PHYSICAL REVIEW B VOLUME 46, NUMBER 22 1 DECEMBER 1992-II

Transition from the orientationally disordered to the quadrupolar glass phase in solid hydrogen

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(Received 26 December 1991; revised manuscript received 9 July 1992)

A quantum Hamiltonian, starting from the electric quadrupole-quadrupole interaction between molecules in solid hydrogen, is constructed for an ortho-para hydrogen mixture with the quadrupolar momenta of the orthohydrogen species randomly frozen out. With use of this Hamiltonian, the effective functional Landau-Ginzburg-Wilson Hamiltonian has been derived. A field-theoretic renormalization-group analysis leads to a conjecture that the system undergoes a discontinuous transition from the orientationally disordered to the quadrupolar glass phase. This transition is smeared out by the influence of the random local crystal field.

In the past 15 years there has been considerable experimental[1-8] and theoretical[8-14] work, including Monte Carlo simulations,[15,16] 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 55% (the crystal lattice is hcp for $x < 55\%$). The static and dynamic NMR data[1-3,5,6] show that, for such concentrations, no long-range order has been observed, and it has been suggested[1-3] that solid ortho-para hydrogen mixtures for $x < 55\%$ form a quadrupolar glass (QG), in which the local orientational order parameters vary randomly from site to site without any long-range spatial correlation. The aim of this paper is to obtain—starting from a microscopic Hamiltonian, which describes electric quadrupole-quadrupole (EQQ) interactions in the ortho-para hydrogen mixture—the effective Landau-Ginzburg-Wilson (LGW) Hamiltonian and, by the renormalization-group (RG) method, to study the phase transition from the orientationally disordered to the QG phase.

As Nakamura[17] has shown, the EQQ interactions are the most important orientational interactions between molecules in solid hydrogen. The Hamiltonian for these interactions is

$$H=\tfrac{1}{2}\sum_{\substack{i,j\\(i\neq j)}} H_{ij} , \tag{1}$$

where

$$H_{ij}=\frac{20\pi}{9}(70\pi)^{1/2}\Gamma\left[\frac{R}{|\mathbf{R}_{ij}|}\right]^5 \times \sum_{M,N=-2}^{+2} C(2,2,4;M,N)Y^{*}_{4,M+N}(\hat{\Omega}_{ij}) \times Y_{2,M}(\hat{\Omega}_i)Y_{2,N}(\hat{\Omega}_j) . \tag{2}$$

Here $C(2,2,4;M,N)$ denotes a Clebsch-Gordan coefficient, $Y_{2,M}$ is a spherical harmonic, and $\hat{\Omega}_i=(\Theta_i,\phi_i)$ and $\hat{\Omega}_{ij}=(\Theta_{ij},\phi_{ij})$ specify the orientations of, respectively, the ith molecule and the intermolecular separation vector $\mathbf{R}_{ij}$ between molecules i and j relative to a coordinate system fixed in the crystal. In Eq. (2),

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

is the EQQ coupling constant for a rigid lattice, where eQ is the molecular quadrupolar momentum and R is the intermolecular separation between nearest neighbors. In solid hydrogen, only the rotational states of molecules with the lowest J are occupied, and therefore Hamiltonian (1) can be rewritten as

$$H=\tfrac{1}{2}\sum_{\substack{i,j\\(i\neq j)}} x_i x_j H_{ij} , \tag{3}$$

where $x_i=0,1$ for p-H_2 and o-H_2 molecules, respectively. Because in the QG state the local averaged quadrupolar momenta of a o-H_2 molecules are randomly frozen out, it is convenient to specify the orientation of the o-H_2 molecule at a given site relative to the local coordinate system chosen so as to coincide with the principal axes of the molecular quadrupolar momentum tensor (cf. Ref. 18). The transformation of $Y_{2,M}(\hat{\Omega}_i)$ to this coordinate system is

$$Y_{2,M}(\hat{\Omega}_i)=\sum_{\mu=-2}^{+2} D^{2*}_{M\mu}(\hat{\chi}_i)Y_{2,\mu}(\hat{\omega}_i) ,$$

where $D^2_{M\mu}$ is a rotation matrix[19] and $\hat{\chi}_i$ denotes the triad of Euler angles α_i, β_i,γ_i specifying the orientation of the local coordinate axes to the coordinate system fixed in the crystal, and $\hat{\omega}_i$ describes the orientation of ith molecule relative to the local axes. In the $J=1$ manifold, one can replace $Y_{2,\mu}(\hat{\omega}_i)$ by their operator equivalences (cf. Ref. 20),

$$Y_{2,\mu}(\hat{\omega}_i)=A_\mu O_i^\mu , \tag{4}$$

where

$$A_0=-\frac{1}{5}\left[\frac{5}{4\pi}\right]^{1/2},$$

$$A_1=\pm\frac{1}{10}\left[\frac{15}{2\pi}\right]^{1/2}, \tag{4a}$$

$$A_{\pm 2}=-|A_{\pm 1}|,$$

and

$$O_i^0=3(J_i^z)^2-2,$$

$$O_i^{\pm 1}=J_i^z J_i^{\pm}+J_i^{\pm}J_i^z,$$

$$O_i^{\pm 2}=(J_i^{\pm})^2,$$

where J_i^z and $J_i^{\pm}=J_i^x \pm iJ_i^y$ are components of angular momentum operator $\mathbf{J}_i$ of ith orthohydrogen molecule. The axis of quantization for $\mathbf{J}_i$ is taken along the local z_i axis. Thus, Hamiltonian (3) can be written in the form

$$H=\sum_{\substack{i,j\\(i\neq j)}}\sum_{\mu,\nu=-2}^{+2} x_i x_j \gamma_{ij}^{\mu\nu} O_i^{\mu} O_j^{\mu} \tag{5}$$

with

$$\gamma_{ij}^{\mu\mu}=\frac{10\pi}{9}(70\pi)^{1/2}\Gamma\left[\frac{R}{|\mathbf{R}_{ij}|}\right]^5 \times\sum_{M,N}C(2,2,4;M,N)Y^{*}_{4,M+N}(\hat{\mathbf{\Omega}}_{ij}) \times D^{2*}_{M\mu}(\hat{\chi}_i)D^{2*}_{N\nu}(\hat{\chi}_j) \tag{6}$$

Because $\hat{\chi}_i$, which specifies the orientation of the local coordinate system, varies randomly from site to site, the coupling constant $\gamma_{ij}^{\mu\nu}$ (6) itself becomes a random quantity. The situation appears to be similar to the models of spin glasses (cf. Ref. 18), though the sources of the randomness of the exchange coupling in the former systems and parameters $\gamma_{ij}^{\mu\nu}$ (6) are quite different. The orientational free energy F of our system is

$$-\beta F=[\ln \mathrm{Tr} e^{-\beta H}]_{\mathrm{av}} \tag{7}$$

with H given by Eq. (5), where the inverse temperature $\beta=1/k_B T$ and $[\cdots]_{\mathrm{av}}$ denotes an averaging over random orientations of local coordinate axes and configurations of o-H_2 molecules. In order to calculate $-\beta F$ we use the well-known replica procedure (cf., e.g., Ref. 18). Thus, one obtains

$$-\beta F=\lim_{n\to 0}\left[\frac{1}{n}Z^{(n)}\right] \tag{8}$$

with

$$\begin{aligned}Z^{(n)}&=\ln\left[\mathrm{Tr}\exp\left[-\beta\sum_{\alpha=1}^{n}H_\alpha\right]\right]_{\mathrm{av}}\\&=\ln\left[\mathrm{Tr}T_\tau\exp\left[-\sum_{\alpha=1}^{n}\int_0^\beta H_\alpha(\tau)d\tau\right]\right]_{\mathrm{av}},\end{aligned} \tag{9}$$

where $\alpha=1,2,\ldots,n$ is a replica index,

$$H_\alpha=\sum_{\substack{i,j\\(i\neq j)}}\sum_{\mu,\nu}x_i x_j \gamma_{ij}^{\mu\nu}O_{i\alpha}^{\mu}O_{j\alpha}^{\nu},$$

$$H_\alpha(\tau)=\sum_{\substack{i,j\\(i\neq j)}}\sum_{\mu,\nu}x_i x_j \gamma_{ij}^{\mu,\nu}O_{i\alpha}^{\mu}(\tau)O_{j\alpha}^{\nu}(\tau),$$

and T_τ denotes the τ ordering operation. A formal dependence of the operators $O_{i\alpha}^{\mu}(\tau)$ on the Matsubara parameter τ has been introduced in order to treat them as c numbers (cf. Ref. 21). In fact, the random variables $\hat{\chi}_i$ are correlated with the spatial distribution of o-H_2 molecules. However, as a first step following Ref. 10, we neglect this correlation, assuming that these variables are statistically independent. This assumption is quite proper for the orientationally disordered phase, where the average components of the local quadrupolar momentum tensor of o-H_2 molecules in the state $J=1$ vanish, and there is a freedom of a choice of the local coordinate systems. Nevertheless, we hope that this is a reasonable approximation for the QG phase, at least just below the transition point. Because of the above-mentioned approximation, we can use techniques developed for spin glasses. Now it is convenient to decompose the operation $[\ldots]_{\mathrm{av}}$ into a sequence of two stages as follows:

$$[\cdots]_{\mathrm{av}}=[[\cdots]_{\hat{\chi}}]_x, \tag{10}$$

where $[\cdots]_{\hat{\chi}}$ denotes an averaging over directions of the local coordinate system at a given distribution of orthohydrogen molecules, and then one averages over configurations of o-H_2 species. Taking into account Eqs. (9) and (10), one obtains

$$Z^{(n)}=\ln\left[\mathrm{Tr}T_\tau\exp\left\{-\sum_{\alpha=1}^{n}\int_0^\beta d\tau[H_\alpha(\tau)[_{\hat{\chi}}+\tfrac{1}{2}\sum_{\alpha,\alpha'=1}\int_0^\beta d\tau\int_0^\beta d\tau'[H_\alpha(\tau)H_{\alpha'}(\tau')]^{c}_{\hat{\chi}}+\cdots\right\}\right]_x, \tag{11}$$

where $[\ldots]^{c}_{\hat{\chi}}$ denotes the cumulant average. The higher-order terms in the exponent in Eq. (11) are less important for the QG problem because they do not contain terms immediately related to the QG order parameter (cf. Ref. 22, where the spin-glass problem has been considered). The averaging over configuration of o-H_2 molecules shall be performed towards the end of the calculations because introducing the operation $[\cdots]_x$ to the exponent in Eq. (11) we wold obtain an incorrect dependence of the QG transition temperature on the concentration of orthohydrogen molecules. We shall approach the QG phase from above (i.e., from the side of the orientationally disordered phase), and the averaging $[\cdots]_{\hat{\chi}}$ should therefore be performed as for a disordered phase assuming that the probability distribution of the orientation of the local coordinate system is the same in each spatial direction. Taking into account (6) with the help of relations known in the theory of angular momentum,[19] one obtains

$$[\gamma_{ij}^{\mu\nu}]_{\hat{\chi}}=0 \tag{12a}$$

and

$$[\gamma_{ij}^{\mu\nu}\gamma_{i'j'}^{\mu'\nu'}]_{\mathrm{av}}^{c}=(\delta_{ii'}\delta_{jj'}\delta_{\mu,-\mu'}\delta_{\nu,-\nu'}+\delta_{ij'}\delta_{ji'}\delta_{\mu,-\nu'}\delta_{\nu,-\mu'})A_{\mu}^{2}A_{\nu}^{2}J_{ij}^{2}\ , \tag{12b}$$

where

$$J_{ij}=J\left[\frac{R}{|\mathbf{R}_{ij}|}\right]^{5}$$

with

$$J=\frac{\pi}{2}\left[\frac{35}{3}\right]^{1/2}\Gamma\ .$$

Taking into account Eqs. (12a) and (12b), we transform $Z^{(n)}$ [Eq. (11)] into the following form:

$$Z^{(n)}=\left[\mathrm{Tr}T_{\tau}\exp\left\{\int_{0}^{\beta}d\tau\int_{0}^{\beta}d\tau' H(\tau,\tau')\right\}\right]_{x}\ , \tag{13}$$

where

$$H(\tau,\tau')=H_{1}(\tau,\tau')+H_{0}(\tau,\tau') \tag{14}$$

is the effective Hamiltonian which depends on two Matsubara parameters τ and τ', with

$$H_{i}(\tau,\tau')=\sum_{\substack{i,j\\(i\neq j)}}\sum_{\alpha,\alpha'=1}^{n}x_{i}x_{j}J_{ij}^{2}\hat{q}_{i}^{\alpha\alpha'}(\tau,\tau')\hat{q}_{j}^{\alpha\alpha'}(\tau,\tau') \tag{15a}$$

and

$$H_{0}(\tau,\tau')=\sum_{\substack{ij\\(i\neq j)}}\sum_{\alpha=1}^{n}x_{i}x_{j}J_{ij}^{2}\hat{p}_{i}^{\alpha}(\tau,\tau')\hat{p}_{j}^{\alpha}(\tau,\tau')\ . \tag{15b}$$

Here the operators $\hat{q}_{i}^{\alpha\alpha'}(\tau,\tau')$ are defined as follows:

$$\hat{q}_{i}^{\alpha\alpha'}(\tau,\tau')=\sum_{\mu}A_{\mu}^{2}O_{i\alpha}^{\mu}(\tau)Q_{i\alpha'}^{-\mu}(\tau')(1-\delta_{\alpha\alpha'}) \tag{16a}$$

and

$$\hat{p}_{i}^{\alpha}(\tau,\tau')=\sum_{\mu}A_{\mu}^{2}O_{i\alpha}^{\mu}(\tau)O_{i\alpha}^{-\mu}(\tau')\ . \tag{16b}$$

The problem now is to obtain the functional Hamiltonian of our system. After a functional Hubbard-Stratonovich transformation (cf. Ref. 21), $Z^{(n)}$ [Eq. (13)] takes the form

$$Z^{(n)}=\left[\int d(q)\exp(-\mathcal{H}([q],\{x_{i}\}))\right]_{x}\ , \tag{17}$$

where $d(q)$ denotes the functional integration over the field $q_{i}^{\alpha\alpha'}(\tau,\tau')$ $[q_{i}^{\alpha,\alpha}(\tau,\tau')=0]$ and

$$\mathcal{H}([q],\{x_{i}\})=\mathcal{H}_{0}(\{x_{i}\})+\tfrac{1}{4}\sum_{i,j}\sum_{\alpha,\alpha'=1}^{n}\int_{0}^{\beta}d\tau\int_{0}^{\beta}d\tau' v_{ij}q_{i}^{\alpha\alpha'}(\tau,\tau')-\ln\left\langle\exp\left[\sum_{i}\sum_{\alpha,\alpha'=1}^{n}x_{i}\int_{0}^{\beta}d\tau\int_{0}^{\beta}d\tau' q_{i}^{\alpha\alpha'}(\tau,\tau')\hat{q}_{i}^{\alpha\alpha'}(\tau,\tau')\right]\right\rangle_{0} \tag{18}$$

with $\sum_{k}v_{ik}J_{kj}^{2}=\delta_{ij}$, where

$$\langle(\cdots)\rangle_{0}=\frac{\mathrm{Tr}T_{\tau}\exp\left[\int_{0}^{\beta}d\tau\int_{0}^{\beta}d\tau' H_{0}(\tau,\tau')\right]\cdots}{\mathrm{Tr}T_{\tau}\exp\left[\int_{0}^{\beta}d\tau\int_{0}^{\beta}d\tau' H_{0}(\tau,\tau')\right]} \tag{19}$$

and

$$\mathcal{H}_{0}(\{x_{i}\})=\ln\int d(q)\exp\left[-\tfrac{1}{4}\sum_{i,j}\sum_{\alpha,\alpha'=1}^{n}\int_{0}^{\beta}d\tau\int_{0}^{\beta}d\tau' v_{ij}q_{i}^{\alpha\alpha'}(\tau,\tau')q_{j}^{\alpha\alpha'}(\tau,\tau')\right]-\ln\mathrm{Tr}T_{\tau}\exp\left[\int_{0}^{\beta}d\tau\int_{0}^{\beta}d\tau' H_{0}(\tau,\tau')\right]\ .$$

It can be shown that $\langle q_{i}^{\alpha,\alpha'}(\tau,\tau')\rangle_{\mathcal{H}}$, where

$$\langle(\cdots)\rangle_{\mathcal{H}}=\frac{\int d(q)\exp\{-\mathcal{H}([q],\{x_{i}\})\}(\cdots)}{\int d(q)\exp\{-\mathcal{H}([q],\{x_{i}\})\}}$$

is related to the QG order parameter defined as follows (cf. Ref. 3):

$$q=A_{0}^{2}[x_{i}|\langle O_{i}^{0}\rangle_{H}|^{2}]_{\mathrm{av}}+2A_{2}[x_{i}|\langle O_{i}^{+2}\rangle_{H}|^{2}]_{\mathrm{av}}=\sum_{\mu=-2}^{+2}A_{\mu}^{2}[x_{i}|\langle O_{i}^{\mu}\rangle_{H}|^{2}]_{\mathrm{av}}\ , \tag{20}$$

where $\langle O_{i}^{\mu}\rangle_{H}$ denotes a thermal average with the Hamiltonian (5). The terms $[x_{i}|\langle O_{i}^{0}\rangle_{H}|^{2}]_{\mathrm{av}}$ and $[x_{i}|\langle O^{+2}\rangle_{H}|^{2}]_{\mathrm{av}}$ in

Eq. (20) measure, respectively, the alignment of orthomolecule along the local axis z_i and eccentricity. The last term on the right-hand side of Eq. (20) results from the fact that in the local coordinate system $\langle O_i^{\pm} \rangle_H = 0$. After detailed calculations, one obtains

$$
\begin{aligned}
q &= \lim_{n\to 0} \left[\frac{\beta^{-2}}{n(n-1)} \sum_{\alpha,\alpha'=1}^{n} \int_0^\beta d\tau \int_0^\beta d\tau' [x_i \langle \hat{q}_i^{\alpha,\alpha'}(\tau,\tau') \rangle]_x \right] \\
&= \frac{1}{2} \lim_{n\to 0} \left[\frac{\beta^{-2}}{n(n-1)} \sum_{\alpha,\alpha'=1}^{n} \int_0^\beta d\tau \int_0^\beta d\tau' v_{ij} [x_j \langle q_j^{\alpha\alpha'}(\tau,\tau') \rangle_{\mathcal{H}}]_x \right]
\end{aligned}
\tag{21}
$$

where

$$
\langle \hat{q}_i^{\alpha\alpha'}(\tau,\tau') \rangle = \frac{\mathrm{Tr} T_\tau \exp \left[\int_0^\beta d\tau \int_0^\beta d\tau' H(\tau,\tau') \right] \hat{q}_i^{\alpha\alpha'}(\tau,\tau')}{\mathrm{Tr} T_\tau \exp \left[\int_0^\beta d\tau \int_0^\beta d\tau' H(\tau,\tau') \right]} \ . \tag{22}
$$

Of course, $[x_i \langle q_i^{\alpha\alpha'}(\tau,\tau') \rangle]_x$ and $[x_i \langle q_i^{\alpha\alpha'}(\tau,\tau') \rangle_{\mathcal{H}}]_x$ are independent of the lattice site i. The calculations leading to Eq. (21) are similar to those used in the theory of quantum spin glasses (cf., e.g., Ref. 23). Thus, $q_i^{\alpha\alpha'}(\tau,\tau')$ represents the QG order parameter field. The effective LGW Hamiltonian, which is the starting point for studies of universal critical behavior, will be calculated with use of $\mathcal{H}([q],\{x_i\})$ [Eq. (18)]. Similarly as in the spin-glass problem,[18,24,25] we assume that the relevant interaction responsible for the transition from the orientationally disordered to the QG phase is the cubic coupling between fields $q_i^{\alpha\alpha'}(\tau,\tau')$. In our calculations we shall not take into account the effect of quantum nature of the system on the universal critical behavior. Therefore, only the Fourier transform of $q_i^{\alpha\alpha'}(\tau,\tau')$ with zero Matsubara frequency will contribute to the LGW Hamiltonian. In other words, we make the replacement

$$
q_i^{\alpha,\alpha'}(\tau,\tau') \to q_i^{\alpha\alpha'} = \beta^{-2} \int_0^\beta d\tau \int_0^\beta d\tau' q_i^{\alpha\alpha'}(\tau,\tau') \ . \tag{23}
$$

The problem now is to expand $\mathcal{H}([q],\{x_i\})$ up to third order in $q_i^{\alpha\alpha'}$ [Eq. (23)]. The coefficients of this expansion include some products of the operators $q_i^{\alpha\alpha'}(\tau,\tau')$ [Eq. (16a)] averaged with $H_0(\tau,\tau')$ according to Eq. (19).

Note, that $H_0(\tau,\tau')$ (15a) is invariant under rotations in the space of angular momenta $\mathbf{J}_{i\alpha}$ for each i and α independently [the operator $A_\mu O_{i\alpha}^\mu(\tau)$ transforms as the spherical harmonic $Y_{2,\mu}$]. Such an internal symmetry is characteristic of the system above the QG transition point and can be taken into account in our calculations because we approach the QG phase from above. As a result, the coefficients of expansion of $\mathcal{H}([q]\{x_i\})$ [Eq. (18)] with respect of $q_i^{\alpha\alpha'}$ [Eq. (23)] are found to be related to the following invariants of the rotation group:

$$
P_i(\{x_i\}) = \beta^{-2} \int_0^\beta d\tau \int_0^\beta d\tau' \sum_{\mu=-2}^{+2} A_\mu^2 \langle O_i^\mu(\tau) O_i^{-\mu}(\tau') \rangle_0 \tag{24a}
$$

and

$$
R_i(\{x_i\}) = \frac{\beta^{-3}}{\sqrt{5}} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \int_0^\beta d\tau_3 \sum_{\mu,\nu=-2}^{+2} A_\mu A_\nu A_{\mu+\nu} C(2,2,2;\mu,\nu) \langle O_i^\mu(\tau_1) O_i^\mu(\tau_2) O_i^{-\mu-\nu}(\tau_3) \rangle_0 \tag{24b}
$$

with $\langle \cdots \rangle_0$ defined by Eq. (19).

We have assumed that $\langle O_{i\alpha}^\mu(\tau) O_{i\alpha}^{-\mu}(\tau') \rangle_0$ and $\langle O_{i\alpha}^\mu(\tau_1) O_{i\alpha}^\nu(\tau_2) O_{i\alpha}^{-\mu-\nu}(\tau_3) \rangle_0$ do not depend on the replica index. After detailed calculations, one obtains

$$
\begin{aligned}
\mathcal{H}([q],\{x_i\}) = {} & \frac{\beta^{-2}}{4} \sum_{i,j} v_{ij} q_i^{\alpha\alpha'} q_j^{\alpha\alpha'} - \tfrac{1}{5} \sum_i \sum_{\alpha,\alpha'} x_i P_i^2(\{x_j\}) (q_i^{\alpha\alpha'})^2 - \tfrac{2}{3} \sum_i \sum_{\alpha,\alpha'} x_i R_i^2(\{x_j\}) (q_i^{\alpha\alpha'})^3 \\
& - \frac{4}{75} \sum_i \sum_{\alpha_1,\alpha_2,\alpha_3} x_i P_i^3(\{x_j\}) q_i^{\alpha_1\alpha_2} q_i^{\alpha_2\alpha_3} q_i^{\alpha_3\alpha_1} + O(q^4) \ .
\end{aligned}
\tag{25}
$$

The inessential term $\mathcal{H}_0(\{x_i\})$ has been omitted. The averaging over distributions of ortho-hydrogen molecules leads to the Hamiltonian $\mathcal{H}[q]$ related to $\mathcal{H}([q],\{x_i\})$ [Eq. (25)] as follows:

$$
\mathcal{H}[q] = -\ln \left[\exp \left\{ -\mathcal{H}([q],\{x_i\}) \right\} \right]_x \ . \tag{26}
$$

We assume that the probability distribution for each random variable x_i has the form

$$
P(x_i) = (1-x)\delta_{x_i 0} + x\delta_{x_i 1} \ ,
$$

where x is the concentration of the o-H_2 species.

Calculating the right-hand side of Eq. (26) we take into account only the first cumulant. The second and next cumulants contribute to the quartic and higher-order coupling of the field $q_i^{\alpha\alpha'}$, which are irrelevant for our analysis.

The result is

$$\mathcal{H}[q]=\frac{\beta^{-2}}{4}\sum_{i,j}v_{ij}q_i^{\alpha\alpha'}q_j^{\alpha\alpha'}-\frac{u}{4}\sum_i\sum_{\alpha,\alpha'}(q_i^{\alpha\alpha'})^2$$
$$-\frac{v_0}{3!}\sum_i\sum_{\alpha,\alpha'}(q_i^{\alpha\alpha'})^3-\frac{w_0}{3!}\sum_i\sum_{\alpha_1,\alpha_2,\alpha_3}q_i^{\alpha_1\alpha_2}q_i^{\alpha_2\alpha_3}q_i^{\alpha_3\alpha_1}+O(q^4) \tag{27a}$$

where

$$u=\tfrac{4}{5}[x_iP_i^2\{x_j\})]_x \ , \tag{27b}$$

$$v_0=4[x_iR_i^2(\{x_j\})]_x \ , \tag{27c}$$

and

$$w_0=\tfrac{8}{25}[x_iP_i^3(\{x_j\})]_x \ . \tag{27d}$$

Now we introduce the spatial Fourier transform of $q_i^{\alpha\alpha'}$ defined as follows:

$$q_i^{\alpha\alpha'}=\int_{\mathbf{k}}e^{-\mathbf{k}\cdot\mathbf{R}_i}q_{\mathbf{k}}^{\alpha\alpha'} \tag{28}$$

where $\mathbf{R}_i$ denotes the lattice vector and

$$\int_{\mathbf{k}}(\cdots)\equiv(2\pi)^{-3}\int d^3\mathbf{k}(\cdots) \tag{29}$$

with $\mathbf{k}$ inside the Brillouin zone. After this, $\mathcal{H}[q]$ [Eq. (27a)] takes the form

$$\mathcal{H}[q]=\tfrac{1}{4}\sum_{\alpha,\alpha'}\int_{\mathbf{k}}u_2(\mathbf{k})q_{-\mathbf{k}}^{\alpha\alpha'}q_{-\mathbf{k}}^{\alpha\alpha'}-\frac{v_0\Omega^{-1}}{3!}\sum_{\alpha,\alpha'}\int_{\mathbf{k}_1}\int_{\mathbf{k}_2}\int_{\mathbf{k}_3}\not\delta\left[\sum\mathbf{k}\right]q_{\mathbf{k}_1}^{\alpha\alpha'}q_{\mathbf{k}_2}^{\alpha\alpha'}q_{\mathbf{k}_3}^{\alpha\alpha'}$$
$$-\frac{w_0\Omega^{-1}}{3!}\sum_{\alpha_1,\alpha_2,\alpha_3}\int_{\mathbf{k}_1}\int_{\mathbf{k}_2}\int_{\mathbf{k}_3}\not\delta\left[\sum\mathbf{k}\right]q_{\mathbf{k}_1}^{\alpha_1\alpha_2}q_{\mathbf{k}_2}^{\alpha_2\alpha_3}q_{\mathbf{k}_3}^{\alpha_3\alpha_1} \ , \tag{30}$$

where

$$\not\delta(\mathbf{k})=(2\pi)^3\delta^{(3)}(\mathbf{k}) \tag{31}$$

and

$$u_2(\mathbf{k})=\Omega^{-1}\left[\frac{\beta^{-2}}{(J^2)(\mathbf{k})}-u\right] \tag{32a}$$

with

$$(J^2)(\mathbf{k})=\sum_{\mathbf{R}_{ij}}J_{ij}^2e^{-i\mathbf{k}\cdot\mathbf{R}_{ij}} \ . \tag{32b}$$

Here Ω denotes the volume of an elementary cell. The EQQ interaction is assumed to be short ranged and the main contribution to the sum in Eq. (32b) comes from the nearest-neighboring sites.[26,1] Therefore, $u_2(\mathbf{k})$ is an analytic function of $\mathbf{k}$, and we expand $u_2(\mathbf{k})$ up to the second order in $|\mathbf{k}|$ as follows:

$$u_2(\mathbf{k})=(z\Omega\beta^2J^2)^{-1}-\Omega^{-1}u+c^{-2}\sum_{\lambda,\lambda'=1,2,3}a_{\lambda\lambda'}k_\lambda k_{\lambda'}+\cdots$$

with

$$c=\Lambda\Omega^{1/2}z^{1/2}\beta J \ ,$$

where Λ and z denote, respectively, the effective radius of the Brillouin zone (in the continuum limit, $\Lambda\rightarrow\infty$) and the number of nearest neighbors, which is $z=12$ for the hcp lattice. After the transformations

$$\mathbf{k}\rightarrow\hat{a}^{-1/2}\mathbf{k}$$

and

$$q_{\hat{a}^{1/2}\mathbf{k}}^{\alpha\alpha'}\rightarrow cq_{\mathbf{k}}^{\alpha\alpha'} \ ,$$

where $\hat{a}=\|a_{\lambda\lambda'}\|$, we obtain a LGW Hamiltonian in the standard form

$$\mathcal{H}[q]=\tfrac{1}{4}\sum_{\alpha,\alpha'}\int_{\mathbf{k}}(r_0+k^2)q_{\mathbf{k}}^{\alpha\alpha'}q_{-\mathbf{k}}^{\alpha\alpha'}$$
$$-\frac{v_0}{3!}\sum_{\alpha\alpha'}\int_{\mathbf{k}}\int_{\mathbf{k}_2}\int_{\mathbf{k}_3}\not\delta\left[\sum\mathbf{k}\right]q_{\mathbf{k}_1}^{\alpha\alpha'}q_{\mathbf{k}_2}^{\alpha\alpha'}q_{\mathbf{k}_3}^{\alpha\alpha'}$$
$$-\frac{w_0}{3!}\sum_{\alpha_1,\alpha_2,\alpha_3}\int_{\mathbf{k}_1}\int_{\mathbf{k}_2}\int_{\mathbf{k}_3}\not\delta\left[\sum\mathbf{k}\right]q_{\mathbf{k}_1}^{\alpha_1\alpha_2}q_{\mathbf{k}_2}^{\alpha_2\alpha_3}q_{\mathbf{k}_3}^{\alpha_3\alpha_1} \tag{33}$$

with

$$r_0=\Lambda^2[1-z(\beta J)^2u] \ . \tag{34}$$

Here, the coefficients v_0 and w_0 differ form those in Eq.

(30) by a factor of $\Omega^{-1}c^3$. In order to study the phase transition by the RG method in our system, the LGW Hamiltonian (33) should be considered in d-dimensional space. This can be easily done by the replacement of the right-hand sides of Eqs. (29) and (31) by $(2\pi)^{-d}\int d^dk \cdots$ and $(2\pi)^d\delta^{(d)}(\mathbf{k})$, respectively, where $\mathbf{k}$ is a d-dimensional wave vector. The second term on the right-hand side of Eq. (33) appears as a consequence of the lack of the reflection operation[27] in the internal symmetry group acting in the space of $O^{\mu}_{l\alpha}$. Therefore, Hamiltonian (33) differs from that describing the Ising spin glass.[24] The standard field-theoretic RG calculation[28,24] to first order in $\epsilon = 6 - d$ yields that the model (34) has the following fixed points (FP's): (i) Gaussian FP unstable for $d < 6$ and stable for $d \geq 6$, (ii) Ising spin-glass FP (Ref. 24) unstable in each spatial dimension with $v^* = 0$ and $S_d w^{*2} = \epsilon/2$ [here $S_d = 2^{1-d}\pi^{-d/2}/\Gamma(d/2)$], and (iii) two unphysical FP's with $v^{*2} < 0$).

The above results lead us to make the conjecture that the unstable Ising spin-glass FP may govern discontinuous transition from the orientationally disordered to the QG phase. This is in agreement with the NMR experiment of Sullivan *et al.*[1], in which rapid variations of the line shapes with temperature have been observed for solid ortho-para hydrogen mixtures with $x < 55\%$. However, such an interpretation should be treated with some caution because, from the experimental point of view, the nature of the transition to the QG phase is not explained unambiguously. At the QG transition point,

$$r_0 = a \ ,$$

where a is some constant. The coefficient r_0 (34) includes u (Eq. (27b)], which can be written in the form

$$u = \tfrac{4}{5}x[P_i^2(x_i = x, \{x_j|_{j\neq i}\})]_x$$

Hence, it is seen that $T_g \sim x^{1/2}$, which is in qualitative agreement with the observed concentration dependence of T_g. In our considerations, we have taken into account only the EQQ coupling, which plays a dominant role as an orientational interaction in solid hydrogen. However, in addition to that interaction in the system, there is a crystal field caused by zero-point motion, which destroys the symmetry of the hcp structure.[29] The crystal field splits the threefold-degenerate $J = 1$ level of orthohydrogen molecules into two levels with $J^z = 0$ and $J^z = \pm 1$. The splitting is about 8 mK.[29] In the solid ortho-para hydrogen mixture, the crystal field randomly varies from site to site. A possible influence of the random crystal field on the QG transition can be a smearing of this transition similar to the classical quadrupolar glasses.[30] Indeed, the experimental studies of Harris and Meyer[7] confirmed by a series of experiments by Sullivan[8] showed a continuous evolution of the QG parameter with changing temperature.

Summarizing, we have applied methods used in theories of quantum spin glasses[21,23] to the QG problem in solid hydrogen. On the basis of RG analysis, the transition from the orientationally disordered to the QG state is found to be discontinuous, but this transition is smeared out by the influence of a random crystal field. However, further studies on this problem with explicit inclusion of the effect of the crystal field are desirable.

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