PHYSICAL REVIEW VOLUME 171, NUMBER 2 10 JULY 1968

Application of the Cluster-Variation Method to the Uniaxial Antiferromagnet FeF_2

TOMOYASU TANAKA*
Catholic University of America, Washington, D. C. and U. S. Naval Ordnance Laboratory, White Oak, Maryland
AND
LOUIS LIBELO AND RONALD KLIGMAN
U. S. Naval Ordnance Laboratory, White Oak, Maryland

(Received 22 June 1967; revised manuscript received 14 March 1968)

Low-temperature nuclear-magnetic-resonance measurements together with antiferromagnetic-resonance observations in FeF_2 furnish a reliable set of values of first- and second-neighbor exchange integrals as well as a uniaxial anisotropy energy. It is the purpose of this paper to see to what extent one can understand the high-temperature properties, such as the Néel temperature and the anisotropic susceptibilities, in terms of the known parameters obtained at low temperatures. To achieve this, the cluster-variation method is used, taking into account spin correlations between the nearest and next-nearest neighbors. The anisotropy energy in FeF_2 is larger than the exchange integrals, and consequently cannot be treated as a small perturbation. After explicit diagonalization of effective two-spin Hamiltonians, we calculate the Néel temperature and the anisotropic susceptibilities for spin $S=2$. The effect of the anisotropy energy on the Néel temperature is shown to be much less pronounced in the cluster approximation than in the Weiss molecular-field approximation. In the neighborhood of the critical temperature, we find that the anisotropic susceptibilities are considerably improved in the cluster approach as compared to the Weiss-theory predictions.

I. INTRODUCTION

EXPERIMENTAL investigation of the magnetic properties of FeF_2 has been rather extensively carried out over the last ten years. In fact, FeF_2 is rapidly becoming one of the most thoroughly researched antiferromagnetic substances. A significant part of the widespread interest in this particular material is the result of two of its characteristics. First, FeF_2 possesses a rather simple magnetic structure. It basically is a two-sublattice, uniaxial antiferromagnet. Second, it possesses a quite large anisotropy energy which is predominantly crystalline field and uniaxial in nature.

The physical properties of FeF_2, such as the crystal structure,[1] anisotropic susceptibilities,[2] specific heat,[3] magnetic structure,[4] antiferromagnetic resonance (AFMR),[5] and sublattice magnetizations,[6] have been measured by a number of investigators. Those experimental observations furnish a reliable set of values for the exchange integrals and the anisotropy constant which characterize the spin Hamiltonian of the magnetic system under investigation. Some of these constants can be determined unambiguously by the observations performed at very low temperatures where there are asymptotically correct theories available. In such a case, therefore, it is very interesting to see to what extent one can predict theoretically the high-temperature properties, entirely in terms of the information obtained at low temperatures. Sometimes, however, one does not necessarily have all the information at low temperatures which is needed for the determination of those constants and one has to resort to use of finite-temperature properties such as the Néel temperature, sublattice magnetizations, and anisotropic susceptibilities. At finite temperatures, however, there is no rigorous theory available and consequently the determination of these constants is not free from uncertainties. Therefore, development of increasingly more accurate theories at finite temperatures is very much desired in order to attain a better understanding of the magnetic properties of a given substance. The status of experimental investigation of FeF_2 seems to be one such situation. Here more complete experimental information is needed at low temperatures.

Recently, many theoretical papers have been published attempting to explain the properties of FeF_2 observed so far. For investigation of low-temperature properties the spin-wave approximation or the Green's-function method is suitable, although there are well-known mathematical difficulties which are characteristic of antiferromagnets if one tries to formulate a more improved spin-wave theory. There are several papers dealing with FeF_2 by the method of the Green's function.[7–9] It has been pointed out by Lines,[9] however, that the crystal-field anisotropy presents a new difficulty in the Green's-function treatment, namely, how to decouple higher-order Green's functions which appear in connection with the anisotropy. As the crystal-field anisotropy increases, the decoupling ap-

---

* Work supported in part by National Aeronautics and Space Administration Research Grant No. SC-09-005(054).

[1] J. W. Stout and S. A. Reed, J. Am. Chem. Soc. **76**, 5279 (1954).

[2] J. W. Stout and L. M. Matarrese, Rev. Mod. Phys. **25**, 338 (1953); S. Foner, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 438.

[3] J. W. Stout and E. Catalano, J. Chem. Phys. **23**, 1803 (1955).

[4] R. A. Erikson, Phys. Rev. **90**, 779 (1953).

[5] R. C. Ohlmann and M. Tinkham, Phys. Rev. **123**, 425 (1961).

[6] V. Jaccarino, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. 2A.

[7] A. Narath, Phys. Rev. **140**, A854 (1965).

[8] F. B. Anderson and H. B. Callen, Phys. Rev. **136**, A1068 (1964).

[9] M. E. Lines, Phys. Rev. **156**, 534 (1967).

proximations introduced by various authors[7–9] seem to become worse, although Lines's decoupling gave among them the best of all the similar Green's-function treatments. At present there is no theoretical treatment known which is satisfactory at high as well as low temperatures. In this paper we will confine our treatment to the high-temperature properties of FeF_2 and sacrifice the low-temperature region. We shall take the following facts more carefully into account: (a) the actual magnitude of the spin angular momentum $(S=2)$, (b) the large crystal-field anisotropy, and (c) the two-spin correlation effects. These are very much the same motivations which led to the development of Cooper's theory.[10] Cooper calculated the sublattice magnetization and the frequency of zero-field AFMR below the Néel temperature for a two-sublattice antiferromagnet with a large uniaxial crystal-field anisotropy in an approximation in which the two-spin correlation is taken into account. The results showed a significant improvement in both these quantities over the Weiss approximation. The actual calculation, however, was performed for a simplified model system with the spin magnitude $S=1$, and therefore a direct comparison with observed values was not possible.

At the present time, the only theoretical method which enables us to accomplish our objectives is the cluster-variation method. In a recent paper[11] the cluster-variation method has been applied to the Heisenberg ferromagnet with arbitrary spin and an extended range of exchange coupling. In that paper, the dependence of the Curie temperature on the ratio of the second-neighbor exchange to the nearest-neighbor exchange, and the temperature dependence of the spontaneous magnetization have been investigated. We shall use a similar method in this paper. It turns out, however, that the application of the method to the present case is not as straightforward as to the ferromagnetic case because of the nonequivalence of the two sublattices, and also because of the presence of a crystal-field anisotropy. Hence, one obtains more complicated effective two-spin Hamiltonians than in the ferromagnetic case. Nevertheless, it will be shown that the effective Hamiltonians can be diagonalized rigorously with reasonable manipulations.

We find that the effect of crystal-field anisotropy on the Néel temperature is much less pronounced in the present two-spin approximation, which is in better agreement with the experimental observation than both the Weiss approximation and that of Lines. There is no limitation on the magnitude of the crystal-field anisotropy in our theory.

II. SPIN HAMILTONIAN, EXCHANGE INTEGRALS, AND CRYSTAL-FIELD ANISOTROPY

Low-temperature investigations of the spin structure by neutron-diffraction techniques together with AFMR measurements yielded quite reliable information concerning the single-crystal spin ordering, the strengths of the exchange coupling, and also the crystal-field anisotropy.

Stout and Reed[1] and Erickson[4] carried out the earliest work to establish the crystal structure and spin ordering of FeF_2. The crystal structure is known to be of the rutile type in which the Fe^{++} ions form a body-centered tetragonal structure and are surrounded by a distorted octahedron of six F^- ions. The symmetry axes at a cation site are the [110], [1$\bar{1}$0], and [001] directions. The axes of the body-centered ion are rotated 90° about the c axis to obtain the equivalent axes at a corner ion, thus causing the macroscopic anisotropy to be uniaxial. The anisotropy, which is relatively large, is due to the effect of the crystalline field upon the spins through the spin-orbit coupling. Below the Néel temperature of 78.35°K,[3] long-range antiferromagnetic order is present and ions may be grouped into two sublattices according to their average spin directions as shown in Fig. 1.

For orthorhombic symmetry, the effect of a spin-orbit coupling may be represented by the spin Hamiltonian as

$$-DS_z^2+E(S_x^2-S_y^2). \tag{2.1}$$

Ohlmann and Tinkham[5] suggested $E\ll D$, based on Tinkham's previous analysis[12] for an Fe^{++} impurity in ZnF_2. Lines[13] has shown that the rhombic anisotropy E contributes to bulk magnetic properties at low temperatures as $(E/D)^2$ and suggested that E may be neglected compared with D. In this approximation a spin Hamiltonian for the entire lattice of Fe^{++} ions can be written in the form

$$\begin{aligned}\mathcal{H}=&-2J_2\sum_{\langle\alpha,\beta\rangle}\mathbf{S}_\alpha\cdot\mathbf{S}_\beta-2J_1\Big[\sum_{\langle j(\alpha),k(\alpha)\rangle}\mathbf{S}_{j(\alpha)}\cdot\mathbf{S}_{k(\alpha)}\\&+\sum_{\langle j(\beta),k(\beta)\rangle}\mathbf{S}_{j(\beta)}\cdot\mathbf{S}_{k(\beta)}\Big]-2J_3\Big[\sum_{\langle j(\alpha),k(\alpha)\rangle}\mathbf{S}_{j(\alpha)}\cdot\mathbf{S}_{k(\alpha)}\\&+\sum_{\langle j(\beta),k(\beta)\rangle}\mathbf{S}_{j(\beta)}\cdot\mathbf{S}_{k(\beta)}\Big]-D\sum_{\alpha}S_{\alpha z}^2-D\sum_{\beta}S_{\beta z}^2,\end{aligned} \tag{2.2}$$

where J_1, J_2, J_3 are exchange integrals along the c axis, the body-diagonal direction, and the a-b axes, re-

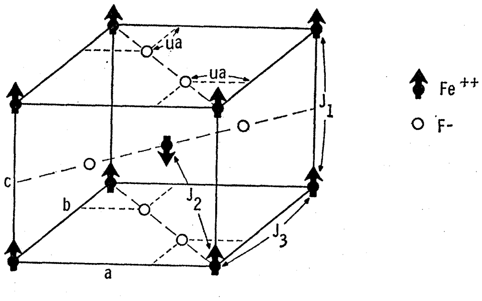

FIG. 1. The crystallographic unit cell of FeF_2. $|a|=|b|=a=4.697$ Å, $c=3.3039$ Å, $u=0.305$.

---

[10] B. R. Cooper, Phys. Rev. **120**, 1171 (1960).

[11] T. Morita and T. Tanaka, Phys. Rev. **145**, 288 (1966).

[12] M. Tinkham, Proc. Roy. Soc. (London) **A236**, 535 (1956).

[13] M. E. Lines, Phys. Rev. **156**, 543 (1967).

spectively. Lines[13] made an analysis of experimental data rather carefully and gave a set of values of these constants. He used AFMR frequency at zero temperature,[5] the low-temperature sublattice magnetization by means of NMR for the fluorine anions in FeF_2,[6] and the high-temperature magnetic susceptibilities.[2] His values are

$$\begin{aligned} D &= 6.5\pm 0.3\ \mathrm{cm}^{-1}, \\ 2J_2 &= -3.85\pm 0.2\ \mathrm{cm}^{-1}, \\ J_1/J_2 &= 0.1\pm 0.25, \\ J_3 &\cong 0. \end{aligned} \tag{2.3}$$

He suggests that the exchange J_1 is small compared with J_2 but the question of its sign must remain open. In view of the fact that in MnF_2, which has the same crystallographic and magnetic structures as FeF_2, the exchange J_1 has been found[14] to be ferromagnetic, we included in our calculation the possibilities of both positive and negative signs of J_1. In this paper we shall use the spin Hamiltonian (2.2) with a set of values (2.3) for the constants.

III. EFFECTIVE HAMILTONIAN

The cluster-variation method[11] will be outlined briefly in the following in order to make this article self-contained.

The Helmholtz free energy F of a system of which the Hamiltonian is $\mathcal{H}$ is calculated by the variational principle.

$$F = \min \mathfrak{F}, \tag{3.1}$$

$$\mathfrak{F} = \mathrm{tr}\rho_t[\mathcal{H} + kT\ \ln\rho_t], \tag{3.2}$$

where the minimum is taken with respect to the trial density matrix ρ_t under the normalization condition

$$\mathrm{tr}\rho_t = 1. \tag{3.3}$$

The Hamiltonian $\mathcal{H}$ is given by

$$\begin{aligned} \mathcal{H} = &-2J_2 \sum_{\langle\alpha,\beta\rangle} \mathbf{S}_\alpha\cdot\mathbf{S}_\beta - J_1\Big(\sum_{j(\alpha)}\sum_{k(\alpha)} \mathbf{S}_{j(\alpha)}\cdot\mathbf{S}_{k(\alpha)} \\ &+ \sum_{j(\beta)}\sum_{k(\beta)} \mathbf{S}_{j(\beta)}\cdot\mathbf{S}_{k(\beta)}\Big) + D\Big(\sum_\alpha S_{\alpha z}^2 + \sum_\beta S_{\beta z}^2\Big) \\ &- H_z\Big(\sum_\alpha S_{\alpha z} + \sum_\beta S_{\beta z}\Big) - H_x\Big(\sum_\alpha S_{\alpha x} + \sum_\beta S_{\beta x}\Big), \end{aligned} \tag{3.4}$$

where $\sum_{\langle\alpha,\beta\rangle}$ is the summation over all α-β pairs, $\sum_{j(\alpha)}\sum_{k(\alpha)}$ (or $\sum_{j(\beta)}\sum_{k(\beta)}$) is the summation over nearest-neighbor α-α (or β-β) pairs in the c-axis direction. J_1, J_2, and D are given by Eq. (2.3). Now the entropy term in Eq. (3.2) is calculated in such an approximate way that the two-spin correlation is retained but the three-spin and higher correlations are ignored. In this approximation the entropy term is written as[11]

$$\begin{aligned} \mathrm{tr}\rho_t \ln\rho_t = &\sum_j \mathrm{tr}_j\rho_t^{(1)}(j)\ \ln\rho_t^{(1)}(j) \\ &+ \sum_{\langle j,k\rangle} [\mathrm{tr}_{jk}\rho_t^{(2)}(j,k)\ \ln\rho_t^{(2)}(j,k) \\ &- \mathrm{tr}_j\rho_t^{(1)}(j)\ \ln\rho_t^{(1)}(j) - \mathrm{tr}_k\rho_t^{(1)}(k)\ \ln\rho_t^{(1)}(k)]. \end{aligned} \tag{3.5}$$

The reducibility conditions for $\rho_t^{(1)}$ and $\rho_t^{(2)}$ are

$$\mathrm{tr}_j\rho_t^{(1)}(j) - 1 = 0, \tag{3.6}$$

$$\mathrm{tr}_k\rho_t^{(2)}(j,k) - \rho_t^{(1)}(j) = 0. \tag{3.7}$$

Since the reducibility condition (3.7) is a matrix equation, it is equivalent to a set of $(2S+1)^2$ scalar equations. One can introduce a complete set of $(2S+1)^2$ matrices, 1 and $M_n(j)$ $[n=1, 2, \cdots, (2S+1)^2-1]$ such that any matrix A of order $2S+1$ can be expanded in terms of the elements of this set:

$$A = a_0 + \sum_n a_n M_n(j). \tag{3.8}$$

Then the reducibility conditions (3.7) for the variation are replaced by

$$\mathrm{tr}_j M_n(j)[\mathrm{tr}_k\rho_t^{(2)}(j,k) - \rho_t^{(1)}(j)] = 0, \qquad n = 1, 2, \cdots, (2S+1)^2-1 \tag{3.9}$$

and

$$\mathrm{tr}_{jk}\rho_t^{(2)}(j,k) = 1. \tag{3.10}$$

Instead of requiring all the reducibility conditions (3.9), we shall be satisfied only with the consistency condition for the first moment of the magnetization. In order to obtain a definite result we shall consider the case in which the external field is in the direction of anisotropy field, i.e., in the z direction; then

$$\mathrm{tr}_j S_{jz}[\mathrm{tr}_k\rho_t^{(2)}(j,k) - \rho_t^{(1)}(j)] = 0. \tag{3.11}$$

As a result of the variational calculation with respect to $\rho_t^{(1)}(j)$ and $\rho_t^{(2)}(j,k)$ one obtains

$$\rho^{(1)}(\alpha) = \exp\theta[f(\alpha) + (H_z + z_1\lambda_{\alpha\alpha} + z_2\lambda_{\beta\alpha})S_{\alpha z} + DS_{\alpha z}^2], \tag{3.12}$$

$$\rho^{(1)}(\beta) = \exp\theta[f(\beta) + (H_z + z_1\lambda_{\beta\beta} + z_2\lambda_{\alpha\beta})S_{\beta z} + DS_{\beta z}^2], \tag{3.13}$$

$$\begin{aligned} \rho^{(2)}(j(\alpha), k(\alpha)) = \exp\theta[&f(\alpha,\alpha) + (H_z + (z_1-1)\lambda_{\alpha\alpha} + z_2\lambda_{\beta\alpha})(S_{j(\alpha)z} + S_{k(\alpha)z}) \\ &+ D(S_{j(\alpha)z}^2 + S_{k(\alpha)z}^2) + 2J_1\mathbf{S}_{j(\alpha)}\cdot\mathbf{S}_{k(\alpha)}], \end{aligned} \tag{3.14}$$

$$\begin{aligned} \rho^{(2)}(j(\beta), k(\beta)) = \exp\theta[&f(\beta,\beta) + (H_z + (z_1-1)\lambda_{\beta\beta} + z_2\lambda_{\alpha\beta})(S_{j(\beta)z} + S_{k(\beta)z}) \\ &+ D(S_{j(\beta)z}^2 + S_{k(\beta)z}^2) + 2J_1\mathbf{S}_{j(\beta)}\cdot\mathbf{S}_{k(\beta)}], \end{aligned} \tag{3.15}$$

$$\rho^{(2)}(\alpha,\beta) = \exp\theta[f(\alpha,\beta) + (H_z + z_1\lambda_{\alpha\alpha} + (z_2-1)\lambda_{\beta\alpha})S_{\alpha z} + (H_z + z_1\lambda_{\beta\beta} + (z_2-1)\lambda_{\alpha\beta})S_{\beta z} + D(S_{\alpha z}^2 + S_{\beta z}^2) + 2J_2\mathbf{S}_\alpha\cdot\mathbf{S}_\beta], \tag{3.16}$$

---

[14] G. G. Low, A. Okazaki, R. W. H. Stevenson, and K. C. Turberfield, J. Appl. Phys. **35**, 998 (1964).

where $\theta=1/kT, f(\alpha), f(\beta), f(\alpha,\alpha), f(\beta,\beta)$, and $f(\alpha,\beta)$ are the normalization constants and $\lambda_{\alpha\alpha}$, $\lambda_{\beta\beta}$, $\lambda_{\alpha\beta}$, and $\lambda_{\beta\alpha}$ are the self-consistent local field parameters which should be determined by the consistency conditions for the first moment of the magnetization, i.e., by the following four equations:

$$\mathrm{tr}_\alpha S_{\alpha z}\rho^{(1)}(\alpha)=\mathrm{tr}_{jk}S_{j(\alpha)z}\rho^{(2)}(j(\alpha),k(\alpha))$$
$$=\mathrm{tr}_{\alpha\beta}S_{\alpha z}\rho^{(2)}(\alpha,\beta), \tag{3.17}$$
$$\mathrm{tr}_\beta S_{\beta z}\rho^{(1)}(\beta)=\mathrm{tr}_{jk}S_{j(\beta)z}\rho^{(2)}(j(\beta),k(\beta))$$
$$=\mathrm{tr}_{\alpha\beta}S_{\beta z}\rho^{(2)}(\alpha,\beta). \tag{3.18}$$

z_1, z_2 in Eqs. (3.12)–(3.16) are the number of neighbors in the c-axis direction and the number of $\beta(\alpha)$ sites around an $\alpha(\beta)$ site, respectively. For FeF_2, $z_1=2$ and $z_2=8$.

IV. MOLECULAR-FIELD APPROXIMATION

Before analyzing the high-temperature properties by the cluster-variation method we shall first find the values for various quantities in the molecular-field approximation for the purpose of a later comparison. In this approximation one has

$$\rho^{(1)}(\alpha)=\exp\theta\{f(\alpha)+[H_z+z_1\lambda_{\alpha\alpha}+z_2\lambda_{\beta\alpha}]S_{\alpha z}+DS_{\alpha z}^2\}, \tag{4.1}$$

$$\rho^{(1)}(\beta)=\exp\theta\{f(\beta)+[H_z+z_1\lambda_{\beta\beta}+z_2\lambda_{\alpha\beta}]S_{\beta z}+DS_{\beta z}^2\}, \tag{4.2}$$

where

$$\lambda_{\alpha\alpha}=2J_1\langle S_{\alpha z}\rangle,\qquad \lambda_{\beta\alpha}=2J_2\langle S_{\beta z}\rangle,$$
$$\lambda_{\beta\beta}=2J_1\langle S_{\beta z}\rangle,\qquad \lambda_{\alpha\beta}=2J_2\langle S_{\alpha z}\rangle. \tag{4.3}$$

The $\langle S_{\alpha z}\rangle$ and $\langle S_{\beta z}\rangle$ must be determined consistently by

$$\langle S_{\alpha z}\rangle=\mathrm{tr}_\alpha S_{\alpha z}\rho^{(1)}(\alpha),\qquad \langle S_{\beta z}\rangle=\mathrm{tr}_\beta S_{\beta z}\rho^{(1)}(\beta). \tag{4.4}$$

Now the sublattice magnetizations can be expressed as

$$\langle S_{\alpha z}\rangle=\langle S_{\alpha z}\rangle_0+\chi_{\parallel}(\alpha)H_z, \tag{4.5}$$
$$\langle S_{\beta z}\rangle=\langle S_{\beta z}\rangle_0+\chi_{\parallel}(\beta)H_z, \tag{4.6}$$

where $\langle S_{\alpha z}\rangle_0$ and $\langle S_{\beta z}\rangle_0$ are the spontaneous sublattice magnetizations below the Néel temperature and $\chi_{\parallel}(\alpha)$, $\chi_{\parallel}(\beta)$ are sublattice susceptibilities. Let us first calculate the susceptibilities above the Néel temperature. For $T>T_N$, the spontaneous magnetizations $\langle S_{\alpha z}\rangle_0$ and $\langle S_{\beta z}\rangle_0$ vanish. In this case, up to the first-order terms in the external field, one has

$$\chi_{\parallel}(\alpha)=\theta[1+2z_1J_1\chi_{\parallel}(\alpha)+2z_2J_2\chi_{\parallel}(\beta)]\varphi_{\parallel}(\theta), \tag{4.7}$$
$$\chi_{\parallel}(\beta)=\theta[1+2z_1J_1\chi_{\parallel}(\beta)+2z_2J_2\chi_{\parallel}(\alpha)]\varphi_{\parallel}(\theta), \tag{4.8}$$

where

$$\varphi_{\parallel}(\theta)=\{\mathrm{tr}S_z^2\exp\theta DS_z^2\}\times\{\mathrm{tr}\exp\theta DS_z^2\}^{-1}. \tag{4.9}$$

Solving these equations for $\chi_{\parallel}(\alpha)$, $\chi_{\parallel}(\beta)$ one finds

$$\chi_{\parallel}=\chi_{\parallel}(\alpha)=\chi_{\parallel}(\beta)=\frac{\theta\varphi_{\parallel}(\theta)}{1-2\theta(z_1J_1+z_2J_2)\varphi_{\parallel}(\theta)}. \tag{4.10}$$

When the external field H_x is applied along the x direction one obtains, again above the Néel temperature,

$$\rho^{(1)}=\exp\theta\{f+H_x[1+2(z_1J_1+z_2J_2)\chi_\perp]S_x+DS_z^2\} \tag{4.11}$$

for both the α and β sites, where $\chi_\perp[=\chi_\perp(\alpha)=\chi_\perp(\beta)]$ is the perpendicular susceptibility per lattice site. $\chi_\perp$ is calculated consistently by the formula

$$\langle S_x\rangle=\chi_\perp H_x=[\mathrm{tr}S_x\exp\theta\{H_x[1+2(z_1J_1+z_2J_2)\chi_\perp]S_x+DS_z^2\}][\mathrm{tr}\exp\theta\{H_x[1+2(z_1J_1+z_2J_2)\chi_\perp]S_x+DS_z^2\}]^{-1}. \tag{4.12}$$

In order to calculate $\chi_\perp$ up to the first order in H_x one uses the usual perturbation expansion for the exponential operator and finds

$$(\chi_\perp)^{-1}=[1/\theta\varphi_\perp(\theta)]-2(z_1J_1+z_2J_2), \tag{4.13}$$

where

$$\theta\varphi_\perp(\theta)=\int_0^\theta d\theta_1\{\mathrm{tr}[S_x\exp(\theta-\theta_1)DS_z^2]S_x$$
$$\times[\exp\theta_1DS_z^2]\}\{\mathrm{tr}\exp\theta DS_z^2\}^{-1}. \tag{4.14}$$

Since $S_x=\frac{1}{2}(S^++S^-)$ and S^+, S^- satisfy the commutation relations

$$S_zS^\pm=S^\pm(S_z\pm1),\qquad F(S_z)S^\pm=S^\pm F(S_z\pm1), \tag{4.15}$$

one finds

$$S_x[\exp(\theta-\theta_1)DS_z^2]S_x[\exp\theta_1DS_z^2]=\tfrac{1}{4}(S^++S^-)$$
$$\times\{S^+\exp[(\theta-\theta_1)D(S_z+1)^2+\theta_1DS_z^2]$$
$$+S^-\exp[(\theta-\theta_1)D(S_z-1)^2+\theta_1DS_z^2]\}. \tag{4.16}$$

Dropping the terms of S^+S^+ and S^-S^- which do not contribute to the trace, and integrating over θ_1, one finds

$$\theta\varphi_\perp(\theta)\{\mathrm{tr}\exp\theta DS_z^2\}=\tfrac{1}{4}\mathrm{tr}\{S^-S^+[\exp\theta D(S_z+1)^2$$
$$-\exp\theta DS_z^2][D(2S_z+1)]^{-1}+S^+S^-[\exp\theta DS_z^2$$
$$-\exp\theta D(S_z-1)^2][D(2S_z-1)]^{-1}\}. \tag{4.17}$$

One may use the identities

$$S^+S^-=S(S+1)-S_z(S_z-1),$$
$$S^-S^+=S(S+1)-S_z(S_z+1), \tag{4.18}$$

and find that the second term goes over into the first term by the transformation $S_z\rightarrow-S_z$. One finally has

$$\theta\varphi_\perp(\theta)\{\mathrm{tr}\exp\theta DS_z^2\}=\tfrac{1}{2}\mathrm{tr}\{(S-S_z)(S+1+S_z)$$
$$\times[\exp\theta D(S_z+1)^2-\exp\theta DS_z^2][D(2S_z+1)]^{-1}\}. \tag{4.19}$$

The magnetic anisotropy, above the Néel temperature, is then given by

$$\chi_{\|}-\chi_{\perp}=\{[1/\theta\varphi_{\|}(\theta)]-2(z_1J_1+z_2J_2)\}^{-1}$$
$$-\{[1/\theta\varphi_{\perp}(\theta)]-2(z_1J_1+z_2J_2)\}^{-1}. \quad (4.20)$$

Second, we shall calculate the spontaneous sublattice magnetizations below the Néel temperature. The consistency equations are

$$\langle S_{\alpha z}\rangle_0=B_{\|}(x,\theta D), \qquad \langle S_{\beta z}\rangle_0=B_{\|}(x',\theta D), \quad (4.21)$$

where

$$B_{\|}(x,\theta D)$$
$$=\{\operatorname{tr}S_z\exp[xS_z+\theta DS_z^2]\}/\operatorname{tr}\exp[xS_z+\theta DS_z^2], \quad (4.22)$$

$$x=2\theta[z_1J_1\langle S_{\alpha z}\rangle_0+z_2J_2\langle S_{\beta z}\rangle_0], \quad (4.23)$$

$$x'=2\theta[z_1J_1\langle S_{\beta z}\rangle_0+z_2J_2\langle S_{\alpha z}\rangle_0]. \quad (4.24)$$

One can easily see that the $B_{\|}(x,\theta D)$ is an odd function of x, and hence $\langle S_{\alpha z}\rangle_0=-\langle S_{\beta z}\rangle_0$ satisfies Eqs. (4.21) consistently. The magnetization $\langle S_z\rangle_0=\langle S_{\alpha z}\rangle_0=-\langle S_{\beta z}\rangle_0$ is then found as the solution of

$$\langle S_z\rangle_0=B_{\|}(x_0,\theta D), \quad (4.25)$$

where

$$x_0=2\theta[z_1J_1-z_2J_2]\langle S_z\rangle_0. \quad (4.26)$$

In order to solve Eq. (4.25) for $\langle S_z\rangle_0$ consistently, one proceeds as follows: From Eq. (4.24) plot $\langle S_z\rangle_0$ as a function of x_0 (a straight line) for the same temperature. From the intersection of the two curves, one finds the spontaneous sublattice magnetization for the given temperature.

Finally, the susceptibility below the Néel temperature will be calculated. For this purpose one sets

$$\langle S_{\alpha z}\rangle=\langle S_{\alpha z}\rangle_0+\chi_{\|}(\alpha)H_z,$$
$$\langle S_{\beta z}\rangle=\langle S_{\beta z}\rangle_0+\chi_{\|}(\beta)H_z. \quad (4.27)$$

Then one finds, up to the linear terms in the external field,

$$\chi_{\|}(\alpha)=\theta[1+2z_1J_1\chi_{\|}(\alpha)+2z_2J_2\chi_{\|}(\beta)]\psi_{\|}(\theta),$$
$$\chi_{\|}(\beta)=\theta[1+2z_1J_1\chi_{\|}(\beta)+2z_2J_2\chi_{\|}(\alpha)]\psi_{\|}(\theta), \quad (4.28)$$

where

$$\psi_{\|}(\theta)=dB_{\|}(x_0,\theta D)/dx_0$$
$$=\langle S_z^2\rangle_0-\langle S_z\rangle_0^2 \quad (4.29)$$

and

$$\langle S_z^2\rangle_0$$
$$=\{\operatorname{tr}S_z^2\exp[x_0S_z+\theta DS_z^2]\}/\{\operatorname{tr}\exp[x_0S_z+\theta DS_z^2]\}. \quad (4.30)$$

One sees again quite easily that $\psi_{\|}(x_0,\theta D_z)$ is an even function of x_0 and hence

$$\chi_{\|}=\chi_{\|}(\alpha)=\chi_{\|}(\beta)$$
$$=1/\{[1/\theta\psi_{\|}]-2(z_1J_1+z_2J_2)\}. \quad (4.31)$$

When the external field is applied along the x direction, one obtains again by the perturbation expansion

$$\chi_{\perp}=\chi_{\perp}(\alpha)=\chi_{\perp}(\beta)=1/\{[1/\theta\psi_{\perp}]-2(z_1J_1+z_2J_2)\}, \quad (4.32)$$

where

$$\psi_{\perp}(\theta)=(1/2\theta)\{\operatorname{tr}(S-S_z)(S+1+S_z)(\exp[x_0(S_z+1)+\theta D(S_z+1)^2]$$
$$-\exp[x_0S_z+\theta DS_z^2])[(x_0/\theta)+D(2S_z+1)]^{-1}\}\{\operatorname{tr}\exp[x_0S_z+\theta DS_z^2]\}^{-1}. \quad (4.33)$$

Now the Néel temperature will be calculated from Eqs. (4.25) and (4.26). At a temperature slightly below the Néel temperature, the sublattice magnetization is vanishingly small. The $B_{\|}(x_0,\theta D)$ is therefore expanded into powers of x_0 and only the lowest-order term is retained. One finds as the condition for the Néel temperature

$$1=2\theta_N(z_1J_1-z_2J_2)\varphi_{\|}(\theta_N), \qquad \theta_N=1/kT_N. \quad (4.34)$$

This is a transcendental equation for T_N. In the absence of the anisotropy this reduces to the usual equation

$$T_N=\tfrac{2}{3}(z_1J_1-z_2J_2)S(S+1). \quad (4.35)$$

TABLE I. Theoretical and experimental values of the Néel temperature of FeF$_2$.

		Mol. field	2-spin cluster	Expt.	Lines
$D=0$	$J_1>0$	91.2°K	78.5°K		
	$J_1<0$	86.7°K	73.8°K		
$D=9.4$°K	$J_1>0$	102.9°K	79.2°K		
	$J_1<0$	95.0°K	74.5°K	79°K	88.5°K

Substituting the values (2.3) and $S=2$, one obtains

$$T_N=91.2°\text{K}, \qquad J_1>0$$
$$T_N=86.7°\text{K}, \qquad J_1<0, \qquad D=0. \quad (4.36)$$

Since $D/kT_N\cong0.1$, $\varphi_{\|}(\theta)$ is approximated by

$$\varphi_{\|}(\theta)=\tfrac{1}{3}S(S+1)[1+(1/15)(4S^2+4S-3)\theta D$$
$$+(1/630)(16S^4+32S^3-56S^2-72S+45)(\theta D)^2].$$

Substituting this value into Eq. (4.34) one finds the corrected Néel temperature

$$T_N=99.1°\text{K}, \qquad J_1>0$$
$$T_N=95.0°\text{K}, \qquad J_1<0, \qquad D=9.4°\text{K}. \quad (4.37)$$

At this point it is instructive to show that $\chi_{\perp}$ reduces to a constant in the limit as $D\rightarrow 0$. In Eq. (4.33) one sets $D=0$,

$$
\begin{aligned}
&2\theta\psi_\perp(\theta)(z_1J_1-z_2J_2)\langle S_z\rangle_0\\
&=\tfrac{1}{4}\mathrm{tr}\{[S(S+1)-S_z(S_z+1)][\exp x_0(S_z+1)-\exp x_0S_z]+[S(S+1)-S_z(S_z-1)][\exp x_0(S_z-1)\\
&\qquad\qquad -\exp x_0S_z]\}\{\exp x_0S_z\}^{-1}\\
&=\tfrac{1}{4}\mathrm{tr}\{S^-(\exp x_0S_z)S^+-S^+(\exp x_0S_z)S^-+2S_z\exp x_0S_z\}\{\exp x_0S_z\}^{-1}\\
&=\langle S_z\rangle_0.
\end{aligned}
$$

Hence

$$\theta\psi_\perp(\theta)=(2z_1J_1-2z_2J_2)^{-1}.$$

Substituting this into (4.32) one obtains

$$\chi_\perp=1/4z_2\,|J_2|.$$

V. NÉEL TEMPERATURE IN THE TWO-SPIN CLUSTER APPROXIMATION

The reducibility conditions (3.11) state that the magnetizations $\langle S_{\alpha z}\rangle$ as calculated from each of the three different density matrices $\rho^{(1)}(\alpha)$, $\rho^{(2)}(j(\alpha),k(\alpha))$, $\rho^{(2)}(\alpha,\beta)$ must be equal to each other. Let us now find explicit forms for the magnetization $\langle S_{\alpha z}\rangle$. Near and below the Néel temperature, the sublattice magnetizations are vanishingly small and all the local field parameters are very small. Therefore, the terms proportional to these parameters can be treated as infinitesimal perturbations. In this limit Eq. (3.17) reduced to

$$\langle S_{\alpha z}\rangle_0=\mathrm{tr}_\alpha S_{\alpha z}\rho^{(1)}(\alpha) \tag{5.1}$$

$$=\theta(z_1\lambda_{\alpha\alpha}+z_2\lambda_{\beta\alpha})\varphi_{||}(\theta), \tag{5.2}$$

where $\varphi_{||}(\theta)$ is the same function as was defined by Eq. (4.9). In the same limit the two-spin magnetizations reduce, respectively, to

$$
\begin{aligned}
\langle S_{\alpha z}\rangle_0&=\tfrac{1}{2}\mathrm{tr}_{j(\alpha),k(\alpha)}[S_{j(\alpha)z}+S_{k(\alpha)z}]\rho^{(2)}(j(\alpha),k(\alpha))\\
&=\theta[(z_1-1)\lambda_{\alpha\alpha}+z_2\lambda_{\beta\alpha}]\varphi_{AA}(\theta),
\end{aligned} \tag{5.3}
$$

$$\langle S_{\alpha z}\rangle_0=[z_1\lambda_{\alpha\alpha}+(z_2-1)\lambda_{\beta\alpha}]\varphi_{AB}(\theta), \tag{5.4}$$

where φ_{AA}, φ_{AB} are given by

$$
\begin{aligned}
\varphi_{AA}=&\tfrac{1}{2}\{\mathrm{tr}_{12}(S_{1z}+S_{2z})^2\exp\theta[D(S_{1z}{}^2+S_{2z}{}^2)+2J_1\mathbf{S}_1\cdot\mathbf{S}_2]\}\\
&\times\{\mathrm{tr}_{12}\exp\theta[D(S_{1z}{}^2+S_{2z}{}^2)+2J_1\mathbf{S}_1\cdot\mathbf{S}_2]\}^{-1},
\end{aligned} \tag{5.5}
$$

$$
\begin{aligned}
\varphi_{AB}=&\sum_j\sum_{j'}\sum_M\langle jM\,|\,S_{1z}\,|\,j'M\rangle\langle j'M\,|\,S_{1z}-S_{2z}\,|\,jM\rangle\\
&\times[\exp(\theta\lambda jM)-\exp(\theta\lambda j'M)][\lambda(j,M)-\lambda(j',M)]^{-1}\\
&\times\{\sum_j\sum_M\exp\theta\lambda(j,M)\}^{-1}.
\end{aligned} \tag{5.6}
$$

In order to obtain Eqs. (5.5) and (5.6) the fact has been used that the two sublattices α and β are equivalent in the absence of the external field except for the spin orientation. This means that

$$\lambda_{\beta\beta}=-\lambda_{\alpha\alpha},\qquad\lambda_{\alpha\beta}=-\lambda_{\beta\alpha}. \tag{5.7}$$

Now the consistency conditions are

$$
\begin{aligned}
&[(z_1-1)\lambda_{\alpha\alpha}+z_2\lambda_{\beta\alpha}]\varphi_{AA}(\theta)=(z_1\lambda_{\alpha\alpha}+z_2\lambda_{\beta\alpha})\varphi_{||}(\theta),\\
&[z_1\lambda_{\alpha\alpha}+(z_2-1)\lambda_{\beta\alpha}]\varphi_{AB}(\theta)=(z_1\lambda_{\alpha\alpha}+z_2\lambda_{\beta\alpha})\varphi_{||}(\theta).
\end{aligned} \tag{5.8}
$$

One can eliminate the λ's from Eq. (5.8) and find

$$z_1/\varphi_{AA}(\theta)+z_2/\varphi_{AB}(\theta)=(z_1+z_2-1)/\varphi_{||}(\theta). \tag{5.9}$$

This is a transcendental equation for the Néel temperature. The separate sides of this equation are plotted as a function of θ and from the intersection the Néel temperature is found. Using the values in Eq. (2.3) one calculates the values summarized in Table I.

VI. SUSCEPTIBILITIES ABOVE THE NÉEL TEMPERATURE

Above the Néel temperature, and in the presence of an infinitesimal external field, the various local fields also become very small, and hence all terms containing the local fields are justifiably treated as infinitesimal perturbations. Since there is no spontaneous sublattice magnetization above the Néel temperature, the two sublattices become equivalent. In this case one can set

$$
\begin{aligned}
\lambda_{\alpha\alpha}&=\lambda_{\beta\beta}=\lambda_{\alpha\alpha}'H_z,\\
\lambda_{\beta\alpha}&=\lambda_{\alpha\beta}=\lambda_{\alpha\beta}'H_z.
\end{aligned} \tag{6.1}
$$

Various magnetizations, up to the linear terms in the H_z, are

$$\langle S_{\alpha z}\rangle^{(1)}=\theta H_z[1+z_1\lambda_{\alpha\alpha}'+z_2\lambda_{\beta\alpha}']\varphi_{||}(\theta), \tag{6.2}$$

$$\langle S_{\alpha z}\rangle_{\alpha,\alpha}{}^{(2)}=\theta H_z[1+(z_1-1)\lambda_{\alpha\alpha}'+z_2\lambda_{\beta\alpha}']\varphi_{AA}(\theta,J_1), \tag{6.3}$$

$$\langle S_{\alpha z}\rangle_{\alpha,\beta}{}^{(2)}=\theta H_z[1+z_1\lambda_{\alpha\alpha}'+(z_2-1)\lambda_{\beta\alpha}']\varphi_{AA}(\theta,J_2), \tag{6.4}$$

where $\varphi_{AA}(\theta,J_1)$ and $\varphi_{AA}(\theta,J_2)$ are the same function as given by Eq. (5.5) except that J_1 is replaced by J_2 in $\varphi_{AA}(\theta,J_2)$. The self-consistency conditions for the magnetization yield equations for the λ's. Solving these equations, one obtains

$$\lambda_{\alpha\alpha}'=\Delta^{-1}\times\begin{vmatrix}\varphi_{||}-\varphi_{AA}(\theta,J_1) & z_2[\varphi_{AA}(\theta,J_1)-\varphi_{||}]\\ \varphi_{||}-\varphi_{AA}(\theta,J_2) & (z_2-1)\varphi_{AA}(\theta,J_2)-z_2\varphi_{||}\end{vmatrix}, \tag{6.5}$$

$$\lambda_{\beta\alpha}'=\Delta^{-1}\times\begin{vmatrix}(z_1-1)\varphi_{AA}(\theta,J_1)-z_1\varphi_{||} & z_2\varphi_{||}(\theta)-\varphi_{AA}(\theta,J_1)\\ z_1[\varphi_{AA}(\theta,J_2)-\varphi_{||}(\theta)] & \varphi_{||}-\varphi_{AA}(\theta,J_2)\end{vmatrix}, \tag{6.6}$$

where

$$\Delta=\begin{vmatrix} (z_1-1)\varphi_{AA}(\theta,J_1)-z_1\varphi_{\|} & z_2[\varphi_{AA}(\theta,J_1)-\varphi_{\|}] \\ z_1[\varphi_{AA}(\theta,J_2)-\varphi_{\|}] & (z_2-1)\varphi_{AA}(\theta,J_2)-z_2\varphi_{\|} \end{vmatrix}. \tag{6.7}$$

The parallel susceptibility is given by

$$\chi_{\|}(\theta)=\theta[1+z_1\lambda_{\alpha\alpha}'+z_2\lambda_{\beta\alpha}']\varphi_{\|}(\theta). \tag{6.8}$$

The perpendicular susceptibility will be calculated in a very similar way:

$$\langle S_{\alpha x}\rangle^{(1)}=\mathrm{tr}S_{\alpha x}\rho^{(1)}(\alpha)=H_x[1+z_1\mu_{\alpha\alpha}'+z_2\mu_{\beta\alpha}']\phi_{\perp}(\theta), \tag{6.9}$$

$$\langle S_{\alpha\alpha}\rangle_{\alpha\alpha}^{(2)}=\mathrm{tr}S_{\alpha x}\rho^{(2)}(\alpha,\alpha)=H_x[1+(z_1-1)\mu_{\alpha\alpha}'+z_2\mu_{\beta\alpha}']\Phi_{AA}(\theta,J_1), \tag{6.10}$$

$$\langle S_{\alpha x}\rangle_{\alpha,\beta}^{(2)}=\mathrm{tr}S_{\alpha x}\rho^{(2)}(\alpha,\beta)=H_x[1+z_1\mu_{\alpha\alpha}'+(z_2-1)\mu_{\beta\alpha}']\Phi_{AA}(\theta,J_2), \tag{6.11}$$

where H_x is the external field in the x direction, $\mu_{\alpha\alpha}'$, $\mu_{\beta\alpha}'$ are the pertinent local fields, and $\phi_{\perp}(\theta)$, $\Phi_{AA}(\theta,J_2)$, and $\Phi_{AA}(\theta,J_1)$ are given by

$$\phi_{\perp}(\theta)=\sum_{m=-S}^{S}\left\{\frac{2[m^2+S(S+1)]\exp(Dm^2\theta)}{(2m+1)(2m-1)}+\frac{(S-m)(S+m+1)\exp[D(m+1)^2\theta]}{2m+1}\right.$$
$$\left.-\frac{(S+m)(S-m+1)\exp[D(m-1)^2\theta]}{(2m-1)}\right\}\Big/\left[4D\sum_{m=-S}^{S}\exp(Dm^2\theta)\right], \tag{6.12}$$

$$\Phi_{AA}(\theta,J)=\tfrac{1}{2}\sum_{(j,M,j',M',\mathcal{S},\mathcal{S}')}\cdots\sum|\langle jM|\mathcal{S}M\rangle\langle\mathcal{S}M|\mathcal{S}_x|\mathcal{S}'M'\rangle\langle\mathcal{S}'M'|j'M'\rangle|^2$$
$$\times\{[\exp(\theta\lambda(j',M'))-\exp(\theta\lambda(j,M))][\lambda(j',M')-\lambda(j,M')]^{-1}\}\{\sum_{j,M}\exp\theta\lambda(j,M)\}^{-1}, \tag{6.13}$$

where $\langle jM|\mathcal{S}M\rangle$'s are elements of the unitary transformation matrix calculated in Sec. VII, λjM's are the eigenvalues of the effective two-spin Hamiltonian [Eq. (7.1)].

Elimination of the local fields gives the following expressions for the susceptibilities:

$$\chi_{\|}(\theta)=\theta\left\{\frac{2}{\varphi_{AA}(\theta,J_1)}+\frac{8}{\varphi_{AA}(\theta,J_2)}-\frac{9}{\varphi_{\|}}\right\}^{-1}, \tag{6.14}$$

$$\chi_{\perp}(\theta)=\left\{\frac{2}{\Phi_{AA}(\theta,J_1)}+\frac{8}{\Phi_{AA}(\theta,J_2)}-\frac{9}{\Phi_{\perp}}\right\}^{-1}. \tag{6.15}$$

The temperature dependence of $\chi_{\perp}$ and $\chi_{\|}$ are calculated from these equations and the results plotted in Fig. 2.

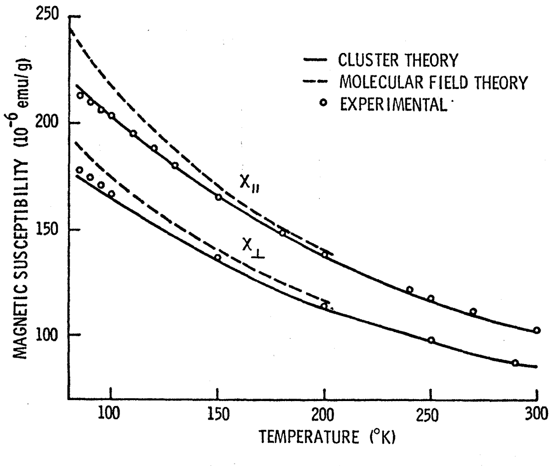

FIG. 2. The paramagnetic susceptibilities for FeF$_2$ as predicted by molecular-field theory and the two-spin-cluster model.

VII. DIAGONALIZATION OF EFFECTIVE HAMILTONIANS

In order to calculate the Néel temperature or the susceptibility above the Néel temperature it is necessary to first diagonalize the effective two-spin Hamiltonian of the following form:

$$D(S_{1z}^2+S_{2z}^2)+2J\mathbf{S}_1\cdot\mathbf{S}_2, \tag{7.1}$$

where D and J are arbitrary constants.

As was pointed out in Sec. I, the anisotropy constant D has been treated as a small perturbation, in the literature, compared with the exchange integrals. But as the recent experimental data[11] and Lines's analysis[13] show, D is not necessarily small. As a matter of fact, D is even larger than the exchange J_2, and therefore one is not justified in treating D as a small perturbation. In this section it will be shown that it is possible to diagonalize the Hamiltonian (7.1) by solving only up to third-order equations (for $S=2$). This means that the diagonalization can be done analytically.

One now introduces, as usual, the operators

$$\mathcal{S}=\mathbf{S}_1+\mathbf{S}_2,\qquad \mathcal{S}_z=S_{1z}+S_{2z}, \tag{7.2}$$

and then uses the representation in which $\mathcal{S}^2$ and $\mathcal{S}_z$ are diagonal simultaneously:

$$\mathcal{S}^2|\mathcal{S},M\rangle=\mathcal{S}(\mathcal{S}+1)|\mathcal{S},M\rangle,\qquad \mathcal{S}_z|\mathcal{S},M\rangle=M|\mathcal{S},M\rangle,$$
$$0\leq\mathcal{S}\leq2S,\qquad -\mathcal{S}\leq M\leq\mathcal{S}. \tag{7.3}$$

Equation (7.1) is now written as

$$D\mathcal{S}_z^2+J[\mathcal{S}^2-2S(S+1)]-2DS_{1z}S_{2z}. \tag{7.4}$$

In Eq. (7.4) only the last term is not diagonal in the new representation (7.3). In our case of Fe^{++} the spin $S=2$, and hence $S_{1z}S_{2z}$ is a 25×25 matrix. It is known however that both S_{1z} and S_{2z} are diagonal and hence $S_{1z}S_{2z}$ is block-wise diagonal with respect to M. Those diagonal subspaces are classified according to M

$$\mathcal{S}_z=M, \qquad |M|\leq\mathcal{S}\leq 2S, \qquad M=0, \pm 1, \cdots, \pm 4.$$

Therefore, even the largest matrix is only a 5×5 matrix. Furthermore, the S_{1z}, S_{2z} have elements between $\mathcal{S}$ and $\mathcal{S}'=\mathcal{S}\pm 1(0)$ and hence the matrix $S_{1z}S_{2z}$ is separated into odd and even spaces. The matrix elements of $S_{1z}S_{2z}$ in this representation are calculated by the standard method. These are

$$\langle\mathcal{S}, M\,|\,S_{1z}S_{2z}\,|\,\mathcal{S}', M\rangle=\langle\mathcal{S}\,|\,(1,2)\,|\,\mathcal{S}\pm 2(0)\rangle_M, \tag{7.5}$$

$$\langle 4\,|\,(1,2)\,|\,4\rangle_4=8J+8D, \tag{7.6}$$

$$\langle\mathcal{S}\,|\,(1,2)\,|\,\mathcal{S}'\rangle_3=\begin{bmatrix}5D & 0\\ 0 & 8J+5D\end{bmatrix}\begin{array}{l}3\\ 4\end{array}, \tag{7.7}$$

$$\langle\mathcal{S}\,|\,(1,2)\,|\,\mathcal{S}'\rangle_2=\begin{bmatrix}-6J+22D/7 & 4\sqrt{3}D/7 & \\ 4\sqrt{3}D/7 & 8J+20D/7 & \\ & & 4D\end{bmatrix}\begin{array}{l}2\\ 4,\\ 3\end{array} \tag{7.8}$$

$$\langle\mathcal{S}\,|\,(1,2)\,|\,\mathcal{S}'\rangle_1=\begin{bmatrix}-6J+31D/7 & 4\sqrt{6}D/7 & & \\ 4\sqrt{6}D/7 & 8J+11D/7 & & \\ & & -10J+13D/5 & 4\sqrt{6}D/5\\ & & 4\sqrt{6}D/5 & 17D/5\end{bmatrix}\begin{array}{l}2\\ 4\\ 1\\ 3\end{array}, \tag{7.9}$$

$$\langle\mathcal{S}\,|\,(1,2)\,|\,\mathcal{S}'\rangle_0=\begin{bmatrix}\langle\mathcal{S}\,|\,(1,2)\,|\,\mathcal{S}'\rangle_{0g} & 0\\ 0 & \langle\mathcal{S}\,|\,(1,2)\,|\,\mathcal{S}'\rangle_{0u}\end{bmatrix}, \tag{7.10a}$$

$$\langle\mathcal{S}\,|\,(1,2)\,|\,\mathcal{S}'\rangle_{0gu}=\begin{bmatrix}-10J+34D/5 & 12D/5\\ 12D/5 & 16D/5\end{bmatrix}\begin{array}{l}1\\ 3\end{array}, \tag{7.10b}$$

$$\langle\mathcal{S}\,|\,(1,2)\,|\,\mathcal{S}'\rangle_{0g}=\begin{bmatrix}-12J+4D & 2\sqrt{70}D/5 & 0\\ 2\sqrt{70}D/5 & -6J+34D/7 & 24\sqrt{5}D/35\\ 0 & 24\sqrt{5}D/35 & 8J+8D/7\end{bmatrix}\begin{array}{l}0\\ 2.\\ 4\end{array}$$

Now five 2×2 and one 3×3 matrices must be diagonalized. This is achieved analytically by the usual method. A symmetric 2×2 matrix of general form is diagonalized by the transformation

$$U_2\begin{bmatrix}a & c\\ c & b\end{bmatrix}U_2^{-1}=\begin{bmatrix}\lambda_1 & \\ & \lambda_2\end{bmatrix}, \tag{7.11}$$

where

$$\lambda_{12}=\tfrac{1}{2}\{(a+b)\pm[(a-b)^2+4c^2]^{1/2}\}, \tag{7.12}$$

$$U_2=\begin{bmatrix}-c/R_2(\lambda_1) & (a-\lambda_1)/R_2(\lambda_1)\\ -c/R_2(\lambda_1) & (a-\lambda_1)/R_2(\lambda_2)\end{bmatrix}, \tag{7.13}$$

and

$$R_2(\lambda)=[(a-\lambda)^2+c^2]^{1/2}. \tag{7.14}$$

Similarly, a symmetric 3×3 matrix is diagonalized:

$$U_3\begin{bmatrix}a & f & 0\\ f & b & g\\ 0 & g & c\end{bmatrix}U_3^{-1}=\begin{bmatrix}\lambda_1 & & \\ & \lambda_2 & \\ & & \lambda_3\end{bmatrix}, \tag{7.15}$$

where

$$U_3=\begin{bmatrix}-f(c-\lambda_1)/R_3(\lambda_1) & (a-\lambda_1)(c-\lambda_1)/R_3(\lambda_1) & -g(a-\lambda_1)/R_3(\lambda_1)\\ -f(c-\lambda_2)/R_3(\lambda_2) & (a-\lambda_2)(c-\lambda_2)/R_3(\lambda_2) & -g(a-\lambda_2)/R_3(\lambda_2)\\ -f(c-\lambda_3)/R_3(\lambda_3) & (a-\lambda_3)(c-\lambda_3)/R_3(\lambda_3) & -g(a-\lambda_3)/R_3(\lambda_3)\end{bmatrix} \tag{7.16}$$

and

$$R_3(\lambda)=[(a-\lambda)^2(c-\lambda)^2+f^2(c-\lambda)^2+g^2(a-\lambda)^2]^{1/2}. \tag{7.17}$$

Once eigenvalues of the effective two-spin Hamiltonian are known, $\varphi_{AA}(\theta)$ of Eq. (5.5) can be calculated. In order to calculate $\varphi_{AB}(\theta)$ of Eq. (5.6), however, one more step is necessary. This is to find diagonal elements of the operator $S_{1z}(S_{1z}-S_{2z})$ in the representation in which the effective two-spin Hamiltonian is diagonal. The matrix elements of this operator in the $(\mathcal{S}, M)$ representation are given in the following:

$$\langle \mathcal{S}, M \mid S_{1z}(S_{1z}-S_{2z}) \mid \mathcal{S}', M' \rangle = \langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_M, \tag{7.18}$$

$$\langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_4 = 0, \tag{7.19}$$

$$\langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_3 = \left[\begin{array}{cc} \frac{1}{2} & \frac{3}{2} \\ \frac{3}{2} & \frac{1}{2} \end{array}\right]\begin{array}{l} 3 \\ 4 \end{array}, \tag{7.20}$$

$$\langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_2 = \left[\begin{array}{ccc} 2 & 4/\sqrt{7} & 2\sqrt{3}/\sqrt{7} \\ 4/\sqrt{7} & 8/7 & 4\sqrt{3}/7 \\ 2\sqrt{3}/\sqrt{7} & 4\sqrt{3}/7 & 6/7 \end{array}\right]\begin{array}{l} 3 \\ 2, \\ 4 \end{array} \tag{7.21}$$

$$\langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_1 = \left[\begin{array}{cc} \langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_{1g} & \langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_{gu} \\ \langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_{gu} & \langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_{1u} \end{array}\right], \tag{7.22}$$

$$\langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_{1g} = \left[\begin{array}{cc} 55/14 & \sqrt{6}/\sqrt{7} \\ \sqrt{6}/\sqrt{7} & 15/14 \end{array}\right]\begin{array}{l} 2 \\ 4 \end{array},$$

$$\langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_{1u} = \left[\begin{array}{cc} 21/10 & 4\sqrt{6}/5 \\ 4\sqrt{6}/5 & 29/10 \end{array}\right]\begin{array}{l} 1 \\ 3 \end{array},$$

$$\langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_{gu} = \left[\begin{array}{cc} \sqrt{21}/2\sqrt{5} & 0 \\ 4\sqrt{2}/\sqrt{35} & \sqrt{15}/2\sqrt{7} \end{array}\right], \tag{7.22$'$}$$

$$\langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_0 = \left[\begin{array}{cc} \langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_{0g} & 0 \\ 0 & \langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_{0u} \end{array}\right], \tag{7.23}$$

$$\langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_{0u} = \left[\begin{array}{cc} 34/5 & 12/5 \\ 12/5 & 16/5 \end{array}\right]\begin{array}{l} 1 \\ 3 \end{array}, \tag{7.23$'$}$$

$$\langle \mathcal{S} \mid (1, 1-2) \mid \mathcal{S}' \rangle_{0g} = \left[\begin{array}{ccc} 4 & 2\sqrt{14/5} & 0 \\ 2\sqrt{14}/\sqrt{5} & 34/7 & 24/7\sqrt{5} \\ 0 & 24/7\sqrt{5} & 8/7 \end{array}\right]\begin{array}{l} 0 \\ 2. \\ 4 \end{array} \tag{7.23$''$}$$

Using the above matrix representation, one can now calculate the diagonal elements of

$$US_{1z}(S_{1z}-S_{2z})U^{-1} \tag{7.24}$$

within a given M subspace. All these can be done independently of the temperature, hence only once.

VIII. RESULTS AND CONCLUSION

One of the principal results of the numerical calculations is that the effect of the crystal-field anisotropy on the Néel temperature is very much less pronounced in the two-spin cluster approximation than in the Weiss approximation. The shift of the Néel temperature due to the anisotropy is 0.9% ($J_1>0$), 0.95% ($J_1<0$) in the two-spin cluster approximation, while in the Weiss approximation it is 12.8% ($J_1>0$), 9.6% ($J_1<0$). This insensitivity of the Néel temperature to the anisotropy is, at first, quite surprising, but this is in general accord with the experimental data for $\mathrm{MnF_2}$ and $\mathrm{FeF_2}$.

The two systems compared have the same crystal structure. The origin of anisotropy in $\mathrm{MnF_2}$ is mainly a dipole-dipole interaction, and hence the anisotropy is not expressible as a uniaxial-energy term except at very low temperatures. Nevertheless, $\mathrm{MnF_2}$ may be regarded as a system which has a relatively small anisotropy, while $\mathrm{FeF_2}$ has a huge anisotropy. A comparison of their Néel temperatures would, therefore, furnish a test of whether the Néel temperature is sensitive to the anisotropy. Table II indicates that the difference in the Néel temperatures is almost accounted for by the difference in the major exchange integrals J_2 and the spin values.

The effect of the crystal-field anisotropy on the Néel temperature was first investigated by Cooper.[10] The analysis is done in both the Weiss approximation and the two-spin cluster approximation, for $S=1$ and with only one exchange constant. The two-spin cluster approximation which Cooper uses is, however, the Oguchi method[15] and therefore the effective field appearing in the effective two-spin Hamiltonian is replaced by $(z_2-1)/z_2$ times the Weiss field. Cooper finds about the same strong sensitivity in the two approximations adopted.

A similar sensitivity analysis for ferromagnetic systems was performed by Callen.[16] He uses the Weiss molecular-field approximation, with only one exchange constant, and for $S=1$ he found a strong sensitivity of the Curie temperature to the uniaxial anisotropy. In more recent papers, Lines[9,13] found the same sensitivity for a more realistic model, i.e., with $S=2$, by the method of the two-time Green's function, although the intrasublattice exchange J_1 was ignored in the treatment.

---

[15] T. Oguchi, Progr. Theoret. Phys. (Kyoto) **13**, 148 (1955).

[16] E. R. Callen, J. Appl. Phys. **32**, 221S (1961); Phys. Rev. **124**, 1373 (1961).

TABLE II. Comparison of the anisotropy, exchange integral, and Néel temperature.

	MnF_2 ($S=\frac{5}{2}$)	FeF_2 ($S=2$)
D/J_2	0.12[a]	3.4
T_N (exp)	67.3°K	79°K
$3T_N/2z_2J_2S(S+1)$	0.85	0.91

[a] Reference 14.

We found a similar strong sensitivity when we worked within the Weiss approximation. The insensitivity we found by the two-spin cluster approximation is in contradiction with the Green's-function approximation which is supposed to be better than the Weiss approximation. At this moment it is not possible to resolve the discrepancy. One possible interpretation of this discrepancy would be the following. The decoupling scheme proposed by Lines is derived for a system which has a vanishingly small anisotropy, nevertheless, as Lines states, the decoupling is used for FeF_2 which has a large anisotropy. In the present formulation the two-spin cluster-variation method is used with both the intersublattice and intrasublattice exchanges, and for $S=2$. There is no limitation on the magnitude of the anisotropy field, because the effective two-spin Hamiltonian is rigorously diagonalized.

The second observation we can make from the present theory concerns the sensitivity of the Néel temperature to the intrasublattice exchange J_1. If one changes the value of J_1 by 20% of J_2, i.e., from $J_1=0.1\,J_2$ to $J_1=-0.1\,J_2$, one finds a change in T_N of about 5% (see Table I). This sensitivity is again quite surprising at first, because of the fact that D is very large and yet has almost no effect on T_N while J_1 is very small but has a large effect on T_N. We have

$$D=3.4J_2, \qquad J_1=\pm 0.1J_2.$$

This is accounted for however by a simple molecular-field-type consideration

$$\Delta T_N/T_N=\Delta\,|\,z_1J_1/z_2J_2\,|$$
$$=5\times 10^{-2} \qquad (z_1=2,\ z_2=8).$$

The susceptibilities $\chi_{\parallel}$ and $\chi_{\perp}$ are shown in Fig. 2. These quantities have been calculated for both signs of J_1, but the difference due to this change is negligibly small.

The close agreement of our calculations with experimental data may be partly accidental. It nevertheless suggests the following method of determining the values of the pertinent constants: The anisotropy field constant D may be determined by the susceptibilities $\chi_{\parallel}$ and $\chi_{\perp}$ above the Néel temperature (where the susceptibilities are insensitive to J_1). J_2 can be determined rather accurately by AFMR frequency at very low temperature when the resonance frequency is a known function of only J_2 and D. With these values of J_2 and D, and experimental Néel temperature the value of J_1 may be fixed.

Our results provide at least one step of improvement over the Weiss approximation in that (a) the Néel temperature is more accurately evaluated in the presence of a large crystal-field anisotropy and (b) the two-spin correlation including up to second neighbors is taken into account. Extension of the calculations to temperatures below the Néel temperature is underway. It is also of considerable interest to see how much improvement would result if three-spin correlation is included. This is a subject of a future investigation.

ACKNOWLEDGMENTS

The authors would like to express their thanks to Dr. Tohru Morita for many valuable suggestions in the early stage of the present investigation. They also thank Dr. Ojiro Nagai. A discussion with him led to a correct proof of the temperature independence of the perpendicular susceptibility below the Néel temperature in the absence of crystal-field anisotropy.