is some inessential constant.

It can be shown that

$$q = \lim_{n\to 0}\frac{1}{n(n-1)}\sum_{\alpha\alpha'}[\langle\hat{q}_i^{\alpha\alpha'}\rangle_{\mathcal{H}}]_{\hat{x}} \, , \tag{43}$$

where

$$\langle\cdots\rangle_{\mathcal{H}} = \operatorname{Tr}\exp(-\beta\mathcal{H}) \, . \tag{44}$$

In Eq. (13), q is equal to the average QG order parameter defined as[7,8,18]

$$q = \left[\sigma_i^2 + \eta_i^2\right]_{\text{av}} \, .$$

We will calculate q within the mean-field method. Such an approach gives exact results in the thermodynamic limit for systems with long-ranged interaction (see, e.g., Ref. 33). This is not the situation for solid hydrogen, where the EQQ interaction is not long ranged (see e.g., Refs. 1 and 12) and effects of correlations should play an important role. However, taking into account the complexity of the problem, we treat the mean-field method as a first step in the calculation of q. Furthermore, the replica symmetric theory will be used. At present the replica symmetry-breaking scheme for quadrupolar glasses is rather an obscure problem.[34]

After a Sherrington-Kirkpatrick type of procedure (cf. Ref. 33) we obtain the free energy (27) with Z_n (40) in the form

$$F = \left[F\{\hat{x}_i\}\right]_{\hat{x}} , \tag{45}$$

where

$$\begin{aligned} F\{\hat{x}_i\} = & -\frac{\beta}{4}\sum_{i\neq j}\tilde{J}^2\hat{x}_i q_i\hat{x}_j q_j + \frac{\beta}{2}\sum_i f_i^2\hat{x}_i \\ & -k_BT\sum_i\frac{1}{2\pi}\int_{-\infty}^{\infty}dxdye^{-\frac{1}{2}(x^2+y^2)} \\ & \times\ln\left[e^{\frac{3}{2}\beta f_i\hat{x}_i x}+2\cosh\left(\frac{\beta\sqrt{3}}{2}f_i\hat{x}_i y\right)\right] \end{aligned} \tag{46}$$

denotes the free energy at the fixed values of the $\hat{x}_i$ numbers. The field f_i which enters Eq. (46) is defined as

$$f_i^2 = \sum_i \tilde{J}_{ij}^2\hat{x}_j q_j + D^2 . \tag{47}$$

The parameter q_i which refers to the fixed distribution of o-H_2 species in the neighborhood of ith site occupied by the o-H_2 molecule is calculated from the extremum condition of $F\{\hat{x}_i\}$ (46)

$$\frac{\partial F\{\hat{x}_j\}}{\partial q_i} = 0, \tag{48}$$

with $\hat{x}_i = 1$. The QG parameter q is obtained as

$$q = [q_i]_{\hat{x}} . \tag{49}$$

We will take into account only the EQQ interaction for nearest neighbors. Finally, from the condition (48) one obtains the following equation

$$\begin{aligned} q(p) = 1 - \frac{3}{2\pi}\int_{-\infty}^{\infty} & dxdye^{-\frac{1}{2}(x^2+y^2)} \\ & \times\frac{1+2e^{ap^{1/2}x}\cosh\left(\frac{a}{\sqrt{3}}p^{1/2}y\right)}{\left[e^{ap^{1/2}x}+2\cosh\left(\frac{a}{\sqrt{3}}p^{1/2}y\right)\right]^2} , \end{aligned} \tag{50}$$

where

$$a = \frac{6}{25}\beta J\left[q(p) + \frac{(\beta J)^2}{5000}[33q(p)+54]\right]^{1/2} \tag{51}$$

and $q(p)$ denote the order parameter assigned to a given site in whose neighborhood there are p molecules of the orthohydrogen. For the hcp lattice the coordination number $z = 12$; therefore $0 \leq p \leq 12$. If we assume that the probabilities to find at a given site an o-H_2 and a p-H_2 molecule are X and $(1 - X)$, respectively, where X is the concentration of the orthohydrogen, the averaged QG parameter q can be calculated as follows

$$q = \sum_{p=1}^{z}\frac{z!}{p!(z-p)!}(1-X)^{z-p}X^p q(p), \tag{52}$$

with $z = 12$. Note that $q(0) = 0$ as it is seen from Eq. (50).

In Ref. 16 a similar equation to (50) has been obtained; however only the contribution due to unrenormalized couplings $J_{ij}^{\mu\nu}$ has been taken into account.

IV. LOW-TEMPERATURE ASYMPTOTIC BEHAVIOR

Now we wish to calculate the low-temperature asymptote of the QG order parameter. The form of Eq. (50) for $T/J \ll 1$ can be conveniently obtained after changing the integration range in (50) for both variables x and y from $(-\infty,\infty)$ to $(0,\infty)$. After this it is easy to see that the most essential contribution in the low-temperature limit to the integrand in (50) is

$$\theta(\alpha_1-\alpha_2)e^{-(\alpha_1-\alpha_2)} + \theta(\alpha_2-\alpha_1)e^{(\alpha_1-\alpha_2)} , \tag{53}$$

where

$$\alpha_1 = ap^{1/2}x , \tag{54a}$$

$$\alpha_2 = \frac{a}{\sqrt{3}}p^{1/2}y . \tag{54b}$$

Here $\theta(x)$ is the step function, equal to zero and one for $x < 0$ and $x > 0$, respectively. After the substitution of (53) together with Eqs. (54) into Eq. (50) and integration over one of the variables, one obtains

$$q(p) = 1 - \frac{6}{\sqrt{\pi}}\left\{\sqrt{\frac{3}{2}}e^{\frac{a^2}{2}}\int_0^{\infty}dxe^{-\frac{3}{2}x^2+ax}\left[1-\operatorname{erf}\left(\frac{x+a}{\sqrt{2}}\right)\right] + \sqrt{\frac{1}{6}}e^{\frac{a^2}{6}}\int_0^{\infty}dxe^{-\frac{x^2}{6}+\frac{a}{\sqrt{3}}x}\left[1-\operatorname{erf}\left(\frac{\sqrt{3}x+a}{\sqrt{6}}\right)\right]\right\} , \tag{55}$$

where $\operatorname{erf}(x)$ is the error function. In the low-temperature limit the parameter a (51) becomes large. Therefore in Eq. (55) we substitute the asymptotic form of the error function for a large argument (cf. Ref. 35). A straightforward calculation leads to the following result

$$q(p) = 1 - 28.736p^{1/2}\left(\frac{T}{\Gamma}\right)^2 + \mathcal{O}\left[\left(\frac{T}{\Gamma}\right)^4\right] . \tag{56}$$

Obviously, the concentration-dependent QG parameter q is calculated with the use of Eq. (52). It can be shown that the temperature-dependent term in Eq. (56) comes from the parts $\Delta J_{ij}^{\mu\nu}$ of the effective couplings $\tilde{J}_{ij}^{\mu\nu}$ [cf. (25), (26a), and (26b)], which take into account the influence of the nondiagonal terms of the EQQ Hamiltonian responsible for the quantum effects. This is in agreement with the opinion that at low temperatures the quantum nature of systems is demonstrated.

V. COMPARISON WITH EXPERIMENT AND CONCLUSIONS

Several groups[1-10] have studied experimentally the orientational ordering in the solid ortho-para hydrogen mixture. The QG order parameter q_{expt} can be observed directly by the NMR technique. For a powdered sample q_{expt} is given by the relation[8]

$$q_{\text{expt}} = \frac{5M_2^{\text{intra}}}{9d^2}, \tag{57}$$

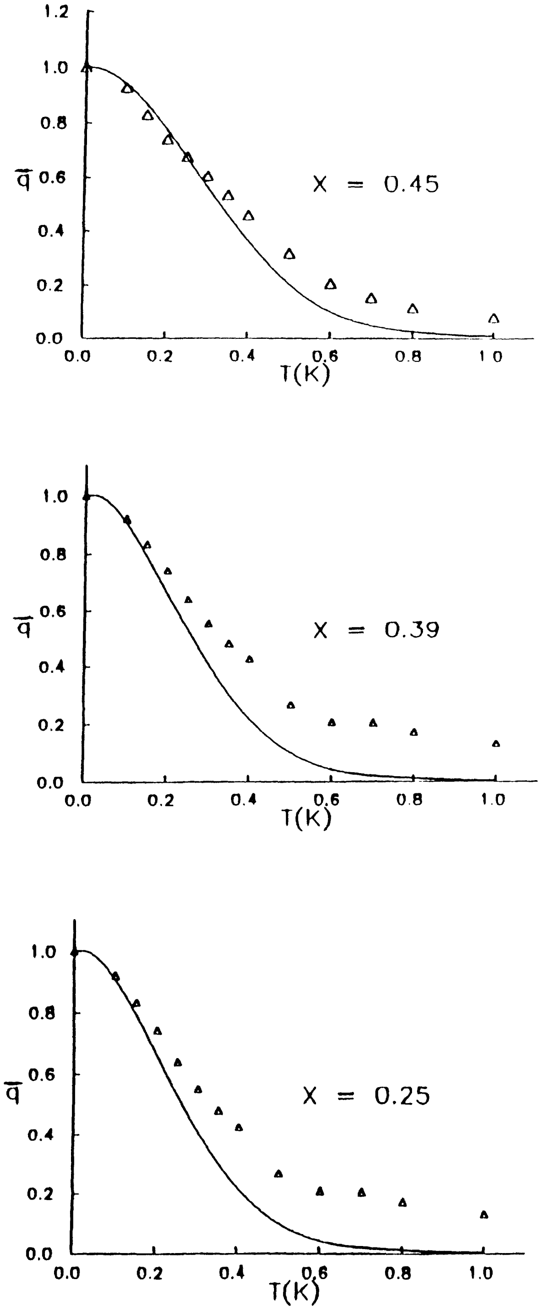

FIG. 1. Calculated temperature dependence of the QG order parameter q for three representative concentrations X of the orthohydrogen. The triangles refer to the data of Meyer and Washburn (Ref. 8) for the reduced parameter $q_{\text{red}} = M_2^{\text{intra}}(T,X)/M_2^{\text{inter}}(0,X)$

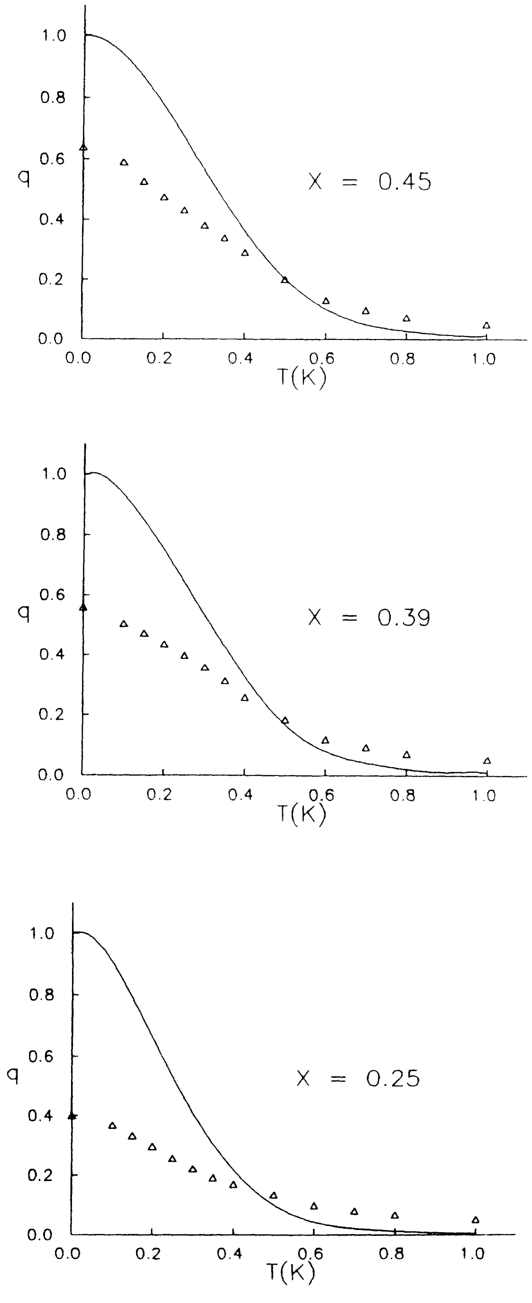

FIG. 2. Comparison of the temperature dependence of the calculated QG order parameter q with that measured experimentally ($\triangle$) by Meyer and Washburn (Ref. 8).

where $M_2^{\rm intra}$ is the intramolecular component of the second moment of the NMR line shape and $d = 57.7$ kHz is the intramolecular nuclear dipole coupling parameter (see, e.g., Ref. 8). The observed second moment M_2 is the sum of $M_2^{\rm intra}$ and $M_2^{\rm inter}$, the latter being the contribution from the intermolecular nuclear dipolar interaction.[8,19] The series of experiments by Meyer and Washburn[8] and Edwards *et al.*[10] showed a continuous evolution of M_2 with temperature, which indicate that the sharp phase transition is suppressed. The results obtained by these two groups are in agreement. Here we will compare the calculated temperature and concentration dependence of q with the data tabulated in Ref. 8. The component $M_2^{\rm inter}$ we take in the form[18]

$$M_2^{\rm inter} = \frac{4}{9} M_2^{\rm VV} = 40X \ ({\rm kHz}^2) , \tag{58}$$

where $M_2^{\rm VV}$ is the Van Vleck second moment and X denotes the concentration of the orthohydrogen.

In Fig. 1 the temperature dependence (T dependence) of the QG average parameter q is shown for three representative concentrations of orthohydrogen ($X = 0.25$, 0.39, and 0.45). The triangles refer to the reduced parameter $q_{\rm red} = M_2^{\rm intra}(T,X)/M_2^{\rm intra}(0,X)$ calculated from data given in Ref. 8. It is seen that agreement of our results with the experiment is quite good for $X = 0.45$. For lower concentrations of orthohydrogen the quantitative agreement is worse, but the qualitative form of the variation of q with temperature is very similar to that obtained from experiment.

Note that the T dependence of q calculated in the present paper is in better agreement with experiment than that obtained in Ref. 17. The T dependence of q presented in Ref. 17 shows in the range $T \sim 0.3$–1.0 K a much slower decrease of q with temperature than that shown here for $q_{\rm red}$. Hence the qualitative form of the T dependence of the average the QG parameter calculated there differs significantly from that measured experimentally.

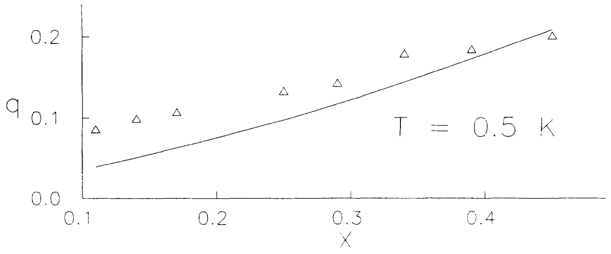

FIG. 3. Calculated concentration dependence of the QG order parameter for $T = 0.5$ K. The triangles refer to the data of Meyer and Washburn (Ref. 8).

In Fig. 2 a comparison of the calculated T dependence of q with that for $q_{\rm expt}$ obtained from the data of Ref. 8 (the triangles) is presented. We see that at low temperatures there are rather large discrepancies between the theory and experiment. This can be explained by the presence of strong zero-point motions,[12,18] which mean that the QG order parameter does not tend to 1. Our effective Hamiltonian (24) takes into account quantum effects only implicitly, and the inclusion in the theory of the nondiagonal part of the EQQ interaction in an explicit form would probably improve the results. Also for this reason the asymptotic behavior of q at low temperatures (56) is only a crude qualitative result.

Finally, in Fig. 3 a comparison of the concentration dependence of q with the experimental data[8] (the triangles) is shown for the temperature $T = 0.5$ K.

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