PHYSICAL REVIEW B VOLUME 18, NUMBER 12 15 DECEMBER 1978

Derivation of the temperature dependence of the order parameter for solid orthohydrogen and paradeuterium

K. Walasek and K. Lukierska-Walasek

Institute of Physics, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

(Received 10 May 1976)

The orientational free energy and order parameter for solid orthohydrogen and paradeuterium are obtained using a Green's-function diagrammatic technique developed by the authors. The orientational interaction is assumed to be electrostatic quadrupole-quadrupole. The zero-phonon, and $J = 1 \rightarrow J = 3$ effects on the order parameter are also taken into account. The expressions for the free energy of the orientationally ordered and disordered phase are obtained in $1/z$ approximation, where $z = 12$ is the number of the nearest neighbors in the fcc lattice. An equation for the order parameter is obtained from the minimum condition for the free energy. The orientational phase transition is predicted to be first order. The critical temperature is found to be 3.64 K for ortho-H_2 and 4.63 K for para-D_2. The temperature T_1 and T_2 which are the maximum (T_1) and minimum (T_2) metastability limit for the ordered and disordered phase, respectively, are also calculated. They are $T_1 = 0.60\ T_0$ and $T_2 = 0.46\ T_0$, where T_0 is the critical temperature obtained from the molecular-field theory. The results are in a good agreement with experimental data.

I. INTRODUCTION

In the past ten years, there has been extensive theoretical and experimental activity directed at solid hydrogen and deuterium. These solids with very high concentration of molecules in a metastable state, $J=1$ (orthohydrogen and paradeuterium), have many properties in common with magnetic systems. In particular, at low temperatures (2.8 K for ortho-H_2 and 3.8 K for para-D_2), there is an orientational ordering of the $J=1$ molecular orbitals, closely analogous to the spin ordering in antiferromagnetic systems.[1] A structural change from a hcp to a fcc lattice accompanies the phase transition from the orientationally disordered to the ordered state.[2] Because of a considerable hysteresis of the structural transition, the fcc phase can be stabilized by thermal cycling and therefore the orientational and structural transitions can be separated[2-4] at least to a certain extent. Thus, to consider the order-disorder phase transition in the fcc lattice it seems to be reasonable.

In the ordered state, the axis of symmetry of a rotating molecule in the $J=1$ state is oriented along one of the [1 1 1] body diagonals of the fcc lattice. The arrangement is such that for each of the four simple cubic sublattices comprising the fcc structure, the molecular axes of symmetry are parallel. Thus, four orientational sublattices exist in a crystal and the space group of the system is $Pa3$ (T_h^6). Various experiments, such as elastic neutron[5] and Raman[6] scattering, provide a firm basis for this assumption. The $Pa3$ structure was also predicted theoretically in the classical[7-10] as well as in the quantum[11-13] cases.

A quantity of particular interest for the investigation of the orientational transition in solid ortho-H_2 and para-D_2 is the order parameter, proportional to $\langle 3\cos^2\theta - 1\rangle$, where θ is the angle between the internuclear axis of a molecule and the molecular symmetry axis, and $\langle\cdots\rangle$ denotes an ensemble average. The nuclear-magnetic-resonance (NMR) experiments performed on polycrystalline samples of high concentration of para-D_2 (Ref. 14) show that below the molecular ordering temperature the NMR line suddenly becomes very broad and assumes the shape of a Pake doublet, whose magnitude of splitting is, accordingly to the theoretical predictions,[15] proportional to $\langle 3\cos^2\theta - 1\rangle$. Such a rapid variation of the order parameter at the critical temperature is characteristic of first-order phase transtions. The temperature dependence of the order parameter for oriented ortho-H_2 and para-D_2 monocrystals was also investigated via Raman scattering.[6] The results are consistent with the assumption of first-order character of the orientational transition.

Several calculations, based on molecular-field (MF) theories,[11,16-18] Green's-function methods (RPA),[19,20] cluster expansions,[21-23] and the Kirkwood technique of restricted traces,[24] have been performed to determine the temperature dependence of the order parameter. All these theories do not take into account, with a satisfactory accuracy, the effect of short-range order on the order parameter, and consequently, they overestimate the transition temperature by a factor ranging from 2 to 1.3. Because of the nature of the orientational interactions between molecules in solid ortho-H_2 and para-D_2,[15,25] the short-range order is indeed important in the critical region. An attempt to investigate the effect of correlation on the transition temperature has been done by Englman and Friedman.[26] They have used an approximation scheme first developed by Lines for a ferroelectric.[27] Unfortunately, this approach is not suitable to calculate the order parameter.

For an efficient study of the effect of short-range order on the order parameter for a wide range of temperatures it is necessary to develop a more general method than MF theory or RPA. For an arbitrary spin and pseudospin system, however, this is a rather difficult task requiring a special diagrammatic Green's-function technique. Such a diagrammatic technique has been originally developed for a few simple models of ferromagnetism by Izyumov *et al.*[28] and was generalized in Ref. 29 to a large class of spin systems, using the formalism of the standard basis operators. Unfortunately, the diagrams of the method of Ref. 29 become rather complicated in dealing with systems having a large number of single-body states, and moreover, the method cannot be applied when the singlebody levels are degenerate.

Another diagrammatic approach, considerably simpler than that of Ref. 29 and applicable to an arbitrary spin and pseudospin system, was proposed by one of the authors.[30] The quantities considered in our method are the many-point irreducible Green's functions (IGF's) for imaginary "time" arguments. In the present paper, we describe this method in application to the phenomenon of orientational ordering in solid ortho-H_2 and para-D_2. As will be seen, the results obtained are in a good agreement with the temperature dependence of the order parameter, determined experimentally via measurements of the Pake doublet splitting.[14]

The remainder of the paper is arranged as follows. In Sec. II we briefly discuss the Hamiltonian of the system and define the order parameter. Section III contains the development of our method. We introduce the generating functional for IGF's and discuss the diagrammatic expansion scheme. Special attention is paid to the diagrammatic series for the orientational free energy in $1/z$ approximation, where $z=12$ is the number of nearest neighbors of a site in the fcc lattice. In Sec. IV we obtain the equation for the order parameter using a minimum condition for the free energy. In Sec. V we calculate the orientational free energy for the disordered phase. The temperature which is the minimum limit of metastability for the disordered phase is also found. In Sec. VI the results are discussed and compared with experimental data and previous theories.

Part of our results have been reported in Ref. 31. Because of some numerical and algebraical errors the results given in[31] differ from those obtained in the present paper.

II. HAMILTONIAN AND ORDER PARAMETER

It has been shown that in solid H_2 and D_2 the dominant contribution to the anisotropic interactions is an electrostatic quadrupole-quadrupole (EQQ) coupling and that the EQQ interaction leads to an orientational ordering.[15,25] Following Raich and Etters[20] we write the EQQ Hamiltonian for the orientationally ordered phase in the form

$$H=\sum_{i,j}\sum_{m,n} v_{ij}^{mn} Y_{2m}(\hat{\omega}_i) Y_{2n}(\hat{\omega}_j)\ , \tag{2.1}$$

where $m,n=0,\pm 1,\pm 2$; $\hat{\omega}_i=(\theta_i,\phi_i)$ describes the orientation of a molecule at the ith site relative to the local coordinate system. The local coordinate system for the ith molecule is chosen in such a way that the z_i axis coincides with the molecular-symmetry axis

$$\begin{aligned} v_{ij}^{mn}=v_{ji}^{nm}=&\tfrac{10}{9}\pi(70\pi)^{1/2}\Gamma_{ij}\\ &\times\sum_{M,n} C(224;MN)Y_{4,M+N}(\hat{\Omega}_{ij})^*\\ &\times D^2_{Mm}(\hat{\chi}_i)^* D^2_{Nn}(\hat{\chi}_j)^*\ , \end{aligned} \tag{2.2}$$

where $C(224;MN)$ is the Glebsch-Gordan coefficient, $D^2_{Mm}(\hat{\chi}_i)$ is a rotation matrix, $\hat{\chi}_i$ is the triad of Euler angles specifying the orientation of the z_i axis with respect to the cubic crystal axes, $\hat{\Omega}_{ij}$ denotes the orientation of the vector $\vec{R}_{ij}$ connecting the ith and jth sites, relative to the crystal axes, and

$$\Gamma_{ij}=\Gamma_0\left(\frac{R_0}{R_{ij}}\right)^5\ , \tag{2.3}$$

where $R_{ij}=|\vec{R}_{ij}|$, R_0 is the distance between the nearest neighbors, and

$$\Gamma_0=6e^2Q^2/25R_0^5 \tag{2.4}$$

is the EQQ-coupling parameter. Here eQ denotes the molecular quadrupole moment. Because of the weakness of EQQ interaction, the rotational quantum number J_i of each molecule remains a good quantum number and the Hamiltonian (2.1) can be projected into the subspace of $J_i=1$ states. So, we get[20]

$$H=\sum_{ij}\sum_{mn}\gamma_{ij}^{mn} O_i^m O_j^n\ , \tag{2.5}$$

where

$$\gamma_{ij}^{mn}=\gamma_{ji}^{nm}=\gamma_{ij}^{-m,-n}=(1/20\pi)A_m A_n v_{ij}^{mn}\ , \tag{2.6}$$

with $A_0=1$, $A_{\pm1}=\mp\sqrt{\frac{3}{2}}$, $A_{\pm2}=\sqrt{\frac{3}{2}}$, and

$$O_i^0=3(J_i^z)^2-2\ , \tag{2.7a}$$

$$O_i^{\pm1}=J_i^z J_i^{\pm}+J_i^{\pm}J_i^z\ , \tag{2.7b}$$

$$O_i^{\pm2}=(J_i^{\pm})^2\ , \tag{2.7c}$$

where

$$J_i^{\pm}=J_i^x \pm iJ_i^y \ . \tag{2.7d}$$

Here J_i^x, J_i^y, and J_i^z are the components of the angular momentum operator $\vec{J}_i$ for a molecule on site i. The axis of quantization for $\vec{J}_i$ is taken along the local z_i axis.

Of course, in ortho-H_2 and para-D_2 crystals several many-body effects modify the EQQ interaction. These effects are[15] (i) static phonon renormalization, (ii) dynamic phonon renormalization, and (iii) screening effects. They lead to the replacement of EQQ interaction parameter Γ_0 by the effective one $\Gamma \simeq 0.8\Gamma_0$.[15] By fitting to Raman experiments one obtains[6]

$$\Gamma_{H_2}=0.582 \pm 0.017 \text{ cm}^{-1}=0.84 \pm 0.02 \text{ K} \ , \tag{2.8a}$$

$$\Gamma_{D_2}=0.747 \pm 0.019 \text{ cm}^{-1}=1.07 \pm 0.03 \text{ K} \ . \tag{2.8b}$$

These values are in a good agreement with other experimental values.

The order parameter is a measure of ordering of average molecular quadrupolar moments. We define it as follows

$$\begin{aligned}\sigma &= -(20\pi)^{1/2}\frac{1}{N_0}\sum_i \langle Y_{20}(\hat{\omega}_i)\rangle \\ &= -\frac{5}{2}\frac{1}{N_0}\sum_i \langle 3\cos^2\theta_i - 1\rangle \ ,\end{aligned} \tag{2.9}$$

where N_0 is the number of molecules in the crystal, and $\langle \cdots \rangle$ denotes the ensemble average. Because of the symmetry of the $Pa3$ space group we have that $\langle Y_{20}(\hat{\omega}_i)\rangle$ is the same for each orientational sublattice, and therefore,

$$\sigma = -\tfrac{5}{2}\langle 3\cos^2\theta - 1\rangle \ , \tag{2.10}$$

where the axial angle θ is related to any molecule. In the manifold $J_i=1$, we obtain

$$\sigma_{J=1}=\frac{1}{N_0}\sum_i \langle O_i^0\rangle = \langle O^0\rangle \ . \tag{2.11}$$

Because of a small admixture of $J_i=3$ states to $J_i=1$ state, σ differs only slightly from $\sigma_{J=1}$. The correction due to $J_i=1 \rightarrow J_i=3$ virtual transition can be taken into account by multiplying of $\sigma_{J=1}$ by a factor ξ_{rot} equal to 1.025 for H_2 and 1.063 for D_2 (see Appendix A). The further renormalization of $\sigma_{J=1}$ is caused by the interaction of the "zero-point" phonon modes with librational degrees of freedom. Harris[15,32] found that then the order parameter is reduced by a factor $\xi_{\text{ph}}=0.98$. So, we have

$$\sigma = \xi_{\text{ph}}\xi_{\text{rot}}\sigma_{J=1} \ . \tag{2.12}$$

The problem now is to separate the effective single-body part H_0 from the Hamiltonian (2.5). Using relations

$$\langle O_i^m\rangle = \delta_{m0}\sigma_{J=1} \tag{2.13a}$$

and

$$\sum_j \gamma_{ij}^{0m} = \sum_j \gamma_{ji}^{m0} = \delta_{m0}\sum_j \gamma_{ij}^{00} \ , \tag{2.13b}$$

which follow from symmetry considerations,[33] we have

$$H_0 = \epsilon \sum_i (J_i^z)^2 \ , \tag{2.14}$$

where

$$\epsilon = -\tfrac{1}{2}\sigma_{J=1}\epsilon_0 \tag{2.15a}$$

and

$$\epsilon_0 = -12\sum_j \gamma_{ij}^{00} \ . \tag{2.15b}$$

If the sum (2.15b) is restricted to the nearest neighbors only, one obtains[20]

$$\epsilon_0 = 19\Gamma \ . \tag{2.16}$$

Taking into account further-neighbor interactions we have[34]

$$\epsilon_0 = 21.20\Gamma \ . \tag{2.17}$$

Introducing the operators

$$\delta O_i^m = O_i^m - \langle O_i^m\rangle \tag{2.18}$$

of the deviations of O_i^m from their average values we write the two-body part of H (2.5) in the form

$$V = \sum_{ij}\sum_{mn} \gamma_{ij}^{mn}\delta O_i^m \delta O_j^n \ . \tag{2.19}$$

In the following, we will assume that $\gamma_{ij}^{mn} \neq 0$ only for nearest neighbors. The total Hamiltonian can be written as follows

$$H = E + H_0 + V \ , \tag{2.20}$$

where

$$E = -\sigma_{J=1}(\sigma_{J=1}+4)\sum_{ij}\gamma_{ij}^{00} \tag{2.21}$$

is the energy of the mean-field ground state.

III. METHOD

The quantities, employed in our method, are the many-point IGF's. They can be defined by means of the generating functional as follows:

$$K(x_1, \ldots, x_k) = \left.\frac{\delta^k \Phi[q]}{\delta q(x_1)\cdots\delta q(x_k)}\right|_{q(x)=0} \ , \tag{3.1}$$

where $K(x_1, \ldots, x_k)$ is the k-point IGF, $x_l = (i_l, m_l, \tau_l)$ $(1 \leqslant l \leqslant k)$, i_l denote a site in a crystal lattice, $m_l = 0, \pm 1, \pm 2$ and $0 \leqslant \tau \leqslant \beta$ is the thermodynamical "time", $q(x)$ is a test function, and $\Phi[q]$ is the generating functional defined as

$$\Phi[q] = \ln Q[q] \ , \tag{3.2}$$

where

$$Q[q]=\mathrm{Tr}e^{-\beta H}T_\tau e^{(\delta\tilde{O},q)} \quad . \tag{3.3}$$

H is the Hamiltonian of the system defined by Eq. (2.5) or (2.20), β is the inverse temperature, T_τ denotes the τ ordering operator,

$$(\delta\tilde{O},q)=\int dx\,\delta\tilde{O}(x)q(x)$$

$$=\sum_i \sum_{m=0,\pm1,\pm2}\int_0^\beta d\tau\,\delta\tilde{O}_i^m(\tau)q_i^m(\tau)\ . \tag{3.4}$$

$\delta\tilde{O}(x)=\delta\tilde{O}_i^m(\tau)=e^{\tau H}\delta O_i^m e^{-\tau H}$ is the operator δO_i^m (2.18) in the Heisenberg representation, and $\int dx\cdots$ denotes the "integration" over the x argument, i.e.,

$$\int dx\cdots=\sum_i \sum_{m=0,\pm1,\pm2}\int_0^\beta d\tau\ldots \quad . \tag{3.5}$$

From Eqs. (3.1)–(3.4), it is easy to see that

$$K(x_1,\ldots,x_k)=K(i_1,m_1,\tau_1;\ldots;i_k,m_k,\tau_k)$$
$$=\langle T_\tau\delta\tilde{O}_{i_1}^{m_1}(\tau_1)\ldots\delta\tilde{O}_{i_k}^{m_k}(\tau_k)\rangle \text{ for } k\leqslant 3\ , \tag{3.6}$$

where $\langle\cdots\rangle=\mathrm{Tr}e^{-\beta H}\cdots/\mathrm{Tr}e^{-\beta H}$. For $k>3$ the relation between $\langle T_\tau\delta\tilde{O}_{i_1}^{m_1}(\tau_1)\cdots\delta\tilde{O}_{i_k}^{m_k}(\tau_k)\rangle$ and IGF's is similar, but more complicated than the relation between the statistical moments and cumulants, respectively.

It is a standard procedure to obtain the functional $Q[q]$ (3.3) in the interaction representation, i.e.,

$$Q[q]=e^{-\beta E}\,\mathrm{Tr}e^{-\beta H_0}T_\tau\exp\left\{(\delta O,q)-\int_0^\beta d\tau\,V(\tau)\right\}$$
$$=e^{-\beta E}\,\mathrm{Tr}e^{-\beta H_0}T_\tau\exp[(\delta O,q)-(\delta O,\hat{\gamma},\delta O)]\ , \tag{3.7}$$

where

$$(\delta O,q)=\int dx\,\delta O(x)q(x)\ , \tag{3.8}$$

$$\delta O(x)=\delta O_i^m(\tau)=e^{\tau H_0}\delta O_i^m e^{-\tau H_0}\ , \tag{3.9}$$

H_0 is the mean-field Hamiltonian (2.14), the constant E is defined by Eq. (2.21),

$$V(\tau)=e^{\tau H_0}Ve^{-\tau H_0}\ , \tag{3.10}$$

where V is the interaction Hamiltonian (2.19),

$$(\delta O,\hat{\gamma}\delta O)=\int\gamma(x,y)\delta O(x)\delta O(y)\,dx\,dy$$
$$=\sum_{ij}\sum_{mn}\gamma_{ij}^{mn}\int_0^\beta d\tau\,\delta O_i^m(\tau)\delta O_j^n(\tau)\ , \tag{3.11}$$

and γ_{ij}^{mn} is an EQQ coupling constant. Here $\hat{\gamma}$ is an integral operator with a kernel $\gamma(x,y)$ defined as

$$\gamma(x,y)=\gamma_{ij}^{mn}\delta(\tau-\tau')\ , \tag{3.12}$$

where $x=(i,m,\tau)$ and $y=(j,n,\tau')$.

It is easy to see that the left-hand side of Eq. (3.7) can be represented in the functional form as follows:

$$Q[q]=e^{-\beta E}\,\mathrm{Tr}\,e^{-\beta H_0}$$
$$\times\exp\left[-\left(\frac{\delta}{\delta q},\hat{\gamma}\frac{\delta}{\delta q}\right)\right]e^{\Phi_0[q]}, \tag{3.13}$$

where

$$\left(\frac{\delta}{\delta q},\hat{\gamma}\frac{\delta}{\delta q}\right)=\int dx\,dy\,\gamma(x,y)\frac{\delta}{\delta q(x)}\frac{\delta}{\delta q(y)}$$
$$=\sum_{ij}\sum_{mn}\int_0^\beta d\tau\,\gamma_{ij}^{mn}\frac{\delta}{\delta q_i^m(\tau)}\frac{\delta}{\delta q_j^n(\tau)}\ , \tag{3.14}$$

$$\Phi_0[q]=\ln Q_0[q]\ , \tag{3.15}$$

and

$$Q_0[q]=\mathrm{Tr}\,e^{-\beta H_0}\tau e^{(\delta O,q)}\ . \tag{3.16}$$

The expansion of $\exp[-(\delta/\delta q,\hat{\gamma}\delta/\delta q)]$ into a power series with respect to $\hat{\gamma}$ leads to a complicated series for $Q[q]$, containing such quantities as the coupling $\gamma(x,y)$, the test functions $q(x)$ and zeroth-order irreducible Green's functions (ZOIGF's) defined for k variables $x_1,\ldots,x_k$ as follows:

$$K_0(x_1,\ldots,x_k)=\left.\frac{\delta^k\Phi_0[q]}{\delta q(x_1)\cdots\delta q(x_k)}\right|_{q(x)=0}\ . \tag{3.17}$$

Note, that $K_0(x_1,\ldots,x_k)$ is restricted to a common site in a crystal lattice, e.g.,

$$K_0(x_1,\ldots,x_k)=K_0(i_1,m_1,\tau_1;\ldots;i_k,m_k,\tau_k)$$
$$=\delta_{ii_1}\delta_{i_1i_2}\cdots\delta_{i_{k-1}i_k}$$
$$\times K_0(i,m_1,\tau_1;\ldots;i,m_k,\tau_k)\ . \tag{3.18}$$

This fact can be easy proved. The functional $Q_0[q]$ (3.15) can be written as follows:

$$Q_0[q]=\prod_i Q_0[q_i]\ , \tag{3.19}$$

where

$$Q_0[q_i]=\mathrm{Tr}\,e^{-\beta H_0(i)}T_\tau\,e^{\{\delta O_i,q_i\}}\ , \tag{3.20}$$

with

$$H_0(i)=\epsilon(J_i^z)^2\ , \tag{3.21}$$

and

$$\{\delta O_i,q_i\}=\sum_m\int_0^\beta d\tau\,\delta O_i^m(\tau)q_i^m(\tau)\ . \tag{3.22}$$

Now, $\Phi_0[q]$ takes the form

$$\Phi_0[q]=\sum_i\Phi_0[q_i]\ , \tag{3.23}$$

where

$$\Phi_0[q_t] = \ln Q_0[q_t] . \tag{3.24}$$

Taking into account Eq. (3.17) we obtain Eq. (3.18) as an obvious consequence of Eq. (3.23).

The functional series for $Q[q]$ can be represented in a simple form using a graphical notation. We introduce the elements (a), (b), and (c) shown in Fig. 1, which correspond to $\gamma(x,y)$, $K_0(x_1,\ldots,x_k)$, and $q(x)$, respectively. Each term of an expansion for $Q[q]$ can be represented as a diagram in which the oval blocks [Fig. 1(b)], are connected by the interaction lines [Fig. 1(a)]. Some vertices in the oval blocks contain dotted lines [Fig. 1(c)]. The vertices in such a diagram are not labeled. This means that the "integration" in the sense of definition (3.5) over the variables assigned to these vertices must be performed. The functional $Q[q]$ can be expanded into connected as well as disconnected diagrams. By virtue of the Mayer theorem (cf., for example, Ref. 35) the diagrammatic series for the functional $\Phi[q]$ (3.2) does not contain disconnected diagrams. The diagrammatic series for $\Phi[q]$ can be formally written as

$$\Phi[q] = -\beta E + \Phi_0[q] + \sum_{n=1} \frac{(-2)^n}{n!} \sum_{\{G_n\}} \frac{2^n n!}{P(G_n)} G_n , \tag{3.25}$$

where G_n denotes the expression associated with the connected diagram G_n having n interaction lines, $\sum_{\{G_n\}}$ denotes the summation over all connected and topologically distinct diagrams with n interaction lines, and $P(G_n)$ is the number of the transformations of the diagram G_n into itself. We note, that the coefficient $2^n n!/P(G_n)$ is the number of the diagrams being topologically equivalent to the given diagram G_n. It is easy to see that each diagram for the k-point IGF defined by Eq. (3.1) must contain k external vertices,[36] representing the variables $x_1,\ldots,x_k$ and no $q(x)$ line.

At this stage, we can discuss the diagrammatic series for the orientational free energy defined as

$$F = -\beta^{-1} \ln Q , \tag{3.26}$$

where

$$Q = \mathrm{Tr}\, e^{-\beta H} . \tag{3.27}$$

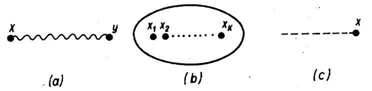

FIG. 1. (a) Diagrams representing the coupling $\gamma(x,y)$, (b) many-point ZOIGF $K_0(x_1,\ldots,x_k)$, and (c) test function $q(x)$.

From Eqs. (3.26), (3.27), (3.2), and (3.3) it is easy to see that

$$F = -\beta^{-1}\Phi[q=0] . \tag{3.28}$$

Taking into account Eqs. (3.28) and (3.25) we can write

$$F = E + F_0 + \Delta F , \tag{3.29}$$

where

$$F_0 = -\beta^{-1}\Phi_0[q=0] = -\beta^{-1} \ln \mathrm{Tr}\, e^{-\beta H_0} \tag{3.30}$$

and

$$\Delta F = -\beta^{-1}\Delta\Phi[q=0] . \tag{3.31}$$

Here. $\Delta\Phi[q=0]$ is the sum of the diagrams without $q(x)$ lines and external vertices. The diagrams can be classified according to powers of $1/z$, where $z=12$ is the number of nearest neighbors of a site in fcc lattice.[37] The $1/z$ expansion scheme, which we shall discuss, is valid near the temperature of the orientational phase transition. It is clear that the diagram with n interaction lines corresponds to an expression in which an n-fold integration over "times" $\tau_1,\ldots,\tau_n$ must be performed. This is an obvious consequence of the locality of EQQ coupling $\gamma(x,y)$ with respect to the τ arguments [see Eq. (3.12)]. Therefore, the expression associated with the diagram having n interaction lines is proportional to the integral

$$\int_0^\beta (\cdots)\, d\tau_1 \cdots d\tau_n . \tag{3.32}$$

From a rough estimation based on the MF theory[16,17] it follows that the inverse critical temperature β_c of the orientational phase transition is of first order in $1/z$. Thus, when $\beta \simeq \beta_c$ the integral (3.32) is of nth order in $1/z$. Each summation over nearest neighbors gives the contribution proportional to z. When a given diagram has n interaction lines and the expression associated with it contains m summation over nearest neighbors then the resulting factor in $1/z$ is $(1/z)^{n-m}$. The corrections of first order in $1/z$ to the free energy corresponds to the sum of diagrams shown in Fig. 2. The number $P(G_n)$ for such a diagram with n interaction lines is $2n$. Introducing the Fourier transform of the ZOIGF $K_0(i,m,\tau;i,n,\tau')$, defined as

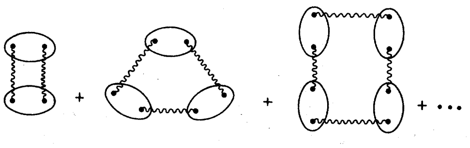

FIG. 2. Sum of the diagrams representing the first-order correction in $1/z$ to the orientational free energy.

$$K_0(i,m;i,n;\omega_\nu)=\int_0^\beta d\tau\, e^{i\omega_\nu\tau}K_0(i,m;i,n;\tau)\,, \qquad (3.33)$$

where $\omega_\nu=2\pi\nu/\beta$, $\nu=0,\pm1,\pm2,\pm3,\ldots$, and

$$K_0(i,m;i,n;\tau)=K_0(i,m,\tau;i,n,0)=\langle T_\tau O_i^m(\tau)O_i^n\rangle_0 - \langle O_i^m\rangle_0\langle O_i^n\rangle_0\,, \qquad (3.34)$$

we attribute to G_n the following expression:

$$\frac{1}{2}\sum_{m,m_1,\ldots,m_{n-1}}\;\sum_{n,n_1,\ldots,n_{n-1}}\;\sum_{i,i_1,\ldots,i_{n-1}}\;\sum_{\omega_\nu}K_0(i,m;i,n;\omega_\nu)\gamma_{ii_1}^{mn_1}K_0(i_1,n_1;i_1,m_1;\omega_\nu) \times\gamma_{i_1i_2}^{m_1n_2}\cdots K_0(i_{n-1},n_{n-1};i_{n-1},m_{n-1};\omega_\nu)\gamma_{i_{n-1},i}^{m_{n-1},n}\,. \qquad (3.35)$$

IV. FREE ENERGY AND ORDER PARAMETER FOR THE ORDERED PHASE

First, we calculate the Fourier-transformed two-point ZOIGF's which are represented in Fig. 2 by the oval blocks. Taking into account Eqs. (3.17), (3.33), and (3.34) we have

$$K_0(i,m;i,n;\omega_\nu)=\int_0^\beta d\tau\, e^{i\omega_\nu\tau}\langle T_\tau O_i^m(\tau)O_i^n\rangle_0 - \beta\langle O_i^m\rangle_0\langle O_i^n\rangle_0\delta_{\nu,0}\,. \qquad (4.1)$$

After straightforward calculations one obtains

$$K_0(i,m;i,n;\omega_\nu)=\delta_{m,-n}K_0(m,\omega_\nu)\,, \qquad (4.2)$$

where

$$K_0(\pm1,\omega_\nu)=2\sigma_0\epsilon/[(i\omega_\nu)^2-\epsilon^2]\,, \qquad (4.3)$$

$$K_0(\pm2,\omega_\nu)=\tfrac{2}{3}\beta(\sigma_0+2)\delta_{\nu,0}\,, \qquad (4.4)$$

and

$$K_0(0,\omega_\nu)=\beta(1-\sigma_0)(\sigma_0+2)\delta_{\nu,0}\,, \qquad (4.5)$$

where

$$\sigma_0=-2(e^{\beta\epsilon}-1)(e^{\beta\epsilon}+2)^{-1}\,. \qquad (4.6)$$

From Eqs. (4.4) and (4.5) we see that the ZOIGF's $K_0(m,\omega_\nu)$ for $m=0,\pm2$ are proportional to σ_0+2, which is a small parameter, as it will be shown below. Therefore, the contribution to ΔF, due to a given diagram from the series shown in Fig. 2, decreases as the number of the oval blocks associated with $K_0(m,\omega_\nu)$ for $m=0,\pm2$ increases. In order to estimate (σ_0+2) we assume that near the orientational phase transition $\sigma\simeq-1.7$ and the critical temperature T_c is approximately equal to $0.5T_0$, where $T_0=\epsilon_0/4\ln 2$ is the critical temperature obtained from the MF theory.[17] The straightforward calculation yields that σ_0+2 is the order of 0.1 and it is really a small parameter.

The next problem is to estimate the contribution due to the oval blocks from Fig. 2 representing $K_0(m,\omega_\nu)$ for $m=\pm1$. Note, that such a block with two adjacent interaction lines corresponds to the expression

$$\frac{2\sigma_0\epsilon}{(i\omega_\nu)^2-\epsilon^2}\sum_j(\gamma_{ij}^{m1}\gamma_{jk}^{-1,n}+\gamma_{ij}^{m,-1}\gamma_{jk}^{1n})\,. \qquad (4.7)$$

The value of (4.7) is well estimated by

$$\epsilon_0^{-1}\sum_j(|\gamma_{ij}^{m1}|^2+|\gamma_{ij}^{m,-1}|^2)\,. \qquad (4.8)$$

Taking the γ constants from Ref. 33 we obtain that (4.8) is of the order of 0.1, and therefore, it can be treated as a small parameter. From the considerations above we conclude that the first diagram from Fig. 2 contributes mainly to ΔF since it is of lowest order with respect to the small parameters (4.8) and (σ_0+2). Therefore, it seems reasonable to simplify our problem retaining only this diagram and neglecting the contribution of other diagrams containing three or more oval blocks. Of course, this approximation is valid for the ordered phase. The expression for ΔF is then the following:

$$\Delta F=-\frac{1}{4\beta}\sum_{ij}\sum_{mn}\sum_{\omega_\nu}|\gamma_{ij}^{mn}|^2K_0(m,\omega_\nu)K_0(n,\omega_\nu)\,. \qquad (4.9)$$

After straightforward although tedious calculations Eq. (4.9) takes the form

$$\frac{\Delta F}{N_0\Gamma}=-\frac{2\beta}{(e^{\beta\epsilon}+2)^2}\sum_{m\geq n}c_{mn}F_{mn}(\beta\epsilon)\,, \qquad (4.10)$$

where $m,n=0,1,2$, N_0 is the number of molecules in the crystal, Γ is the EQQ-coupling parameter (2.8a) or (2.86b),

$$F_{22}(x)=16\,, \qquad (4.11\text{a})$$

$$F_{21}(x)=32x^{-1}(e^x-1)\,, \qquad (4.11\text{b})$$

$$F_{20}(x)=72e^x(e^x+2)^{-1}\,, \qquad (4.11\text{c})$$

$$F_{11}(x)=4x^{-1}(e^{2x}+2xe^x-1)\,, \qquad (4.11\text{d})$$

$$F_{10}(x)=72x^{-1}e^x(e^x-1)(e^x+2)^{-1}\,, \qquad (4.11\text{e})$$

$$F_{00}(x)=81e^{2x}(e^x+2)^{-2}\,, \qquad (4.11\text{f})$$

and

$$c_{mn}=\sum_j(|\gamma_{ij}^{mn}|^2+|\gamma_{ij}^{-m,n}|^2)\,. \qquad (4.12)$$

The sum in Eq. (4.12) runs over the nearest neighbors of the ith site. In order to calculate c_{mn}, the following relations are helpful (cf. Ref. 33):

$$c_{00}=24|\gamma^{00}|^2\,, \tag{4.13a}$$

$$c_{11}=12(|\gamma^{11}|^2+|\gamma^{1,-1}|^2)\,, \tag{4.13b}$$

$$c_{22}=12(|\gamma^{22}|^2+|\gamma^{2,-2}|^2)\,, \tag{4.13c}$$

$$c_{10}=12(|\gamma^{10}|^2+|\gamma^{01}|^2)\,, \tag{4.13d}$$

$$c_{20}=12(|\gamma^{20}|^2+|\gamma^{02}|^2)\,, \tag{4.13e}$$

and

$$c_{21}=6(|\gamma^{21}|^2+|\gamma^{12}|^2+|\gamma^{2,-1}|^2+|\gamma^{-1,2}|^2)\,, \tag{4.13f}$$

where γ^{mn} is the constant of the EQQ interaction for the sites connected by the vector$(\frac{1}{2},\frac{1}{2},0)$.

In order to obtain the total free energy F (3.29) we must calculate the molecular-field free energy F_0 (3.30). Taking into account Eqs. (3.30) and (2.14), we get

$$F_0/N_0\Gamma=-(\beta\Gamma)^{-1}\ln(1+2e^{-\beta\epsilon}) \tag{4.14}$$

and

$$\frac{F}{N_0\Gamma}=\frac{\epsilon_0}{12\Gamma}\sigma_{J=1}(\sigma_{J=1}+4)$$
$$-\frac{1}{\beta\Gamma}\ln(1+2e^{-\beta\epsilon})+\frac{\Delta F}{N_0\Gamma}\,. \tag{4.15}$$

The equation for the order parameter $\sigma_{J=1}$ is obtained using the condition

$$\frac{\partial F}{\partial\sigma_{J=1}}=0\,. \tag{4.16}$$

After straightforward calculations in Eq. (4.16) takes the form

$$\sigma_{J=1}=-2(e^{\beta\epsilon}-1)(e^{\beta\epsilon}+2)^{-1}$$
$$+12\beta^2(e^{\beta\epsilon}+2)^{-3}\sum_{m\geq n}c_{mn}f_{mn}(\beta\epsilon)\,, \tag{4.17}$$

where $m,n=0,1,2,$

$$f_{22}(x)=16e^x\,, \tag{4.18a}$$

$$f_{21}(x)=16x^{-2}[e^{2x}(x+1)-e^x(4x-1)-2]\,, \tag{4.18b}$$

$$f_{20}(x)=72e^x(e^x-1)(e^x+2)^{-1}\,, \tag{4.18c}$$

$$f_{11}(x)=2x^{-2}[e^{3x}+2e^{2x}(x-1)^2$$
$$-e^x(4x^2+2x+2)-2]\,, \tag{4.18d}$$

$$f_{10}(x)=36x^{-2}e^x[e^{2x}(x+1)-e^x(6x-1)$$
$$+2(x-1)](e^x+2)^{-1}\,, \tag{4.18e}$$

and

$$f_{00}(x)=81e^{2x}(e^x-2)(e^x+2)^{-2}\,. \tag{4.18f}$$

Equation (4.17) was solved numberically for $\epsilon_0=21.2\Gamma$. The values of constants γ^{mn} are taken from Ref. 33. The plot of $\sigma_{J=1}$ versus the reduced temperature T/T_0 is presented in Fig. 3, where T_0 denotes the critical temperature obtained from the MF theory.[17] Equation (4.17) has three solutions represented in Fig. 3 by the lines A, B, and C. The solution C is zero at all temperatures and corresponds to the phase with no long-range orientational ordering. The nonzero solutions A and B exist below the temperature $T_1=0.60\ T_0$, which is the maximum limit of metastability for the ordered phase.

V. FREE ENERGY AND THE PROBLEM OF STABILITY OF THE DISORDERED PHASE

In order to calculate free energy in $1/z$ approximation for the disordered phase ($\sigma=0$), we must sum the whole diagrammatic series shown in Fig. 2. In general, the problem is complicated, however some simplifications can be made. Note, that for $\sigma=0$ the ZOIGF's (4.3)–(4.5) takes the form

$$K_0(\pm1,\omega_\nu)=K_0(\pm2,\omega_\nu)=\tfrac{4}{3}\beta\delta_{\nu,0}\,, \tag{5.1}$$

$$K_0(0,\omega_\nu)=2\beta\delta_{\nu,0}\,. \tag{5.2}$$

The constant $\gamma_{ij}^{m,-n}$ can be written as follows [cf. Eqs. (2.6) and (2.2)]

$$\gamma_{ij}^{m,-n}=(-1)^nA_mA_{-n}\{\hat{D}^+(\hat{\chi}_i)\hat{a}_{ij}\hat{D}(\hat{\chi}_j)\}_{m,n}\,, \tag{5.3}$$

where $\hat{D}(\hat{\chi}_i)$and $\hat{a}_{ij}$ are the 5×5 matrices defined as follows:

$$\{\hat{D}(\hat{\chi}_i)\}_{M,m}=D^2_{Mm}(\hat{\chi}_i) \tag{5.4}$$

and

$$\{\hat{a}_{ij}\}_{M,N}=(-1)^N\tfrac{1}{18}(70\pi)^{1/2}$$
$$\times\Gamma_{ij}C(224;M,-N)Y_{4,M-N}(\Omega_{ij})^*\,, \tag{5.5}$$

where $m,M,N=0,\pm1,\pm2$.

Now, it is convenient to attribute to the oval blocks in diagrams from Fig. 2 the following quantity:

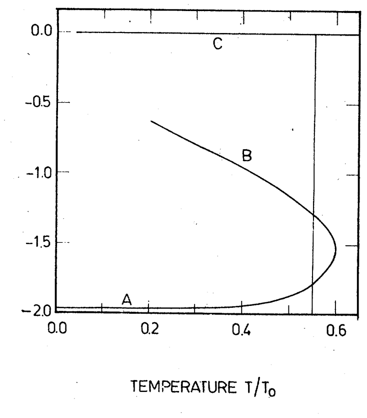

FIG. 3. Order parameter $\sigma_{J=1}$ vs the reduced temperature T/T_0. The lines A, B, and C represent the solutions of Eq. (4.17). The vertical line marks the first-order phase transition.

$$(-1)^m K_0(m,\omega_\nu) A_m A_{-m} = 2\beta\delta_{\nu,0}\,, \tag{5.6}$$

instead of $K_0(m,\omega_\nu)$. Then, the interaction line is connected with

$$\{\hat{D}^+(\hat{\chi}_i)\hat{a}_{ij}\hat{D}(\hat{\chi}_j)\}_{m,n}\,. \tag{5.7}$$

In the terms of the matrices $\hat{D}(\hat{\chi}_i)$ and $\hat{a}_{ij}$, the expression associated with the diagrammatic series for ΔF can be written as follows:

$$\begin{aligned}\Delta F &= \frac{1}{2\beta}\sum_{n=1}^{\infty}\frac{(-4\beta)^{n+1}}{n}\sum_{i,i_1\cdots i_{n-1}}\mathrm{Tr}[\hat{D}^+(\chi_i)\hat{a}_{ii_1}\hat{D}(\hat{\chi}_{i_1})\cdots\hat{D}^+(\chi_{i_{n-1}})(\hat{a}_{i_{n-1},i}\hat{D}(\hat{\chi}_i)]\\ &= \frac{1}{2\beta}\sum_{n=1}^{\infty}\frac{(-4\beta)^{n+1}}{n}\sum_{i,i_1\cdots i_n}\mathrm{Tr}(\hat{a}_{ii_1}\cdots\hat{a}_{i_{n-1},i})\,.\end{aligned} \tag{5.8}$$

We now introduce the Fourier-transformed matrix $\hat{a}(\vec{k})$ defined as

$$\hat{a}(\vec{k}) = \sum_{\vec{R}_{ij}} e^{i\vec{k}\cdot\vec{R}_{ij}}\hat{a}_{ij}\,, \tag{5.9}$$

where $\sum_{\vec{R}_{ij}}$ is the sum over the nearest neighbors of the ith site. The elements of $\hat{a}(\vec{k})$ are tabulated in Appendix B. Using the matrix $\hat{a}(\vec{k})$, we can write Eq. (5.8) in the form

$$\begin{aligned}\Delta F &= \frac{1}{2\beta}\sum_{n=1}^{\infty}\frac{(-4\beta)^{n+1}}{n}\sum_{\vec{k}}\mathrm{Tr}[\hat{a}(\vec{k})]^n\\ &= \frac{1}{2\beta}\sum_{\vec{k}}\mathrm{Tr}\ln[1+4\beta\hat{a}(\vec{k})]\\ &= \frac{1}{2\beta}\sum_{\vec{k}}\ln\det[1+4\beta\hat{a}(\vec{k})]\,.\end{aligned} \tag{5.10}$$

If we take into account that

$$a(\vec{k}) = a(-\vec{k})\,, \tag{5.11}$$

the expression for ΔF can be rewritten as follows:

$$\begin{aligned}\Delta F &= \frac{1}{2\beta}\ln\det[1+4\beta\hat{a}(0)]\\ &\quad + \frac{1}{2\beta}\sum_{\vec{k}\neq 0}\ln\{\det[1+4\beta\hat{a}(\vec{k})]\}^2\,,\end{aligned} \tag{5.12}$$

where $\sum_{\vec{k}\neq 0}$ runs over half of the Brillouin zone for the fcc lattice.

The temperature T_2 which is the minimum limit of metastability of disordered phase can be obtained from the following considerations. Let us write $\ln\det[1+4\beta\hat{a}(0)]$ in the form

$$\ln\det[1+4\beta\hat{a}(0)] = \sum_{\lambda=1}^{5}\ln[1+4\beta\hat{a}_\lambda(0)]\,, \tag{5.13}$$

where $a_\lambda(0)$ is the eigenvalue of the matrix $\hat{a}(0)$. The quantity (5.13) has a real value when $[1+4\beta a_\lambda(0)]>0$ for each $\lambda = 1,\ldots,5$. This condition is satisfied at temperatures higher than the certain temperature T_2 which is determined as

$$T_2 = -4\min_\lambda a_\lambda(0)\,. \tag{5.14}$$

Since the minimum eigenvalue of $4\hat{a}(0)/T_0 = -0.46$ (see Appendix B), we have

$$T_2 = 0.46 T_0\,. \tag{5.15}$$

It is easy to see that for $T > T_2$, ΔF (5.10) has a real value and T_2 may be regarded as the minimum limit of metastability for the disordered phase. The same result one obtains by investigating of the isothermal susceptibility for $\vec{k}=0$ which is made in Appendix C.

Note that Eq. (5.12) is equivalent to the following:

$$\begin{aligned}\frac{\Delta F}{N_0} &= \frac{1}{2\beta}\sum_{\vec{k}}\ln|\det[1+4\beta\hat{a}(\vec{k})]|\\ &= \frac{1}{2\beta}\frac{\Omega}{(2\pi)^3}\int d^3k\,\ln|\det[1+4\beta\hat{a}(\vec{k})]|\,,\end{aligned} \tag{5.16}$$

where Ω is the volume of the elementary cell of the fcc lattice. For the numerical calculation of $\Delta F/N_0\Gamma$ we use Eq. (5.16). Putting

$$\vec{k} = x_1\vec{\kappa}_1 + x_2\vec{\kappa}_2 + x_3\vec{\kappa}_3\,, \tag{5.17}$$

where $\vec{\kappa}_1$, $\vec{\kappa}_2$, $\vec{\kappa}_3$ are the basis vectors of the inverse lattice and $-\frac{1}{2} < x_1, x_2, x_3 < \frac{1}{2}$ we transform Eq. (5.16) to the form

$$\frac{\Delta F}{N_0} = \frac{1}{2\beta}\int_{-1/2}^{1/2}dx_1\int_{-1/2}^{1/2}dx_2\int_{-1/2}^{1/2}dx_3\,\ln|\det[1+4\beta\hat{a}(x_1,x_2,x_3)]|\,. \tag{5.18}$$

In order to calculate the threefold integral in Eq. (5.18) we apply the Gauss method with $n=2$ (cf. for example, Ref. 38) for each integration. The total free energy per one molecule is the following

$$F/N_0 = -(1/\beta)\ln 3 + \Delta F\,, \tag{5.19}$$

where $(-1/\beta)\ln 3$ is the molecular-field free energy of the disordered phase.

VI. DISCUSSION AND RESULTS

The stability of the three phases A, B, and C corresponding to the solutions of Eq. (4.17) (see Fig. 3) are investigated by comparing of the free energies of these phases. The plot of $F/N_0\Gamma$ versus the reduced temperature T/T_0 is presented in Fig. 4. The lines A, B, and C refer to the phases A, B, and C, respectively. At the temperature T_c near the maximum limit of metastability for the ordered phase $T_1 = 0.60T_0$ line C intersects line A. When the temperature is less than T_c, phase A is stable, whereas above T_c phase A destabilizes and disordered phase C becomes stable. At T_c two phases A and C coexist. From Fig. 3, it is seen that at T_c, marked by the vertical line, the order parameter $\sigma_{J=1}$ varies discontinuously from the value characteristic for the phase A to zero. Thus, we conclude that T_c is the critical temperature of the first-order orientational phase transition. The value T_c is estimated as $T_c = 0.57T_0$. Phase B is not stable and rather does not correspond to the physical situation. Therefore it does not matter that curve B implies a negative heat capacity.

The plot of σ_{D_2} vs T/T_0 is represented in Fig. 5. Here σ_{D_2} denotes the order parameter for solid para-D_2 with zero-phonon and $J_i = 1 \rightarrow J_i = 3$ corrections calculated as

$$\sigma_{D_2} = \xi_{ph}\xi_{rot}\sigma_{J=1}, \tag{6.1}$$

where $\xi_{rot}(D_2) = 1.063$ (see Appendix A) and $\xi_{ph} = 0.98$.[15,32] The dashed line in Fig. 5 shows the variation σ_{D_2} with T/T_0 obtained via measurement of Pake doublet splitting[14] and extrapolation of the data to pure para-D_2. We see that our results are in a good agreement with the experiment. Taking the EQQ-coupling parameters as $\Gamma_{H_2} = 0.84$ K and $\Gamma_{D_2} = 1.07$ K we obtain the following values of transition temperature

$$T_c(H_2) = 3.64 \text{ K} \quad \text{and} \quad T_c(D_2) = 4.63 \text{ K},$$

whereas the values obtained from the extrapolation of experimental data are

$$T_c(H_2) = 2.8 \text{ K} \quad \text{and} \quad T_c(D_2) = 3.8 \text{ K}.$$

The comparison of our results with previous theories is shown in Fig. 6, where the plots of $\sigma_{J=1}$ versus reduced temperature T/T_0 are presented. The lines A, B, C, and D are obtained from our theory (A), cluster expansion method[23] (B), the Kirkwood technique of restricted traces[24] (C), and

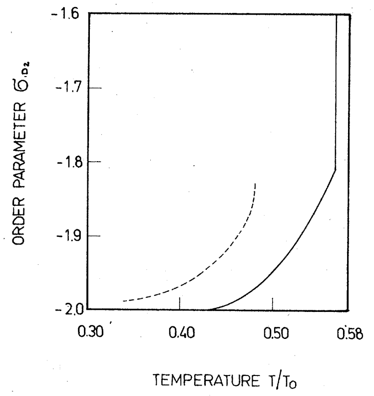

FIG. 5. Renormalized order parameter σ_{D_2} of solid para-D_2 vs reduced temperature T/T_0 (solid line). The order parameter σ_{D_2} obtained from NMR experiment (Ref. 14) (dashed line).

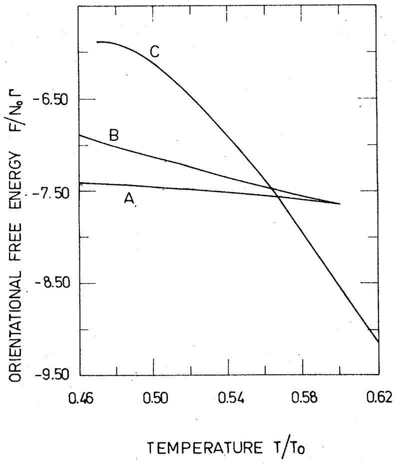

FIG. 4. Orientational free energies per molecule scaled by EQQ coupling parameter Γ vs the reduced temperature T/T_0. The lines A and B correspond to the branches A and B of the solution of Eq. (4.17), and line C represents $F/N_0\Gamma$ for the disordered phase.

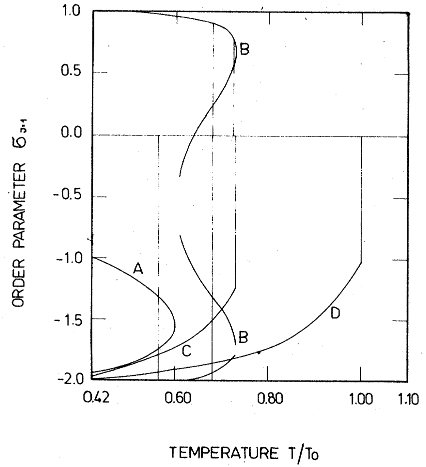

FIG. 6. Order parameter $\sigma_{J=1}$ vs the reduced temperature T/T_0: A—present theory, B—cluster-expansion method, (Ref. 23), C—the Kirkwood technique of restricted traces (Ref. 24), and D—molecular-field theory (Ref. 17).

MF theory[17] (D). The vertical lines mark the first-order transitions. From Fig. 6, we see that the present method yields the most exact value of T_c.

In summary, we conclude that the diagrammatic method presented above is a useful tool for the systematic investigation of cooperative phenomena in spinlike systems. This method can be also applied to study of the elementary excitations which can be done by the diagrammatic expansion of two-point IGF's. We hope that this approach will be helpful in derivation of the libron spectrum in solid ortho-H_2 and para-D_2 at nonzero temperature. This work is in progress.

APPENDIX A: EFFECT OF $J=1 \rightarrow J=3$ VIRTUAL TRANSITION ON ORDER PARAMETER

Let us write the Hamiltonian (2.1) in the form

$$H = H_0 + H_1 , \tag{A1}$$

where

$$H_0 = -(20\pi)^{1/2} x \sum_i Y_{20}(\hat{\omega}_i) \tag{A2}$$

is the mean-field part of H, $H_1 = H - H_0$ and

$$x = 2\sigma \sum_j \gamma_{ij}^{00} . \tag{A3}$$

The order parameter σ can be written as

$$\sigma = \frac{\partial F}{\partial x} , \tag{A4}$$

where $F = -\beta^{-1} \ln \operatorname{Tr} \exp[-\beta(H_0 + H_1)]$ is the free energy of the system. Let us split the Hamiltonian (2.1) into two parts

$$H = H_{J=1} + \Delta H , \tag{A5}$$

where $H_{J=1}$ is the projection of H into $J_i = 1$ subspace [see Eq. (2.5)] and

$$\Delta H = H - H_{J=1} . \tag{A6}$$

Now, the free energy of the system can be written as follows:

$$F = F_{J=1} + \Delta F , \tag{A7}$$

where $F_{J=1} = -\beta^{-1} \ln \operatorname{Tr} \exp(-\beta H_{J=1})$ and $\Delta F = F - F_{J=1}$. Since $\Gamma_0 / B \ll 1$, where Γ_0 is the nonrenormalized EQQ coupling parameter and B is the rotational constant of the H_2 or D_2 molecule, we can treat ΔH (A6) as a small perturbation. We take ΔH in the following approximated form:

$$H = (1 - P) H_0 P , \tag{A8}$$

where P is the projection operator into $J_i = 1$ subspace and H_0 is the mean-field Hamiltonian (A2). Applying the thermodynamical perturbation method (see, for example Ref. 39) we get the following expression for ΔF:

$$\Delta F = \frac{1}{3} \sum_{MN} \frac{|\langle J=3, N | \Delta H | J=1, M \rangle|^2}{E_{J=1} - E_{J=3}} = -(3x^2/10B) , \tag{A9}$$

where $E_J = BJ(J+1)$. A splitting of the rotational levels is neglected here. With the help of Eqs. (A4), (A8) and the relation

$$x = -\tfrac{1}{6} \sigma \epsilon_0 , \tag{A10}$$

where $\epsilon_0 = -12 \sum_j \gamma_{ij}^{00} = 21.2\,\Gamma_0$, with the further neighbor interaction taken into account, we obtain the following expression for σ:

$$\sigma = \sigma_{J=1} + 2.12 (\Gamma_0 / B) \sigma , \tag{A11}$$

where

$$\sigma_{J=1} = \frac{\partial F_{J=1}}{\partial x} .$$

Hence, we obtain

$$\sigma = \xi_{\text{rot}} \sigma_{J=1} , \tag{A12}$$

where $\xi_{\text{rot}} = (1 - 2.12\,\Gamma_0 / B)^{-1}$. Putting $\Gamma_0 = 0.698$ cm^{-1} and $B = 59.34$ cm^{-1} for H_2, and $\Gamma_0 = 0.8931$ cm^{-1} and $B = 29.91$ cm^{-1} for D_2,[15] we get

$$\xi_{\text{rot}}(H_2) = 1.025 \quad \text{and} \quad \xi_{\text{rot}}(D_2) = 1.063 .$$

This result differs slightly from that given in Ref. 32, where the rotational renormalization of σ was calculated for $T = 0$.

APPENDIX B: TABULATION OF $4\hat{a}(\vec{k})/T_0$

The elements of the 5×5 matrix $\hat{a}(\vec{k})$ are given by Eqs. (5.5) and (5.9). In order to calculate the matrix $4\hat{a}(\vec{k})/T_0$ we use the following relations:

$$\{\hat{a}(\vec{k})\}_{M,N} = \{\hat{a}(\vec{k})\}^*_{N,M} = (-1)^{M+N} \{\hat{a}(\vec{k})\}_{-M,-N} , \tag{B1}$$

and

$$\{\hat{a}(\vec{k})\}_{2,2} = \tfrac{1}{6} \{\hat{a}(\vec{k})\}_{0,0} = -\tfrac{1}{4} \{\hat{a}(\vec{k})\}_{1,1} , \tag{B2}$$

$$\{\hat{a}(\vec{k})\}_{1,0} = -\sqrt{6}\, \{\hat{a}(\vec{k})\}_{2,1} , \tag{B3}$$

$$\{\hat{a}(\vec{k})\}_{1,-1} = -\sqrt{\tfrac{8}{3}}\, \{\hat{a}(\vec{k})\}_{2,0} . \tag{B4}$$

Thus, we must to calculate five independent elements of $4\hat{a}(\vec{k})/T_0$ which are the following:

$$\begin{aligned} (4/T_0)\{\hat{a}(\vec{k})\}_{2,2} &= 0.0653 C_1 C_2 - 0.1413 C_3 C_4 C_5 , \\ (4/T_0)\{\hat{a}(\vec{k})\}_{2,1} &= 0.0544 (S_2 + i S_1) S_3 , \\ (4/T_0)\{\hat{a}(\vec{k})\}_{2,0} &= 0.6674 C_3 S_4 S_5 - i\,0.2669 S_1 S_2 , \\ (4/T_0)\{\hat{a}(\vec{k})\}_{1,-2} &= -0.3814 (S_2 + i S_1) S_3 , \end{aligned} \tag{B5}$$

and

$$(4/T_0)\{\hat{a}(\vec{k})\}_{2,-2} = 0.3814 C_3 C_4 C_5 - 0.7628 C_1 C_2 ,$$

where $C_1 = \cos\pi(x_1 + x_2)$, $C_2 = \cos\pi(x_1 - x_2)$, $C_3 = \cos\pi(x_1 + x_2 - 2x_3)$, $C_4 = \cos\pi x_1$, $C_5 = \cos\pi x_2$, $S_1 = \sin\pi(x_1 + x_2)$, $S_2 = \sin\pi(x_1 - x_2)$, $S_3 = \sin\pi(x_1 + x_2 - 2x_3)$, $S_4 = \sin\pi x_1$, $S_5 = \sin\pi x_2$, and $k = x_1\vec{\kappa}_1 + x_2\vec{\kappa}_2 + x_3\vec{\kappa}_3$, where $\vec{\kappa}_1$, $\vec{\kappa}_2$, and $\vec{\kappa}_3$ are the basic vectors of the inverse fcc lattice, and $-\frac{1}{2} < x_1, x_2, x_3 < \frac{1}{2}$. The eigenvalues of $4\hat{a}(\vec{k})/T_0$ for $\vec{k} = 0$ are the following: $a_1 = 0.3054$, $a_2 = a_3 = 0.3040$, $a_4 = 0.4560$, and $a_5 = 0.4574$.

APPENDIX C: THE ISOTHERMIC SUSCEPTIBILITY FOR DISORDERED PHASE

In this appendix, we show that investigating the isothermic quadrupolar susceptibility the same result for T_2 as presented in Sec. V is obtained. The isothermic quadrupolar susceptibility χ_{ij}^{mn} ($m, n = 0, \pm 1, \pm 2$) for solid ortho-H_2 (para-D_2) we define as follows

$$\chi_{ij}^{mn} = \int_0^\beta d\tau K(i,m,\tau;j,n,0)\,, \tag{C1}$$

where $K(i,m,\tau;j,n,\tau')$ is the two-point IGF defined by Eq. (3.6) for $k=2$. Introducing the Fourier transform of $K(i,m,\tau;j,n,0)$, e.g.,

$$K(i,m;j,n;\omega_\nu) = \int_0^\beta d\tau K(i,m,\tau;j,n,0)e^{i\omega_\nu\tau} \tag{C2}$$

we have

$$\chi_{ij}^{mn} = \sum_{\omega_\nu} K(i,m;j,n;\omega_\nu)\,. \tag{C3}$$

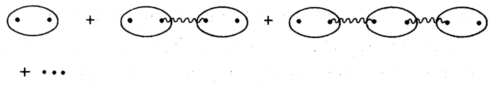

FIG. 7. Sum of the simplest reducible (with respect to the interaction line) diagrams for the two-point IGF $K(i,m;j,n;\omega_\nu)$.

In order to calculate $K(i,m;j,n;\omega_\nu)$, we sum the diagrammatic series shown in Fig. 7. The result is the following:

$$\chi_{ij}^{mn} = \frac{(-1)^m}{A_m A_{-n}} \sum_{M,N} D^2_{-m,M}(\hat{\chi}_i)^*(\hat{\chi}_{ij})^{M,N} D^2_{N,n}(\hat{\chi}_j)\,, \tag{C4}$$

where $\hat{\chi}_{ij}$ is the 5×5 susceptibility matrix determined in the cubic crystal coordinate system defined as

$$\hat{\chi}_{ij} = \frac{1}{N_0} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}_{ij}}\hat{\chi}(\vec{k})\,, \tag{C5}$$

where $\vec{R}_{ij}$ is a vector of fcc lattice,

$$\hat{\chi}(\vec{k}) = 2\beta/[1 + 4\beta\hat{a}(\vec{k})] \tag{C6}$$

is the 5×5 susceptibility matrix transformed to the inverse space and $\hat{a}(\vec{k})$ is defined by Eqs. (5.9) and (5.5). In order to calculate the temperature T_2 we consider $\hat{\chi}(\vec{k})$ for $\vec{k} = 0$. Using the eigenvalues of $4\hat{a}(0)/T_0$ tabulated in Appendix B we see that the maximum temperature at which $\hat{\chi}(0)$ diverges is $T_2 = 0.46T_0$. Hence we conclude that T_2 is really the minimum limit of metastability of the disordered phase.

---

[1] A. B. Harris, J. Appl. Phys. 42, 1574 (1971).

[2] A. F. Schuch, R. L. Mills, and D. A. Depatie, Phys. Rev. 165, 1032 (1968).

[3] K. F. Mucker, S. Talhouk, P. M. Harris, D. White, and R. A. Erickson, Phys. Rev. Lett. 16, 799 (1966).

[4] D. Ramm, H. Meyer, and R. L. Mills, Phys. Rev. B 1, 2763 (1970).

[5] R. L. Mills, J. L. Yarnell, and A. F. Schuch, in *Proceedings of the Thirteenth International Conference of Low-Temperature Physics*, edited by W. J. O'Sullivan, K. D. Timmerhaus, and E. F. Hammel (Plenum, New York, 1974).

[6] W. N. Hardy, J. F. Silvera, and J. P. McTague, Phys. Rev. B 12, 753 (1975), and references cited therein.

[7] O. Nagai and T. Nakamura, Prog. Theor. Phys. 24, 432 (1960).

[8] J. Felsteiner, Phys. Rev. Lett. 15, 1025 (1965); Phys. Lett. A 28, 288 (1968).

[9] H. Miyagi and T. Nakamura, Prog. Theor. Phys. 37, 641 (1967).

[10] E. E. Tareyeva and T. I. Trapezina, Teor. Mat. Fiz. 26, 269 (1976).

[11] H. M. James and J. C. Raich, Phys. Rev. 162, 649 (1967); H. M. James, Phys. Rev. B 2, 2213 (1970); Phys. Rev. Lett. 24, 970(E) (1970); 24, 815 (1970).

[12] J. Felsteiner and Z. Friedman, Phys. Rev. B 8, 3996 (1973).

[13] E. E. Tareyeva and T. I. Trapezina, Teor. Mat. Fiz. 29, 136 (1976).

[14] H. Meyer, F. Weinhaus, and B. Maraviglia, Phys. Rev. B 6, 112 (1972); see also B. Maraviglia, F. Weinhaus, H. Meyer, and R. L. Mills, Solid State Commun. 8, 815 (1970); 8, 1683 (1970).

[15] A. B. Harris, Phys. Rev. B 1, 1881 (1970).

[16] J. C. Raich and H. M. James, Phys. Rev. Lett. 16, 173 (1966).

[17] J. C. Raich and R. D. Etters, Phys. Rev. 155, 457 (1967); 161, 439 (1967).

[18] H. Moraal, Phys. Status Solidi 50, 327 (1972).

[19] H. Ueyama and T. Matsubara, Prog. Theor. Phys. 38, 784 (1967).

[20] J. C. Raich and R. D. Etters, Phys. Rev. 168, 425 (1968).

[21] J. C. Raich and R. D. Etters, J. Phys. Chem. Solids 29, 1561 (1968); Solid State Commun. 7, 1031 (1969).

[22] R. J. Lee, J. C. Raich, and R. D. Etters, Solid State Commun. 8, 1803 (1970).

[23] R. J. Lee and J. C. Raich, Phys. Rev. Lett. 27, 1137 (1971); Phys. Rev. B 5, 1591 (1972).

[24] N. S. Sullivan J. Phys. (Paris) 37, 981 (1976).

[25] T. Nakamura, Prog. Theor. Phys. 20, 542 (1958).

[26] R. Englman and Z. Friedman, Phys. Rev. Lett. 13, 816 (1973).

[27] M. E. Lines, Phys. Rev. B 5, 3690 (1972).

[28] Yu. A. Izyumov, F. A. Kassan-ogly, and Yu. N. Skryabin, *Field Methods in Theory of Ferromagnetism* (Nauka, Moscow, 1974) (in Russian).

[29] D. H.-Y. Yang and Y.-L. Wang, Phys. Rev. B 10, 4714 (1974).

[30] K. Walasek, Physica (to be published).

[31] K. Walasek and K. Lukierska-Walasek, Phys. Lett. A 56, 397 (1976).

[32] A. B. Harris. Int.J. Quantum Chem. II S, 347 (1968).

[33] C. F. Coll, III and A. B. Harris, Phys. Rev. B 2, 1176 (1970).

[34] A. J. Berlinsky, A. B. Harris, and C. F. Coll, III, Solid State Commun. 7, 1491 (1969).

[35] G. Uhlenbeck and G. W. Ford, *Lectures in Statistical Mechanics* (American Mathematical Society, Providence, Rhode Island, 1963).

[36] We call the vertex connected with the interaction line "internal vertex." The vertex connected with no line is called "external vertex" (cf. Ref. 28).

[37] The $1/z$ expansion scheme at $T=0$ for the self-energy part of the libron Green's function has been developed by C. F. Coll, III and A. B. Harris [Phys. Rev. B 4, 2781 (1971)].

[38] G. A. Korn and T. M. Korn, *Mathematical Handbook* (McGraw-Hill, New York, 1968).

[39] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Nauka, Moscow, 1964) (in Russian).