CONCLUSIONS

The critical field H_0 is quite large at most temperatures. The simplest method of obtaining such high fields is by utilizing pulsed-field techniques, but, with this method, it is difficult to measure the weak ferromagnetic moment directly, in the absence of spin flop. A measurement of H_0 using a magnetic-resonance method could avoid this difficulty. Using such magnetic-resonance studies, the theoretical rotating AF-axis picture could be investigated. Also, more information about the canting mechanism, especially at low temperatures, could be obtained, and, from a knowledge of $H_0(T)$, it would be possible to find the temperature dependence of the uniaxial magnetocrystalline anisotropy constant. To calculate the resonance modes in the case where the applied field deviates slightly from the special directions considered here is somewhat more difficult as the symmetry of the equilibrium configuration is reduced. All the above calculations were performed at essentially 0°K using the molecular-field approximation.

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Orientational Order in fcc Solid Ortho-H_2. Green's-Function Treatment of the Internal-Field Approximation

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The technique of temperature-dependent Green's functions is applied to a molecular-field model of the orientational order-disorder transition of ortho-H_2 molecules on a face-centered-cubic (fcc) lattice. The chain of equations for the various Green's functions is decoupled by an approximation similar to the one used by Tahir-Kheli and ter Haar, which enables one to solve the three remaining Green's-function equations of motion. It is shown that the Green's-function approach leads to the same results as the more conventional methods.

I. MODEL

A THEORETICAL discussion of the cooperative orientational ordering of ortho-H_2 molecules on both face-centered-cubic (fcc) and hexagonal-close-packed (hcp) lattices has recently been given by Raich and James.[1,2] For the case of a rigid fcc lattice it was shown that the internal-field approximation (or molecular-field approximation) leads to a first-order phase transition between an orientationally ordered phase, stable at low temperatures, and an orientationally disordered phase, stable at high temperatures.

The purpose of this paper is to indicate how the technique of temperature-dependent Green's functions can be applied to a model of the ordering of ortho-H_2 molecules on a rigid fcc lattice, valid within the framework of the internal-field approximation. It is shown that this technique leads to the same results as the more conventional one, based on the minimization of the free energy.

Leaving off the rotational energy of the molecules, the Hamiltonian for the model to be considered is

$$H=\tfrac{1}{2}\sum_{i,j} V_{ij}(\mathbf{\Omega}_i,\mathbf{\Omega}_j)\,, \tag{1}$$

where $\mathbf{\Omega}_i=(\theta_i,\phi_i)$ specifies the orientation of molecule i. If we assume that the orientational coupling of the molecules arises from quadrupole-quadrupole coupling, the potential energy of interaction of molecules i and j, V_{ij} can be written as[3]

$$V_{ij}=(20\pi/9)(70\pi)^{1/2}\Gamma_{ij}\sum_{MN} C(224;MN) \times Y_{2M}(\mathbf{\Omega}_i)Y_{2N}(\mathbf{\Omega}_j)Y_{4,M+N}(\mathbf{\Omega}_{ij})^*\,. \tag{2}$$

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[1] J. C. Raich and H. M. James, Phys. Rev. Letters **16**, 173 (1966). This paper gives a list of references to previous experimental and theoretical work on this problem.

[2] H. M. James and J. C. Raich (to be published).

[3] H. P. Gush and J. Van Kranendonk, Can. J. Phys. **40**, 1461 (1962).

Here $C(224;\,MN)$ is a Clebsch-Gordan coefficient,[4] and

$$\Gamma_{ij}=6e^2Q^2/(25R_{ij}^5)\,, \tag{3}$$

where Q is the molecular quadrupole moment, and $\mathbf{R}_{ij}$ is the vector connecting sites i and j, measured relative to the crystal axis.

The space group $Pa3$ (T_h^6) assumed[1] for the crystal structure of fcc solid ortho-H_2 is in good agreement with experiment.[5] In this structure the molecules are distributed over four simple cubic sublattices. The molecular orientational distributions on each sublattice are axially symmetric about equilibrium configurations oriented along a different threefold axis of the crystal. Through the center of each molecular distribution passes a threefold axis of the average charge distribution of the rest of the crystal. Thus, the average charge distribution around the molecule on site i will have a threefold axis of symmetry in the equilibrium direction assumed to be characteristic of molecules on that sublattice.

Because of this threefold axis of symmetry, one can, within the internal-field approximation, replace the interaction (2) by the effective interaction, valid for the particular crystal structure assumed above,[1,6]

$$V_{ij}=-(95\pi/18)\Gamma_{ij}Y_{20}(\omega_i)Y_{20}(\omega_j)\,, \tag{4}$$

where ω_i specifies the orientation of molecule i relative to its symmetry axis. For the case of solid ortho-H_2, the temperature is so low and the orientational interactions so small that $J=1$ can be considered a good quantum number. Then the effective Hamiltonian, given by Eqs. (1) and (4), can be written in operator form[7]:

$$H=\sum_{i,j}\gamma_{ij}[3(J_i^z)^2-2][3(J_j^z)^2-2]\,, \tag{5}$$

where $\gamma_{ij}=-(19/144)\Gamma_{ij}$. Here and below units where $\hbar=1$ are used. $\mathbf{J}_i$ is the angular-momentum operator for a molecule on site i, with the z_i axis taken along the axis of symmetry for molecule i. The components of $\mathbf{J}_i$ satisfy the basic commutation relations:

$$[J_i^+,J_j^-]_-=2J_j^z\delta_{ij},\quad [J_i^\pm,J_j^z]_-=\mp J_j^\pm\delta_{ij}\,, \tag{6}$$

where

$$J_j^\pm=J_j^x\pm iJ_j^y\,. \tag{7}$$

For $J=1$ the following relations hold:

$$J^-J^+=2-J^z-(J^z)^2\,, \tag{8}$$

$$(J^-)^2(J^+)^2=-6J^z+(J^z)^2+4(J^z)^3+(J^z)^4\,, \tag{9}$$

$$(J^z)^3=J^z\,. \tag{10}$$

For the sake of simplicity let us assume

$$\begin{aligned}\gamma_{ij}&=\gamma, && \text{if } i \text{ and } j \text{ are nearest neighbor sites}\\ &=0, && \text{otherwise.}\end{aligned} \tag{11}$$

II. EQUATIONS OF MOTION FOR THE GREEN'S FUNCTIONS

Temperature-dependent Green's functions have been applied to a variety of problems in solid-state physics. A review of this application of Green's functions has been given by Zubarev.[8] The Green's-function technique was first applied to the theory of the Heisenberg ferromagnet with spin $\frac{1}{2}$ by Tyablikov.[9] An extension of this theory to higher spin has been given by Tahir-Kheli and ter Haar[10] and by Callen.[11]

The Fourier transform of the Green's function, $\langle\langle A;\,B\rangle\rangle$, involving the two operators A and B satisfies the equation of motion[8]

$$E\langle\langle A;\,B\rangle\rangle=(1/2\pi)\langle[A,B]_-\rangle+\langle\langle[A,H]_-;\,B\rangle\rangle\,, \tag{12}$$

where the double brackets $\langle\langle\ \rangle\rangle$ indicate Fourier forms of Green's functions, and the single brackets $\langle\ \rangle$ indicate averages over the canonical ensemble at temperature T. The correlation function is found from the relation[8]

$$\langle B(t')A(t)\rangle = \lim_{\epsilon\to+0} i\int_{-\infty}^{+\infty}\frac{\langle\langle A;\,B\rangle\rangle_{E+i\epsilon}-\langle\langle A;\,B\rangle\rangle_{E-i\epsilon}}{e^{\beta E}-1}e^{-iE(t-t')}dE\,, \tag{13}$$

where $\beta=1/kT$. The Green's-function approach yields solutions for the desired expectation values (13) in the form of a large number of coupled equations. A common feature of this technique is that in order to obtain a solution it becomes necessary to decouple these equations of motion. In the description of the application of the temperature-dependent Green's functions to the present model for the orientational ordering of ortho-H_2 molecules on a rigid fcc lattice, we shall follow treatment of the Heisenberg ferromagnet by Tahir-Kheli and ter Haar,[10] and use a somewhat similar decoupling approximation.

By Eq. (12), the equation of motion for the Fourier transform of the Green's function $\langle\langle J_g^+;\,B\rangle\rangle$ is

$$E\langle\langle J_g^+;\,B\rangle\rangle=(1/2\pi)\langle[J_g^+,B]_-\rangle+\langle\langle[J_g^+,H]_-;\,B\rangle\rangle\,, \tag{14}$$

where, following Tahir-Kheli and ter Haar,[10] one takes

$$B=(J_f^-)^n(J_f^+)^{n-1},\quad n=1,2. \tag{15}$$

From Eq. (5) and the commutation relations (6), one finds

$$\begin{aligned}E\langle\langle J_g^+;\,B\rangle\rangle&=(1/2\pi)\langle[J_g^+,B]_-\rangle\\ &\quad+6\textstyle\sum_i \gamma_{ig}\langle\langle[3(J_i^z)^2-2](1-2J_g^z)J_g^+;\,B\rangle\rangle.\end{aligned} \tag{16}$$

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[4] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

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

[6] B. C. Kohin, J. Chem. Phys. **33**, 882 (1960).

[7] T. Nakamura, Progr. Theoret. Phys. (Kyoto) **14**, 135 (1955).

[8] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

[9] S. V. Tyablikov, Ukr. Mat. Zh. **112**, 87 (1959); see also Ref. 8.

[10] R. Tahir-Kheli and D. ter Haar, Phys. Rev. **127**, 88 (1962). This paper gives also a fairly complete list of references for the application of Green's-function techniques to ferromagnetism.

[11] H. B. Callen, Phys. Rev. **130**, 890 (1963).

It is seen that Eq. (16) involves higher-order Green's functions, and it now becomes necessary to decouple this equation of motion. The decoupling procedure which will be used here is

$$\langle\langle (J_i^z)^2 J_g^+; B\rangle\rangle \underset{i\neq g}{\rightarrow} \langle (J_i^z)^2\rangle \langle\langle J_g^+; B\rangle\rangle, \tag{17}$$

$$\langle\langle (J_i^z)^2 J_g^z J_g^+; B\rangle\rangle \underset{i\neq g}{\rightarrow} \langle (J_i^z)^2\rangle \langle\langle J_g^z J_g^+; B\rangle\rangle. \tag{18}$$

This decoupling approximation ignores any fluctuations in $(J_i^z)^2$, replacing this operator by its average value. From the translational invariance of the lattice it follows that all averages are independent of the lattice index, or $\langle J_i^z\rangle = \langle J^z\rangle$, and $\langle (J_i^z)^2\rangle = \langle (J^z)^2\rangle$.

Then using Eq. (11), Eq. (16) is written

$$E\langle\langle J_g^+; B\rangle\rangle = (1/2\pi)\langle [J_g^+,B]_-\rangle + 6\gamma\mathfrak{z}(3\langle (J^z)^2\rangle - 2)(\langle\langle J_g^+; B\rangle\rangle - 2\langle\langle J_g^z J_g^+; B\rangle\rangle), \tag{19}$$

where $\mathfrak{z}$ is the number of nearest neighbors (12, for the fcc lattice). Equation (19) can be rewritten in the form

$$\langle\langle J_g^+; B\rangle\rangle = \frac{\langle [J_g^+,B]_-\rangle}{2\pi(E-E_0)} - \frac{2E_0\langle\langle J_g^z J_g^+; B\rangle\rangle}{E-E_0}, \tag{20}$$

where

$$E_0 = 6\gamma\mathfrak{z}(3\langle (J^z)^2\rangle - 2). \tag{21}$$

Note that Eq. (20) still involves the higher-order Green's function $\langle\langle J_g^z J_g^+; B\rangle\rangle$. It therefore becomes necessary to develop a system of equations for the three Green's functions: $\langle\langle J_g^+; B\rangle\rangle$, $\langle\langle J_g^z J_g^+; B\rangle\rangle$, and $\langle\langle (J_g^z)^2 J_g^+; B\rangle\rangle$. By Eq. (12), the equations of motion for the last two Green's functions are

$$E\langle\langle J_g^z J_g^+; B\rangle\rangle = (1/2\pi)\langle [J_g^z J_g^+,B]_-\rangle + \langle\langle [J_g^z J_g^+,H]_-; B\rangle\rangle, \tag{22}$$

and

$$E\langle\langle (J_g^z)^2 J_g^+; B\rangle\rangle = (1/2\pi)\langle [(J_g^z)^2 J_g^+,B]_-\rangle + \langle\langle [(J_g^z)^2 J_g^+,H]_-; B\rangle\rangle. \tag{23}$$

By Eqs. (5), (6), (10) and the decoupling approximations (17) and (18), the equations of motion (22) and (23) become, respectively,

$$E\langle\langle J_g^z J_g^+; B\rangle\rangle = (1/2\pi)\langle [J_g^z J_g^+,B]_-\rangle + E_0(\langle\langle J_g^z J_g^+; B\rangle\rangle - 2\langle\langle (J_g^z)^2 J_g^+; B\rangle\rangle) \tag{24}$$

and

$$E\langle\langle (J_g^z)^2 J_g^+; B\rangle\rangle = (1/2\pi)\langle [(J_g^z)^2 J_g^+,B]_-\rangle + E_0[\langle\langle (J_g^z)^2 J_g^+; B\rangle\rangle - 2\langle\langle J_g^z J_g^+; B\rangle\rangle]. \tag{25}$$

It is seen that Eqs. (24) and (25) involve only the two Green's functions: $\langle\langle J_g^z J_g^+; B\rangle\rangle$ and $\langle\langle (J_g^z)^2 J_g^+; B\rangle\rangle$. Solving Eqs. (24) and (25) for $\langle\langle J_g^z J_g^+; B\rangle\rangle$, the Green's function that occurs on the right-hand side of Eq. (20), one obtains

$$\langle\langle J_g^z J_g^+; B\rangle\rangle = [(E_0/\pi)\langle (J_g^z)^2 J_g^+,B]_-\rangle - (1/2\pi)(E-E_0)\langle [J_g^z J_g^+,B]_-\rangle]/[4E_0^2 - (E-E_0)^2]. \tag{26}$$

Substituting Eq. (26) into Eq. (20), we find

$$\langle\langle J_g^+; B\rangle\rangle = \frac{\langle [J_g^+,B]_-\rangle}{2\pi(E-E_0)} - \frac{E_0\langle [J_g^z J_g^+,B]_-\rangle}{\pi(E+E_0)(E-3E_0)} + \frac{2E_0^2\langle [(J_g^z)^2 J_g^+,B]_-\rangle}{\pi(E+E_0)(E-E_0)(E-3E_0)}. \tag{27}$$

Using Eq. (13), an elementary complex integration yields the following relation for the correlation function $\langle BJ_g^+\rangle$:

$$\langle BJ_g^+\rangle = \langle [J_g^+,B]_-\rangle \Phi(E_0) + \tfrac{1}{2}\langle [J_g^z J_g^+,B]_-\rangle [\Phi(-E_0) - \Phi(3E_0)] + \tfrac{1}{2}\langle [(J_g^z)^2 J_g^+,B]_-\rangle [\Phi(-E_0) - 2\Phi(E_0) + \Phi(3E_0)], \tag{28}$$

where

$$\Phi(E) = (e^{\beta E} - 1)^{-1}. \tag{29}$$

For $B = (J_g^-)^n (J_g^+)^{n-1}$, with $n=1$, 2 and $J=1$, the expectation values occurring in Eq. (28) are (in units where $\hbar = 1$),

for $n=1$:

$$\begin{aligned} \langle [J_g^+,J_g^-]_-\rangle &= 2\langle J^z\rangle, \\ \langle [J_g^z J_g^+,J_g^-]_-\rangle &= \langle [(J_g^z)^2 J_g^+,J_g^-]_-\rangle \\ &= -2 + \langle J^z\rangle + 3\langle (J^z)^2\rangle; \end{aligned} \tag{30}$$

for $n=2$:

$$\begin{aligned} \langle [J_g^+,(J_g^-)^2 J_g^+]_-\rangle &= 4 + 2\langle J^z\rangle - 6\langle (J^z)^2\rangle, \\ \langle [J_g^z J_g^+,(J_g^-)^2 J_g^+]_-\rangle & \\ &= \langle [(J_g^z)^2 J_g^+,(J_g^-)^2 J_g^+]_-\rangle = 0. \end{aligned} \tag{31}$$

For $n=1$, combining Eqs. (8), (28), and (30), one can write both the left- and right-hand sides of Eq. (28) as a sum of averages of J^z and $(J^z)^2$:

$$2 - \langle J^z\rangle - \langle (J^z)^2\rangle = 2\langle J^z\rangle \Phi(E_0) + [-2 + \langle J^z\rangle + 3\langle (J^z)^2\rangle][\Phi(-E_0) - \Phi(E_0)]. \tag{32}$$

Similarly, combining Eqs. (9), (10), (28), and (31), for $n=2$, one finds

$$-\langle J^z\rangle + \langle (J^z)^2\rangle = [2 + \langle J^z\rangle - 3\langle (J^z)^2\rangle]\Phi(E_0). \tag{33}$$

III. ORDER-DISORDER TRANSITION

Equations (32) and (33) are solved for $\langle J^z\rangle$ and $\langle (J^z)^2\rangle$ to give

$$\langle J^z\rangle = 0, \tag{34}$$

$$3E_0 \coth(\tfrac{1}{2}\beta E_0) = E_0 - 24\gamma\mathfrak{z}. \tag{35}$$

For $E_0 \neq 0$, Eq. (35) can be rewritten in the form

$$6\beta\gamma\mathfrak{z}[3\langle (J^z)^2\rangle - 2] - \ln 2 = \ln\{[1 - \langle (J^z)^2\rangle]/\langle (J^z)^2\rangle\}. \tag{36}$$

Similary, the internal energy, approximated by the same technique used to decouple the Green's functions (17) and (18), is, by Eq. (5),

$$\langle H\rangle = -(19/3)N\Gamma[1 - 3\langle (J^z)^2\rangle + (9/4)\langle (J^z)^2\rangle^2]. \tag{37}$$

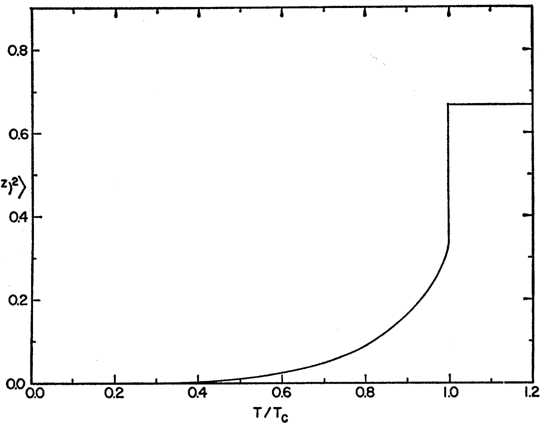

FIG. 1. The average value $\langle (J^z)^2 \rangle$ as a function of temperature.

Equation (34) implies that the $M_J = \pm 1$ states must contribute equally, i.e., that they correspond to a two-fold degenerate level in the internal-field approximation. The relation (36), specifying $\langle (J^z)^2 \rangle$ as a function of temperature, is the same as the one obtained by the more conventional internal-field approximation, based on the minimization of the free energy.[1,12] In that treatment it was found[1] that the model undergoes a first-order orientational transition at a temperature given by $kT_c = 19\Gamma/(4 \ln 2)$. Figure 1 shows $\langle (J^z)^2 \rangle$ as a function of temperature. At $T=0$ there is an ordered phase with $\langle (J^z)^2 \rangle = 0$. At $T=T_c$, we see that $\langle (J^z)^2 \rangle$ abruptly assumes the value $\frac{2}{3}$, characteristic of the orientationally disordered phase, which is stable at all higher T. A complete discussion of this transition is given elsewhere.[1,2]

In order to obtain a higher-order treatment (than the internal-field approximation) of the orientational order-disorder transition in fcc (or hcp) solid ortho-H_2, it is of course necessary to consider the more general Hamiltonian, given by Eqs. (1) and (2).

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[12] See Eq. (6) of S. Strässler and C. Kittel [Phys. Rev. **139**, A758 (1965)], with $g_0/g_1 = \frac{1}{2}$.

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Ferromagnetic Transitions in Dilute Solutions of Cobalt in Palladium[*]

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Ferromagnetic transitions have been observed in dilute random solutions of Co in Pd having Co concentrations between 0.07 and 4.5 at.%. The transition regions near T_c have been explored by using the Mössbauer effect of Fe^{57} present as a very dilute impurity in the alloys. The hyperfine fields have been measured by the standard Doppler technique at low temperatures and by a thermal scanning method near the transition temperatures. Data have been interpreted as showing the effects of statistical fluctuations in the concentration of the alloys, and have been analyzed to yield values for the mean Curie temperature and the mean-square deviation in Curie temperature as a function of concentration. These values have been related to the spatial dependence of the exchange interaction through a molecular-field calculation. It is found that if one assumes the interaction is given by a Gaussian $J(r) = \exp(-r^2/4\sigma^2)$, in correspondence with neutron diffraction results in Co-Pd alloys, then the values deduced from this study are $\sigma = 11.5 \pm 1.2$ Å and $J_0/k = 0.02$°K. However, comparison of the effective range obtained in the present study with the neutron data and the total localized moment suggest that the Gaussian form factor is incorrect at large distances and that the interaction has a more slowly varying and weak tail.

INTRODUCTION

In certain solid solutions of magnetic ions in a nonmagnetic material, the variation of Curie temperature with concentration may provide information on the range of the magnetic interaction. It has been shown[1,2] that, within the Bethe-Peierls-Weiss approximation with nearest-neighbor interactions, such a solid solution will not support long-range magnetic order if the concentration is less than a critical value c_0, where

$$c_0 = 1/(z-1). \tag{1}$$

Here z is the number of nearest-neighbor sites. If the interaction is assumed to be constant over a larger number of sites N in the magnetic cluster, then z in Eq. (1) is replaced by N. If in some alloy system one observes a concentration below which the Curie temperature is zero, then the inverse of this concentration gives the approximate number of sites enclosed by the interaction.

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[1] J. S. Smart, J. Phys. Chem. Solids **16**, 169 (1960).

[2] D. H. Lyons, Phys. Rev. **128**, 2022 (1962).