THE

PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. **150**, NO. 2 14 OCTOBER 1966

Magnetic Properties of Magnetite

EARL CALLEN

Department of Physics, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan

and

U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland

(Received 9 May 1966)

Below the Verwey transition the Fe^{2+} and Fe^{3+} ions on B sites in magnetite are magnetically coupled to A-site ions by different exchange constants. We calculate the six-sublattice spin-wave spectrum of this ordered orthorhombic structure, for arbitrary spin quantum numbers and for arbitrary ferrimagnetic nearest-neighbor exchange interactions coupling A ions with two different kinds of B-site ions. Inelastic neutron scattering by Verwey-ordered magnetite, which has not been studied, will allow evaluation of the two exchange constants and of the dynamics of their averaging through the transition. In spite of differences of the exchange constants and of the numbers of nearest neighbors (an A-site ion has twice as many nearest neighbors as does a B-site ion), we show that all sublattices and the net moment have the same temperature dependence, in the spin-wave region, apart from their proportionality to their 0°K value. This holds also if intrasublattice exchange, which we ignore, is included, and for other symmetries. Besides sublattice magnetizations we also calculate the ferrimagnetic-resonance g factor and specific heat, both above and below the Verwey transition. The observed Mössbauer spectrum is explained, but many other experiments remain unexplained.

I. INTRODUCTION

MAGNETITE undergoes an electronic ordering transition at 119°K.[1] Below that temperature the octahedral (B-site) Fe^{3+} and Fe^{2+} ions, which are randomly distributed above the transition, arrange themselves on alternate (001) planes. Bickford[2] showed that if a magnetite crystal is cooled in a magnetic field along a cube edge, the ordered planes lie perpendicular to the field direction. If the field is then rotated to a different symmetry axis the ordering will slowly follow the field. An orthorhombic distortion accompanies the transition. There is a net moment both above and below the Verwey transition, the spins forming a Néel structure, with the orthorhombic c axis easy. The octahedral ferric ions lie in rows along the orthorhombic a axis and the ferrous ions in rows along the shorter b axis, the cubic face diagonals. Pressure along a cubic [110] removes twinning in the orthorhombic phase. In a paper with extensive references, Hamilton,[3] by means of neutron diffraction, directly confirmed the Verwey structure, which had first been inferred from a resistivity jump. Crystal distortion should stabilize this ordering, which shall herein be approximated as complete below the transition.

Specific heat,[4] ferrimagnetic resonance,[5,6] inelastic neutron scattering,[7] nuclear magnetic resonance (NMR),[8,9] moment measurements[8,10] and the Mössbauer spectrum[11–13] have all been studied on magnetite, and considerable theoretical analysis[14–16] has been

---

[1] E. J. Verwey and E. L. Hailmann, J. Chem. Phys. **15**, 174 (1947); E. J. W. Verwey, P. H. Haayman, and F. C. Romeijn, *ibid.* **15**, 181 (1947).

[2] L. R. Bickford, Jr., Rev. Mod. Phys. **25**, 75 (1953).

[3] Walter C. Hamilton, Phys. Rev. **110**, 1050 (1958).

[4] J. S. Kouvel, Phys. Rev. **102**, 1489 (1956).

[5] L. R. Bickford, Phys. Rev. **76**, 137 (1949).

[6] D. B. Bonstrom, A. H. Morrish, and L. A. K. Watt, J. Appl. Phys. **32**, 272S (1961).

[7] H. Watanabe and B. N. Brockhouse, Phys. Letters **1**, 189 (1962).

[8] E. L. Boyd, Phys. Rev. **129**, 1961 (1963).

[9] S. Ogawa and S. Morimoto, J. Phys. Soc. Japan **17**, 654 (1962); S. Ogawa, S. Morimoto, and Y. Kimura, *ibid.* **17**, 1671 (1962).

[10] A. H. Eschenfelder (private communication).

[11] I. Solomon, Compt. Rend. **251**, 2675 (1960).

[12] R. Bauminger, S. G. Cohen, A. Marinov, S. Ofer, and E. Segal, Phys. Rev. **122**, 1447 (1961).

[13] K. Ono, Y. Ishikawa, A. Ito, and E. Hirahara, J. Phys. Soc. Japan **17**, Suppl. B-1, 125 (1962); A. Ito, K. Ono and Y. Ishikawa, *ibid.* **18**, 1465 (1963).

[14] J. S. Kouvel, Technical Report 210, Cruft Laboratory, Harvard, 1955 (unpublished).

[15] F. J. Milford and M. L. Glasser, Phys. Letters **2**, 248 (1962); M. Lawrence Glasser and Frederick J. Milford, Phys. Rev. **130**, 1783 (1963).

[16] Richard P. Kenan, M. Lawrence Glasser, and Frederick J. Milford, Phys. Rev. **132**, 47 (1963).

applied to their interpretation. However, serious discrepancies exist, both qualitative and numerical. For example, the Mössbauer spectrum below the Verwey transition consists of but two sets of lines, one from Fe^{2+} ions, and one from Fe^{3+} ions on both tetrahedral and octahedral sites; it had been expected that, corresponding to the three types of sites, three sets of lines would be observed. As for quantitative analysis every observation appears to suggest different exchange constants.

It was consideration of exchange interactions that motivated the present work. Lithium ferrite, $Fe^{3+}[Li^{1+}{}_{0.5}\,Fe^{3+}{}_{2.5}]O_4$, has a Néel temperature of 953°K. From molecular field theory, with $\frac{3}{4}$ of the B sites effective,

$$kT_N=\frac{1}{2\sqrt{3}}(z_Az_B)^{1/2}J_3S(S+1)\,. \tag{1.1}$$

With $z_A=2z_B=12$, $S=\frac{5}{2}$, we find

$$J_3/k=45°\mathrm{K}. \tag{1.2}$$

Now consider magnetite. We take it that sufficiently above the Verwey transition electron exchange between B sites is so rapid that these sites are effectively occupied by a single ionic species, of spin $\bar{S}$, AB exchange constant $\bar{J}$ and g factor $\bar{g}$. As a zeroth approximation (we shall not get to first) we may even at times consider that

$$\bar{S}=\tfrac{1}{2}(S_{B(2)}+S_{B(3)})\,, \tag{1.3a}$$

$$\bar{J}=\tfrac{1}{2}(J_2+J_3)\,, \tag{1.3b}$$

$$\bar{g}=\tfrac{1}{2}(g_2+g_3)\,, \tag{1.3c}$$

although the implications of these latter assumptions are not the substance of this paper. Here $S_{B(2)}$ is the spin of Fe^{2+}, and $S_{B(3)}$ that of the Fe^{3+} ion. J_2 is the exchange constant between Fe^{2+} on a B site and Fe^{3+} on A. From the Néel temperature of magnetite, $T_N=855°K$, and molecular field theory we then find

$$\bar{J}/k=37.5°\mathrm{K} \tag{1.4a}$$

and, from Eqs. (1.2) and (1.3b),

$$J_2/k=30°\mathrm{K}. \tag{1.4b}$$

So one wonders what are the implications of different AB exchange constants for Fe^{2+} and Fe^{3+} B-site ions.

In this paper we calculate the six-sublattice spin-wave spectrum of ordered magnetite, for arbitrary spin quantum numbers and for arbitrary ferrimagnetic nearest-neighbor exchange interactions coupling A ions with two kinds of B-site ions. We then calculate the sublattice magnetizations, and show that all sublattices and the net moment have the same temperature dependence in the low-temperature region, apart from a proportionality to their magnitudes at 0°K. This result applies even if intrasublattice exchange constants J_{AA} and J_{BB} are included, and holds also in other symmetries, although we shall ignore intrasublattice exchange because it has been shown experimentally to be small,[15] and shall consider only the spinel structure. After presenting equations for the ferrimagnetic resonance g factor and specific heat of the ordered structure, we give the simple formulas relevant well above the Verwey transition, when electrons on B sites hop around so rapidly that these sites may be considered to be populated with a single ionic species of some unspecified "average" nature. In the final section we compare calculations of the magnetic properties of both ordered and disordered states with experiment.

II. SPIN-WAVE SPECTRUM OF THE ORDERED STRUCTURE

The magnetization is taken along the z axis, with the ordered layers in (001) planes. Because the magnetic properties are rather insensitive to structure, we ignore the effect of noncubic crystal distortion on the spin-wave spectrum (through γ_k), although the orthorhombic *magnetic* structure will indeed be apparent in our results. The method and notation follow closely those of Kaplan.[17] Kouvel[14] has also considered the effect of ordering.

The Hamiltonian is

$$\mathcal{H}=J_2\sum_{\langle ij\rangle}\mathbf{S}_i{}^A\cdot\mathbf{S}_j{}^{B(2)}+J_3\sum_{\langle il\rangle}\mathbf{S}_i{}^A\cdot\mathbf{S}_l{}^{B(3)}\,. \tag{2.1}$$

$S_i{}^A$ is the spin operator for an octahedral ion, $S_j{}^{B(2)}$ is the spin operator for a nearest-neighbor tetrahedral ion of species $B(2)$, coupled to ion i with exchange constant J_2. Ionic species $B(3)$ populates B sites, labeled l. The six magnetic atoms in a primitive unit cell are shown in Fig. 1. The two types of A sites are labeled by an index $\alpha=1,2$ while index $\beta=1,3$ goes over the two $B(2)$ sites

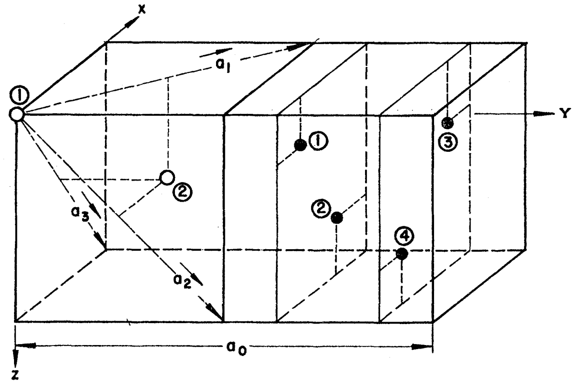

FIG. 1. The sites in a primitive unit cell of the spinel structure. ○ = A sites; ● ① and ● ③ = $B(2)$; ● ② and ● ④ = $B(3)$ sites. (Oxygen not shown.) The primitive translations of the rhombohedral unit cell are shown as $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$. Considerably after T. A. Kaplan, Phys. Rev. **109**, 782 (1958).

---

[17] T. A. Kaplan, Phys. Rev. **109**, 782 (1958).

and $\beta'=2,4$ covers the $B(3)$ sites. Within linear spin-wave theory the Holstein-Primakoff spin operators for the six-sublattices are then

$$\begin{aligned} S_{i\alpha}{}^{+}&=(2S_A)^{1/2}a_{i\alpha}\,, \\ S_{i\alpha}{}^{-}&=(2S_A)^{1/2}a_{i\alpha}{}^{\dagger}\,, \qquad \alpha=1,2 \qquad &(2.2\text{a}) \\ S_{i\alpha}{}^{z}&=S_A-a_{i\alpha}{}^{\dagger}a_{i\alpha}\,, \end{aligned}$$

$$\begin{aligned} S_{j\beta}{}^{+}&=(2S_{B(2)})^{1/2}b_{j\beta}{}^{\dagger}\,, \\ S_{j\beta}{}^{-}&=(2S_{\beta(2)})^{1/2}b_{j\beta}\,, \qquad \beta=1,3 \qquad &(2.2\text{b}) \\ S_{j\beta}{}^{z}&=-S_{B(2)}+b_{j\beta}{}^{\dagger}b_{j\beta}\,, \end{aligned}$$

$$\begin{aligned} S_{l\beta'}{}^{+}&=(2S_{B(3)})^{1/2}b_{l\beta'}{}^{\dagger}\,, \\ S_{l\beta'}&=(2S_{B(3)})^{1/2}b_{l\beta'}\,, \qquad \beta'=2,4 \qquad &(2.2\text{c}) \\ S_{l\beta'}{}^{z}&=-S_{B(3)}+b_{l\beta'}{}^{\dagger}b_{l\beta'}\,. \end{aligned}$$

These all satisfy the boson commutation relations, for example,

$$(a_{i\alpha},a_{i'\alpha'}{}^{\dagger})=\delta_{ii'}\delta_{\alpha\alpha'}\,, \tag{2.3}$$

while operators for different sites commute.

With a periodic region of N primitive rhombohedral cells, we transform to the momentum representation:

$$a_{n\alpha}=N^{-1/2}\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}_{n\alpha}{}^{A}}a_{k\alpha}\,, \tag{2.4a}$$

$$b_{n\beta}=N^{-1/2}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_{n\beta}{}^{B(2)}}b_{k\beta}\,, \tag{2.4b}$$

$$b_{n\beta'}=N^{-1/2}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_{n\beta'}{}^{B(3)}}b_{k\beta'}\,. \tag{2.4c}$$

The inverse transforms, and transforms of the adjoint operators are evident. These operators again all satisfy the boson commutation relations, for example,

$$(b_{k\beta},b_{k'\mu}{}^{\dagger})=\delta_{kk'}\delta_{\beta\mu}\,, \tag{2.5}$$

with operators for different momenta or sublattices commuting. Following Kaplan, the Hamiltonian is now reduced to

$$\begin{aligned} \mathcal{H}=\tfrac{1}{2}z_A(J_2S_{B(2)}+J_3S_{B(3)})&\sum_{k\alpha} a_{k\alpha}{}^{\dagger}a_{k\alpha} \\ &+z_BJ_2S_A\sum_{k\beta} b_{k\beta}{}^{\dagger}b_{k\beta}+z_BJ_3S_A\sum_{k\beta'} b_{k\beta'}{}^{\dagger}b_{k\beta'} \\ &+J_2(S_AS_{B(2)})^{1/2}\sum_{k\alpha\beta}[\zeta_{\alpha\beta}(-\mathbf{k})a_{k\alpha}{}^{\dagger}b_{k\beta}{}^{\dagger} \\ &+\zeta_{\alpha\beta}(\mathbf{k})a_{k\alpha}b_{k\beta}]+J_3(S_AS_{B(3)})^{1/2} \\ &\quad\times\sum_{k\alpha\beta'}[\zeta_{\alpha\beta'}(-\mathbf{k})a_{k\alpha}{}^{\dagger}b_{k\beta'}{}^{\dagger}+\zeta_{\alpha\beta}(\mathbf{k})a_{k\alpha}b_{k\beta'}]\,. \end{aligned} \tag{2.6}$$

Here

$$\zeta_{\alpha\beta}(\mathbf{k})\equiv\sum_{u=1}^{3} e^{i\mathbf{k}\cdot\boldsymbol{\tau}_{\alpha\beta}{}^{u}}\,. \tag{2.7}$$

The $24\boldsymbol{\tau}_{\alpha\beta}{}^{u}$, listed by Kaplan, are, for each particular α and β (or β'), the three vectors from an α site to the nearest-neighbor β (or β') sites.

The $\zeta_{\alpha\beta}(\mathbf{k})$ can be decomposed into even and odd parts relative to the inversion operation $\mathbf{k}\rightarrow-\mathbf{k}$:

$$\zeta_{\alpha\beta}(\mathbf{k})=\zeta_{\alpha\beta}{}^{e}(\mathbf{k})+i\zeta_{\alpha\beta}{}^{o}(\mathbf{k})\,, \tag{2.8}$$

with

$$\zeta_{1\beta}{}^{e}(\mathbf{k})=\zeta_{2\beta}{}^{e}(\mathbf{k}) \tag{2.9a}$$

and

$$\zeta_{1\beta}{}^{o}(\mathbf{k})=-\zeta_{2\beta}{}^{o}(\mathbf{k})\,. \tag{2.9b}$$

We shall be interested in the eigenvalues only up to quadratic terms in k. Then

$$\zeta_{\alpha\beta}{}^{e}=3-(11/128)k^2a_0{}^2-(\tfrac{1}{2})x_{\alpha\beta}\equiv\eta-(\tfrac{1}{2})x_{\alpha\beta}\,, \tag{2.10}$$

with

$$\begin{aligned} x_{11}&=-(5/32)a_0{}^2(k_xk_y+k_yk_z+k_zk_x)\,, \\ x_{12}&=(5/32)a_0{}^2(k_xk_y+k_yk_z-k_zk_x)\,, \\ x_{13}&=(5/32)a_0{}^2(-k_xk_y+k_yk_z+k_zk_x)\,, \\ x_{14}&=(5/32)a_0{}^2(k_xk_y-k_yk_z+k_zk_x)\,, \end{aligned} \tag{2.11}$$

and

$$x_{1\beta}=x_{2\beta}\,. \tag{2.12}$$

The odd functions are

$$\begin{aligned} \zeta_{11}{}^{o}&=-\tfrac{1}{8}a_0(k_x+k_y+k_z)\,, \\ \zeta_{12}{}^{o}&=\tfrac{1}{8}a_0(k_x-k_y+k_z)\,, \\ \zeta_{13}{}^{o}&=\tfrac{1}{8}a_0(k_x+k_y-k_z)\,, \\ \zeta_{14}{}^{o}&=\tfrac{1}{8}a_0(-k_x+k_y+k_z)\,. \end{aligned} \tag{2.13}$$

For succinctness, define

$$\begin{aligned} &A=(z_A/2)(J_2S_{B(2)}+J_3S_{B(3)}) \\ &B=z_BJ_2S_A\,; \qquad B'=z_BJ_3S_A \\ &\gamma=J_2(S_AS_{B(2)})^{1/2}; \quad \gamma'=J_3(S_AS_{B(3)})^{1/2}. \end{aligned} \tag{2.14}$$

The symmetry of $\zeta_{\alpha\beta}$ suggests transformations to acoustic and optic combinations:

$$m_k=\frac{a_{k1}+a_{k2}}{\surd2}\,; \quad \phi_{k5}=-i\frac{a_{k1}-a_{k2}}{\surd2} \tag{2.15a}$$

$$p_k=\frac{b_{k1}+b_{k3}}{\surd2}\,; \quad \phi_{k2}=\frac{b_{k1}-b_{k3}}{\surd2} \tag{2.15b}$$

$$r_k=\frac{b_{k2}+b_{k4}}{\surd2}\,; \quad \phi_{k4}=\frac{b_{k2}-b_{k4}}{\surd2}\,. \tag{2.15c}$$

The adjoints and inverses are obvious, and the boson commutation relations are preserved;

$$(\phi_{ki},\phi_{k'j}{}^{\dagger})=\delta_{kk'}\delta_{ij}\,. \tag{2.16}$$

The Hamiltonian becomes

$$\begin{aligned}\mathcal{H}=\sum_k\{&A[m_k^\dagger m_k+\phi_{k5}^\dagger\phi_{k5}]+B[p_k^\dagger p_k+\phi_{k2}^\dagger\phi_{k2}]+B'[r_k^\dagger r_k+\phi_{k4}^\dagger\phi_{k4}]+2\gamma[(\eta+(5/64)a_0^2k_xk_y)(m_k^\dagger p_k^\dagger+m_kp_k)\\&+(5/64)a_0^2(k_yk_z+k_zk_x)(m_k^\dagger\phi_{k2}^\dagger+m_k\phi_{k2})+(a_0/8)(k_x+k_y)(\phi_{k5}^\dagger\phi_{k2}^\dagger+\phi_{k5}\phi_{k2})+(a_0/8)k_z(\phi_{k5}^\dagger p_k^\dagger+\phi_{k5}p_k)]\\&+2\gamma'[(\eta-(5/64)a_0^2k_xk_y)(m_k^\dagger r_k^\dagger+m_kr_k)-(5/64)a_0^2(k_yk_z-k_zk_x)(m_k^\dagger\phi_{k4}^\dagger+m_k\phi_{k4})\\&-(a_0/8)(k_x-k_y)(\phi_{k5}^\dagger\phi_{k4}^\dagger+\phi_{k5}\phi_{k4})-(a_0/8)k_z(\phi_{k5}^\dagger r_k^\dagger+\phi_{k5}r_k)]\}.\end{aligned}\qquad(2.17)$$

This can be diagonalized very easily by consideration of the Hamiltonian at $k=0$:

$$\begin{aligned}\mathcal{H}_0=&A(m^\dagger m+\phi_5^\dagger\phi_5)+B(p^\dagger p+\phi_2^\dagger\phi_2)+B'(r^\dagger r+\phi_4^\dagger\phi_4)\\&+2\gamma\eta_0(m^\dagger p^\dagger+mp)+2\gamma'\eta_0(m^\dagger r^\dagger+mr).\end{aligned}\qquad(2.18)$$

ϕ_5, ϕ_2, and ϕ_4 are optic modes with eigenvalues A, B, and B'. By the equations-of-motion method we find the other three modes (at $k=0$) to be

$$\phi_0=N_0\left[m^\dagger+\frac{2\eta_0\gamma}{B}p+\frac{2\eta_0\gamma'}{B'}r\right],\qquad(2.19\text{a})$$

with normalization

$$N_0^2=\frac{S_A}{S_{B(2)}+S_{B(3)}-S_A},\qquad(2.19\text{b})$$

and eigenvalue $\qquad \epsilon_0=0;\qquad(2.19\text{c})$

$$\phi_1^\dagger=N_1\left[m^\dagger+\frac{2\eta_0\gamma}{B+\epsilon_1}p+\frac{2\eta_0\gamma'}{B'+\epsilon_1}r\right],\qquad(2.20\text{a})$$

with normalization

$$N_1^2=\left[1-\left(\frac{2\eta_0\gamma}{B+\epsilon_1}\right)^2-\left(\frac{2\eta_0\gamma'}{B'+\epsilon_1}\right)^2\right]^{-1},\qquad(2.20\text{b})$$

and eigenvalue

$$\begin{aligned}\epsilon_1=\frac{A-B-B'}{2}+\frac{1}{2}\bigg[&A^2+2(B'-B)\\&\times\left(\frac{(2\eta_0\gamma)^2}{B}-\frac{(2\eta_0\gamma')^2}{B'}\right)+(B'-B)^2\bigg]^{1/2};\end{aligned}\qquad(2.20\text{c})$$

and

$$\phi_3=N_3\left[m^\dagger+\frac{2\eta_0\gamma}{B-\epsilon_3}p+\frac{2\eta_0\gamma'}{B'-\epsilon_3}r\right],\qquad(2.21\text{a})$$

with normalization

$$N_3^2=\left[-1+\left(\frac{2\eta_0\gamma}{B-\epsilon_3}\right)^2+\left(\frac{2\eta_0\gamma'}{B'-\epsilon_3}\right)^2\right]^{-1},\qquad(2.21\text{b})$$

and eigenvalue

$$\begin{aligned}\epsilon_3=\frac{-A+B+B'}{2}+\frac{1}{2}\bigg[&A^2+2(B'-B)\\&\times\left(\frac{(2\eta_0\gamma)^2}{B}-\frac{(2\eta_0\gamma')^2}{B'}\right)+(B'-B)^2\bigg]^{1/2}.\end{aligned}\qquad(2.21\text{c})$$

All three modes ϕ_0, ϕ_1, and ϕ_3 are acoustic, but ϕ_3 precesses in the opposite sense from ϕ_1, and has a higher energy. All six modes satisfy the boson commutation relation

$$(\phi_i,\phi_j^\dagger)=\delta_{ij}.\qquad(2.22)$$

The six modes reduce to those of Kaplan when $B=B'$ and $\gamma=\gamma'$, that is when there is only one species of ion on the B sites with spin quantum number S_B and AB exchange constant J. We have ordered the eigenvalues to conform to his sequence, but the triple degeneracy of modes ϕ_2, ϕ_3, and ϕ_4 of Kaplan's special case is now removed. In Fig. 2 we show the dependence of the eigenvalues on J_2/J_3, for the case of interest in magnetite, $S_A=S_{B(3)}=\frac{5}{2}$, $S_{B(2)}=2$. There is a crossing of levels at $J_2/J_3\cong0.67$, and the triple degeneracy is apparent at $J_2/J_3=1$.

An interesting question arises concerning the "antiferromagnetic" condition (although the spinel differs from a true antiferromagnet in that the several sites are crystallographically distinct). In the case of a single type of ion on the B sites the condition for the degeneracy of two levels at $k=0$ and $\epsilon=0$ is that

$$2S_B=S_A.\qquad(2.23)$$

Diagonalizing the degenerate operators yields the linear k dependence of the energy of the antiferromagnet. In the present case the result is similar but less evident. For mode ϕ_2 to have zero energy we must have $B=0$, or $J_2=0$, in which case sublattice $B_{(2)}$ is unmagnetized and $S_A=S_{B(3)}$. For mode ϕ_4 the argument is similar. Mode ϕ_5 has zero energy only in the absence of any exchange interactions at all. For modes ϕ_1 and/or ϕ_3 to be degenerate with ϕ_0 at $k=0$, we must have

$$\begin{aligned}(A-B-B')^2=&A^2+2(B'-B)\\&\times\left(\frac{(2\eta_0\gamma)^2}{B}-\frac{(2\eta_0\gamma')^2}{B'}\right)+(B'-B)^2.\end{aligned}\qquad(2.24)$$

Substitution from (2.14) (recall that $\eta_0=3$) leads, irrespective of J_2 and J_3 to

$$S_A=S_{B(2)}+S_{B(3)},\qquad(2.25)$$

the condition for "antiferromagnetism."

To continue with the diagonalization of the Hamiltonian at nonzero k we must invert (2.19a), (2.20a), and (2.21a) and substitute into Eq. (2.17). It is profit-

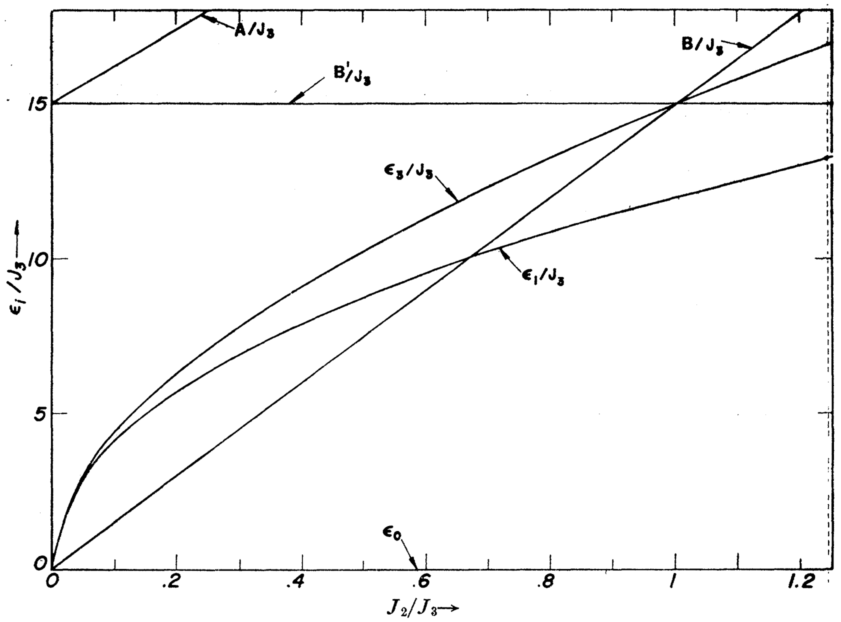

FIG. 2. Energies (divided by J_3) of the six spin-wave modes, at $k=0$, as functions of J_2/J_3. $S_A=S_{B(3)}=\frac{5}{2}$, $S_{B(2)}=2$.

able to anticipate that our attention is confined to the low-temperature approximation, with only the small-k region of the lowest branch populated. We are thus interested in the projections of $m^\dagger$, p, and r only on ϕ_0. Let

$$\begin{aligned} m^\dagger &= c\phi_0+\text{other terms},\\ p&=d\phi_0+\text{other terms},\\ r&=g\phi_0+\text{other terms}. \end{aligned} \tag{2.26}$$

Algebra produces

$$\begin{aligned} c&=-N_0=-\left(\frac{S_A}{S_{B(2)}+S_{B(3)}-S_A}\right)^{1/2},\\ d&=\left(\frac{S_{B(2)}}{S_{B(2)}+S_{B(3)}-S_A}\right)^{1/2},\\ g&=\left(\frac{S_{B(3)}}{S_{B(2)}+S_{B(3)}-S_A}\right)^{1/2}. \end{aligned} \tag{2.27}$$

To obtain the energy of the lowest branch up to at most second-order terms in k, only very few terms in Eq. (2.17) need be retained. Off-diagonal terms between branches other than ϕ_{k0} can be dropped. Terms in which ϕ_{k0} occurs only once can contribute only if the coupling is linear in k. Main-diagonal terms in $\phi_{k0}{}^\dagger\phi_{k0}$ can be second order in k. Concentrating attention on the lowest branch, the relevant terms in Eq. (2.17) reduce to

$$\mathcal{H}=\sum_k\Big\{\left[\mathfrak{D}_0a_0{}^2k^2+\tfrac{5}{16}a_0{}^2k_xk_yc(\gamma d-\gamma' g)\right]\phi_{k0}{}^\dagger\phi_{k0} +A\phi_{k5}{}^\dagger\phi_{k5}+\frac{a_0}{4}k_z(\gamma d-\gamma' g) \times(\phi_{k0}{}^\dagger\phi_{k5}{}^\dagger+\phi_{k0}\phi_{k5})\Big\}. \tag{2.28}$$

This is again diagonalized by the rhythm method or the Bogoliubov transformation, with the result

$$\psi_{k0}=\mathfrak{N}_0\left[\phi_{k0}+\frac{a_0k_z}{4A}(\gamma d-\gamma' g)\phi_{k5}{}^\dagger\right], \tag{2.29a}$$

$$\mathfrak{N}_0{}^2=1+\frac{a_0{}^2k_z{}^2}{16A^2}(\gamma d-\gamma' g)^2, \tag{2.29b}$$

and

$$\epsilon_{k0}=\mathfrak{D}_0a_0{}^2k^2+\tfrac{5}{16}a_0{}^2k_xk_yc(\gamma d-\gamma' g) -\frac{a_0{}^2k_z{}^2}{16A}(\gamma d-\gamma' g)^2. \tag{2.29c}$$

The first term on the right of Eq. (2.29c) is the isotropic term in k^2 which reduces to Kaplan's result. The third term shows a dependence of the energy on $k_z{}^2$, which exists because the B-site atoms are layered in (001) planes. The orthorhombic symmetry of the spin-wave spectrum which comes from the arrangement of $B(2)$ and $B(3)$ ions in [110] lines, and which is closely related to the orthorhombic lattice distortion, is made more manifest in the second term of Eq. (2.29c) by rotation of coordinates around z by $-\pi/4$:

$$k_x=\frac{k_\xi-k_\eta}{\sqrt{2}},\quad k_y=\frac{k_\xi+k_\eta}{\sqrt{2}}. \tag{2.30}$$

Then the energy of the lowest branch of the spin-wave spectrum becomes

$$\epsilon_{k0}=\mathfrak{D}_0a_0{}^2k^2+\mathfrak{D}_ta_0{}^2(k_\xi{}^2-k_\eta{}^2)-\mathfrak{D}_la_0{}^2k_z{}^2, \tag{2.31a}$$

with

$$\mathfrak{D}_0=\frac{11}{32}\frac{S_A}{S_{B(2)}+S_{B(3)}-S_A}(J_3S_{B(3)}+J_2S_{B(2)}), \quad (2.31b)$$

$$\mathfrak{D}_t=\frac{5}{32}\frac{S_A}{S_{B(2)}+S_{B(3)}-S_A}(J_3S_{B(3)}-J_2S_{B(2)}), \quad (2.31c)$$

$$\mathfrak{D}_l=\frac{1}{96}\frac{S_A}{S_{B(2)}+S_{B(3)}-S_A}\frac{(J_3S_{B(3)}-J_2S_{B(2)})^2}{J_3S_{B(3)}+J_2S_{B(2)}}. \quad (2.31d)$$

Note that when $J_2S_{B(2)}=J_3S_{B(3)}$, both $\mathfrak{D}_t$ and $\mathfrak{D}_l$ vanish and cubic symmetry is restored. Note also that

$$0\leqslant|\mathfrak{D}_t|/\mathfrak{D}_0<1, \quad (2.32a)$$

and

$$0\leqslant\mathfrak{D}_l/\mathfrak{D}_0<1, \quad (2.32b)$$

so that the excitation energy of the Néel structure is non-negative and the structure is stable.

By algebra identical to that culminating in Eq. (2.31), all six branches of the spin-wave spectrum are easily obtained to order k^2.

III. STATISTICAL MECHANICS OF THE ORDERED STRUCTURE

Having reduced the Hamiltonian to number operators in the lowest modes, inversion of transformations (2.26) and (2.29a) gives

$$\langle m_k{}^\dagger m_k\rangle=\left(\frac{S_A}{S_{B(2)}+S_{B(3)}-S_A}\right)\left(1+\frac{a_0{}^2k_z{}^2\mathfrak{D}_l}{A}\right)\times\langle\psi_{k0}\psi_{k0}{}^\dagger\rangle, \quad (3.1a)$$

$$\langle p_k{}^\dagger p_k\rangle=\left(\frac{S_{B(2)}}{S_{B(2)}+S_{B(3)}-S_A}\right)\left(1+\frac{a_0{}^2k_z{}^2\mathfrak{D}_l}{A}\right)\times\langle\psi_{k0}{}^\dagger\psi_{k0}\rangle, \quad (3.1b)$$

$$\langle r_k{}^\dagger r_k\rangle=\left(\frac{S_{B(3)}}{S_{B(2)}+S_{B(3)}-S_A}\right)\left(1+\frac{a_0{}^2k_z{}^2\mathfrak{D}_l}{A}\right)\times\langle\psi_{k0}{}^\dagger\psi_{k0}\rangle, \quad (3.1c)$$

$$\langle\phi_{k5}{}^\dagger\phi_{k5}\rangle=\frac{a_0{}^2k_z{}^2\mathfrak{D}_l}{A}\langle\psi_{k0}{}^\dagger\psi_{k0}\rangle, \quad (3.1d)$$

$$\langle\phi_{k4}{}^\dagger\phi_{k4}\rangle=\langle\phi_{k2}{}^\dagger\phi_{k2}\rangle=0, \quad (3.1e)$$

when only modes of the lowest branch are thermally excited.

A. Sublattice Magnetizations

From Eq. (2.2a) the average z component of spin per molecule unit, of the A sublattice is

$$\langle S_A{}^z\rangle=\tfrac{1}{2}\langle S_{A1}{}^z+S_{A2}{}^z\rangle=S_A-\frac{1}{2N}\sum_{i\alpha}\langle a_{i\alpha}{}^\dagger a_{i\alpha}\rangle,$$

$$\langle S_A{}^z\rangle=S_A-\frac{1}{2N}\sum_{k\alpha}\langle a_{k\alpha}{}^\dagger a_{k\alpha}\rangle,$$

and from (2.15a), (3.1a), and (3.1d),

$$\langle S_A{}^z\rangle=S_A-\mathfrak{z}_A-\frac{1}{2N}\frac{S_A}{S_{B(2)}+S_{B(3)}-S_A}\sum_k\langle\chi_{k0}{}^\dagger\psi_{k0}\rangle-\frac{1}{2N}\times\frac{S_{B(2)}+S_{B(3)}}{S_{B(2)}+S_{B(3)}-S_A}\frac{a_0{}^2\mathfrak{D}_l}{A}\sum_k k_z{}^2\langle\psi_{k0}{}^\dagger\psi_{k0}\rangle. \quad (3.2)$$

The average z component of spin per molecule unit, of the $B(2)$ ions is

$$\langle S_{B(2)}{}^z\rangle=\tfrac{1}{2}\langle S_{B(2)1}{}^z+S_{B(2)3}{}^z\rangle=-S_{B(2)}+\frac{1}{2N}\sum_{k\beta}\langle b_{k\beta}{}^\dagger b_{k\beta}\rangle \quad (3.3)$$

and from (2.15b), (3.1b), and (3.1e),

$$\langle S_{B(2)}{}^z\rangle=-S_{B(2)}+\mathfrak{z}_{B(2)}+\frac{1}{2N}\frac{S_{B(2)}}{S_{B(2)}+S_{B(3)}-S_A}\times\sum_k\langle\psi_{k0}{}^\dagger\psi_{k0}\rangle+\frac{1}{2N}\frac{S_{B(2)}}{S_{B(2)}+S_{B(3)}-S_A}\frac{a_0{}^2\mathfrak{D}_l}{A}\times\sum_k k_z{}^2\langle\psi_{k0}{}^\dagger\psi_{k0}\rangle, \quad (3.4)$$

and similarly

$$\langle S_{B(3)}{}^z\rangle=-S_{B(3)}+\mathfrak{z}_{B(3)}+\frac{1}{2N}\frac{S_{B(3)}}{S_{B(2)}+S_{B(3)}-S_A}\times\sum_k\langle\psi_{k0}{}^\dagger\psi_{k0}\rangle+\frac{1}{2N}\frac{S_{B(3)}}{S_{B(2)}+S_{B(3)}-S_A}\frac{a_0{}^2\mathfrak{D}_l}{A}\times\sum_k k_z{}^2\langle\psi_{k0}{}^\dagger\psi_{k0}\rangle. \quad (3.5)$$

The three quantities $\mathfrak{z}_i$ are the small zero-point sublattice reductions, which we shall not calculate. The statistical average of the occupation number is of course the Bose distribution function, and converting the summation to an integral,

$$\sum_k\langle\psi_{k0}{}^\dagger\psi_{k0}\rangle=\frac{Na_0{}^3}{4(2\pi)^3}\int\frac{1}{e^{\beta\epsilon_{k0}}-1}d\mathbf{k}. \quad (3.6)$$

The integral is to extend over a Brillouin zone corresponding to the rhombohedral unit cell. The integration can be performed in a fashion described by Keffer.[18] Expand the Bose factor as

$$[\exp(\beta\epsilon_{k0})-1]^{-1}=\sum_{p=1}^{\infty}\exp(-p\beta\epsilon_{k0}). \qquad (3.7)$$

As the three terms in ϵ_{k0} which depend upon $\mathfrak{D}_t k_\xi^2$, $\mathfrak{D}_t k_\eta^2$, and $\mathfrak{D}_l k_z^2$ are small compared to $\mathfrak{D}_0 k^2$, from (2.32), expand the former as

$$\exp(-p\beta\mathfrak{D}_t a_0^2 k_\xi^2)=\sum_{l=0}^{\infty}\frac{1}{l!}(-p\beta\mathfrak{D}_t a_0^2 k_\xi^2)^l,$$

$$\exp(p\beta\mathfrak{D}_t a_0^2 k_\eta^2)=\sum_{m=0}^{\infty}\frac{1}{m!}(p\beta\mathfrak{D}_t a_0^2 k_\eta^2)^m,$$

$$\exp(p\beta\mathfrak{D}_l a_0^2 k_z^2)=\sum_{n=0}^{\infty}\frac{1}{n!}(p\beta\mathfrak{D}_l a_0^2 k_z^2)^n.$$

These are all then substituted into (3.6), the integration can be restricted to the first octant of the Brillouin zone by symmetry, and extended out to infinity. The integral factors into three integrals, in k_ξ, k_η, and k_z. Employing

$$\int_0^\infty e^{-\alpha x^2}x^{2l}dx=\frac{(2l+1)!!}{2^{l+1}}\left(\frac{\pi}{\alpha^{2l+1}}\right)^{1/2},$$

we have

$$\sum_k\langle\psi_{k0}^\dagger\psi_{k0}\rangle=\frac{N}{32(\pi\beta\mathfrak{D}_0)^{3/2}}\left[\sum_{p=1}^{\infty}p^{-3/2}\right]$$
$$\times\left[\sum_{l=0}^{\infty}\frac{1}{l!}\frac{(2l-1)!!}{2^l}\left(\frac{-\mathfrak{D}_t}{\mathfrak{D}_0}\right)^l\right]$$
$$\times\left[\sum_{m=0}^{\infty}\frac{1}{m!}\frac{(2m-1)!!}{2^m}\left(\frac{\mathfrak{D}_t}{\mathfrak{D}_0}\right)^m\right]$$
$$\times\left[\sum_{n=0}^{\infty}\frac{1}{n!}\frac{(2n-1)!!}{2^n}\left(\frac{\mathfrak{D}_l}{\mathfrak{D}_0}\right)^n\right].$$

The summation on p is the zeta function

$$\sum_{p=1}^{\infty}p^{-3/2}=\zeta(\tfrac{3}{2})=2.612=\frac{\pi^{3/2}}{2.1315}$$

and as

$$(a+b)^{-1/2}=\sum_{n=0}^{\infty}(-1)^n\frac{(2n-1)!!}{n!\,2^n}\left(\frac{b}{a}\right)^n\frac{1}{a^{1/2}};\quad |b|\leqslant|a|,$$

we have finally

$$\sum_k\langle\psi_{k0}^\dagger\psi_{k0}\rangle=\frac{N(kT)^{3/2}}{68.21(\mathfrak{D}_0+\mathfrak{D}_t)^{1/2}(\mathfrak{D}_0-\mathfrak{D}_t)^{1/2}(\mathfrak{D}_0-\mathfrak{D}_l)^{1/2}}. \qquad (3.8)$$

There is also the summation

$$\sum_k k_z^2\langle\psi_{k0}^\dagger\psi_{k0}\rangle$$

in Eqs. (3.2) to (3.5), but it will be evident that such a summation, which can be performed from the integration culminating in (3.8) above by differentiation, will contain an addition factor of kT, and is therefore beyond the present approximation.

Neglecting the small zero-point reductions, and substituting (3.8) into (3.2) to (3.5), the sublattice magnetizations are simply

$$\langle S_A^z\rangle/S_A=1-aT^{3/2}, \qquad (3.9)$$

with

$$a=k^{3/2}[136.4(S_{B(2)}+S_{B(3)}-S_A)(\mathfrak{D}_0+\mathfrak{D}_t)^{1/2}\times(\mathfrak{D}_0-\mathfrak{D}_t)^{1/2}(\mathfrak{D}_0-\mathfrak{D}_l)^{1/2}]^{-1}. \qquad (3.10)$$

Likewise

$$-\frac{\langle S_{B(2)}^z\rangle}{S_{B(2)}}=-\frac{\langle S_{B(3)}^z\rangle}{S_{B(3)}}=1-aT^{3/2} \qquad (3.11)$$

and the reduced net magnetization is

$$M(T)/M(0)=1-aT^{3/2}, \qquad (3.12)$$

where the zero-degree moment per molecule unit is

$$M(0)=-\mu_B(g_{B(2)}S_{B(2)}+g_{B(3)}S_{B(3)}-g_AS_A). \qquad (3.13)$$

μ_B is the Bohr magneton and g the g factor. Equation (3.9) reduces to that of Heeger and Houston[19] and Eq. (3.12) to that of Kaplan[20] when the appropriate simplifications to a single type of ion on the B sites are made.

The contrast between these results and molecular field theory may justify emphasis. In the molecular-field approximation the A-sublattice magnetization falls more slowly with increasing temperature than that of the B sublattices because of the greater number of nearest neighbors of an A ion; $z_A=2z_B$. This is not true of the leading term in spin-wave theory. Further, although the B ions are magnetically coupled to the A ions by different exchange constants, J_2 and J_3, all the A and B sublattices have the same temperature dependence apart from the proportionality to the intrinsic spin S_A, $S_{B(2)}$ or $S_{B(3)}$. Although we have demonstrated the calculation only for AB interactions and for the spinel structure these conclusions are

---

[18] Frederic Keffer, in *Handbuch der Physik*, edited by S. Flügge, (Springer-Verlag, Berlin, to be published), Vol. 18.

[19] A. J. Heeger and T. W. Houston, Phys. Rev. **135**, A661 (1964).

[20] H. Kaplan, Phys. Rev. **86**, 121 (1952).

unaltered even if there are AA and BB exchange interactions, and for other symmetries, so long as only acoustic modes, which produce the $T^{3/2}$ magnetization law, are excited.

B. Ferrimagnetic-Resonance *g* Factor

According to the Wangsness[21]–Tsuya[22] formula, the effective g factor is

$$g_{\mathrm{eff}}=\frac{g_{B(2)}|\langle S_{B(2)}{}^z\rangle|+g_{B(3)}|\langle S_{B(3)}{}^z\rangle|-g_A|\langle S_A{}^z\rangle|}{|\langle S_{B(2)}{}^z\rangle|+|\langle S_{B(3)}{}^z\rangle|-|\langle S_A{}^z\rangle|}. \quad (3.14)$$

In the case of magnetite, in which $S_A=S_{B(3)}$ and Eqs. (3.9) and (3.11) require $\langle S_A{}^z\rangle=|\langle S_{B(3)}{}^z\rangle|$, formula (3.14) predicts a temperature-independent g_{eff}. This badly fails to reproduce the observed strong temperature dependence, as will be discussed later in a section on such comparisons.

C. Specific Heat

The internal energy per molecule unit is

$$U=\frac{1}{2N}\sum_k \epsilon_{k0}\langle\psi_{k0}{}^\dagger\psi_{k0}\rangle=\frac{a_0{}^3}{8(2\pi)^3}\int\frac{\epsilon_{k0}}{e^{\beta\epsilon_{k0}}-1}d\mathbf{k}\,. \quad (3.15)$$

The procedure described following Eq. (3.6) is again employed, and the additional factor of ϵ_{k0} in Eq. (3.15) is introduced by differentiation. This creates a factor of $(\frac{3}{2})(\beta p)^{-1}$ leading to the $T^{5/2}$ dependence of the magnetic energy, and converts the ζ function to $\zeta(\frac{5}{2})=1.341$. Differentiation with respect to the temperature, to find the specific heat, introduces a factor of $\frac{5}{2}$, and thus the magnetic specific heat per mole is

$$C_V=\frac{0.0137R(kT)^{3/2}}{(\mathfrak{D}_0+\mathfrak{D}_t)^{1/2}(\mathfrak{D}_0-\mathfrak{D}_t)^{1/2}(\mathfrak{D}_0-\mathfrak{D}_l)^{1/2}}\ \mathrm{erg/mole\ ^\circ K}. \quad (3.16)$$

R is the gas constant per mole. The specific heat can be related to the magnetizations through the coefficient a defined in (3.10):

$$C_V=1.87(S_{B(2)}+S_{B(3)}-S_A)RaT^{3/2}. \quad (3.17)$$

The specific heat measures the same combination of exchange constants as does the sublattice magnetizations. When there is only a single intersublattice exchange constant, $J_2=J_3$, our formula (3.16) reduces to the expression given by Kouvel,[4] who employs an exchange constant $\frac{1}{2}$ that defined in Eq. (2.1). Comparison with Kouvel's experimental specific heat is deferred until Sec. V.

IV. ABOVE THE TRANSITION

At temperatures above 119°K, magnetite disorders and cubic symmetry is restored. As the Verwey temperature is only about 13% of the Néel temperature, we might hope that the leading $T^{3/2}$ term of spin-wave theory should still suffice. We assume that sufficiently above the transition the B-site electron hopping rate is rapid enough that we can consider there to be a single type of B-site ion with spin $\bar{S}$, exchange constant $\bar{J}$ and g factor $\bar{g}$. These need not necessarily be related to the individual low-temperature ionic constants by the zeroth approximation of Eqs. (1.3).

From Eq. (2.31) we have at once

$$\langle\mathfrak{D}_0\rangle_{\mathrm{av}}=\frac{11}{16}\frac{\bar{J}\bar{S}S_A}{2\bar{S}-S_A}, \quad (4.1)$$

$$\langle\mathfrak{D}_t\rangle_{\mathrm{av}}=\langle\mathfrak{D}_l\rangle_{\mathrm{av}}=0. \quad (4.2)$$

Assuming the same plausible ordering of levels suggested by Kaplan,[17] the energies of the two lowest levels are

$$\epsilon_{k0}=\langle\mathfrak{D}_0\rangle_{\mathrm{av}}a_0{}^2k^2 \quad (4.3\mathrm{a})$$

and

$$\epsilon_{k1}=6\bar{J}(2\bar{S}-S_A)+\langle\mathfrak{D}_0\rangle_{\mathrm{av}}a_0{}^2k^2. \quad (4.3\mathrm{b})$$

The coefficient a of Eq. (3.10) reduces to

$$\bar{a}=\frac{k^{3/2}}{136.4(2\bar{S}-S_A)\langle\mathfrak{D}_0\rangle_{\mathrm{av}}{}^{3/2}}=\frac{k^{3/2}(2\bar{S}-S_A)^{1/2}}{77.8(\bar{J}\bar{S}S_A)^{3/2}}, \quad (4.4)$$

and the sublattice magnetizations and reduced moment are

$$|\langle S_i{}^z\rangle|/Si=1-\bar{a}T^{3/2} \quad (4.5)$$

in analogy with (3.9) to (3.12). The moment per molecule unit "normalizing" Eq. (3.13) is

$$M(\text{“}0\text{”})=-\mu_B(2\bar{g}\bar{S}-g_AS_A). \quad (4.6)$$

From Eq. (3.14) the ferrimagnetic-resonance g factor becomes

$$g_{\mathrm{eff}}=\frac{2\bar{g}|\langle\bar{S}^z\rangle|-g_A\langle S_A{}^z\rangle}{2|\langle\bar{S}^z\rangle|-\langle S_A{}^z\rangle}. \quad (4.7)$$

From Eq. (3.16) the molar specific heat is

$$C_V=0.0137R(kT/\langle\mathfrak{D}_0\rangle_{\mathrm{av}})^{3/2}. \quad (4.8)$$

V. COMPARISON WITH EXPERIMENT

A. Neutron Diffraction

We have mentioned that Hamilton[3] by means of elastic neutron diffraction confirmed the Verwey structure. Watanabe and Brockhouse[7] have studied the spin-wave spectrum at room temperature by inelastic neutron scattering. At small momentum

---

[21] R. K. Wangsness, Phys. Rev. **86**, 146 (1952).

[22] N. Tsuya, Progr. Theoret. Phys. (Kyoto) **7**, 263 (1952).

transfer the absorption corresponds closely to the spectrum of Eqs. (4.1) to (4.3), with $\bar{S}=2.25$ and

$$\bar{J}/k \cong 56°\text{K}. \qquad (5.1)$$

This evaluation, which is not very sensitive to the choice of $\bar{S}$ within the plausible range $S_{B(2)}<\bar{S}<S_{B(3)}$, is properly larger than the molecular-field Néel-temperature evaluation, of Eq. (1.4a), as will be shown in Eq. (5.10). Note that from Eq. (2.1) our exchange constant is defined to be twice that of Watanabe and Brockhouse. Milford and Glasser[15] showed that the important inclusion of terms in the spin-wave energies of degree higher than k^2 bring the theoretical spectrum into close agreement with the observations of Watanabe and Brockhouse, and a nonessential inclusion of BB exchange interaction with $J_{BB}=-0.1\,J_{AB}$ brings complete consonance.

Inelastic neutron scattering has not been studied on the ordered structure; such observation, particularly of an excited branch, would allow evaluation of J_2 and J_3 separately. The form of "averaging" as electrons begin to hop between B sites near the Verwey transition is a very interesting question, bearing upon the NMR linewidth. Perhaps the most unambiguous observation relating to this question would be a neutron-diffraction study of an excited branch of the spin-wave spectrum through the transition region. The zeroth approximation, applied to (2.29c) and (4.3a), suggests that, up to k^2, the curvature of the lowest branch will be unaffected by the Verwey transition.

B. Mossbauer Spectrum

Following the suggestion[23] that Mössbauer absorption should provide interesting information on the electronic order-disorder transformation in magnetite, this spectrum was observed both above[11–13] and below[12–13] the Verwey temperature. Above the transition, if the B-site electronic exchange is faster than the Larmor frequencies of an iron nucleus in the hyperfine fields, there should be an effective hyperfine field for B-site ions, different from the A-site hyperfine field, and hence only two sets of lines should appear, as is in fact observed.

Below the Verwey temperature three sets of lines were expected, one from the A sites and one set each from Fe^{2+} and from Fe^{3+} on B sites. This is not observed, but rather, one set of lines from Fe^{2+} ions and, at approximately twice the intensity, another set of lines from Fe^{3+} ions on both sites.[12,13] Through Eqs. (3.9) and (3.11) we can understand this result if we assume that, apart from the sublattice magnetization, the hyperfine field at the nucleus of Fe^{3+} ions is the same on both octahedral and tetrahedral sites, within the Mössbauer resolution. For the hyperfine field is proportional to the sublattice $\langle S_i^z\rangle$ and since $S_A=S_{B(3)}$, the two sublattice magnetizations should be equal. The Fe^{2+} ion has both a different spin quantum number and a different hyperfine field.

C. Nuclear Magnetic Resonance and Magnetization

Explanation of the Mössbauer spectrum is confronted with the NMR evidence. Above the transition we expect the hyperfine coupling constant and spin quantum number of the "averaged" B sites to differ from those for the A sites, so that two NMR absorption frequencies should be observed. However, if only small-k acoustic modes are excited, we expect from Eq. (4.5) that, normalized by their extrapolated value at 0°K, both sublattice magnetizations and the net moment should have the same slope on a $T^{3/2}$ plot. This is not observed. Boyd[8] reports that both the A and B site NMR frequencies, and the magnetization vary as $T^{3/2}$, but the slopes of his normalized curves differ and suggest exchange constants $\bar{J}$ very different from that of Watanabe and Brockhouse.[7] The moment data is in agreement with that of Eschenfelder.[10] One would like to escape by invoking higher energy modes in the spin-wave spectrum at these elevated temperatures, but excitation of such modes would cause deviations from the $T^{3/2}$ law reported.

Below the Verwey transition there is little evidence, and that conflicting. Boyd sees the two resonances continuing unaffected by the transition down to 90°K, where Mössbauer[12,13] evidence and neutron diffraction[3] indicates that the Verwey ordering is complete. Ogawa *et al.*[9] see the B-site resonance so broadened as to be unobservable below the Verwey temperature, and the A sublattice resonance frequency to increase appreciably and discontinuously upon lowering the temperature into the ordered domain.

From the zeroth approximation of Eqs. (1.3) we can arrive at some qualitative estimate of what might be expected. Above the transition we expect two NMR resonances:

$$h\nu_A=A_A\langle S_A{}^z\rangle=A_AS_A[1-\bar{a}T^{3/2}], \qquad (5.2a)$$

and

$$h\nu_{\bar{B}}=\bar{A}_B\langle\bar{S}_{\bar{B}}{}^z\rangle=\bar{A}_B\bar{S}[1-\bar{a}T^{3/2}]. \qquad (5.2b)$$

Below the transition the possibilities are

$$h\nu_A=A_A\langle S_A{}^z\rangle=A_AS_A[1-aT^{3/2}], \qquad (5.3a)$$

$$h\nu_{B(3)}=A_{B(3)}\langle S_{B(3)}{}^z\rangle=A_{B(3)}S_{B(3)}[1-aT^{3/2}], \qquad (5.3b)$$

$$h\nu_{B(2)}=A_{B(2)}\langle S_{B(2)}{}^z\rangle=A_{B(2)}S_{B(2)}[1-aT^{3/2}]. \qquad (5.3c)$$

However, $S_A=S_{B(3)}$, and from the Mössbauer evidence we wish to believe that $A_A\cong A_{B(3)}$. So we should expect only two lines sufficiently below the transition, or perhaps two Fe^{3+} lines close together, and Fe^{2+} resonance well separated.

The reported shift in frequency of the "A" line can be estimated from a comparison of the coefficients a

---

[23] P. W. Anderson, University of Illinois Report AFOSR-TN 60-698, 1960, p. 39 (unpublished).

and $\bar{a}$ in Eqs. (5.2a) and (5.3a), (5.3b). From Eq. (4.4) we have

$$\bar{a}=1.36\times10^{-3}(k/\bar{J})^{3/2}. \tag{5.4}$$

From Eqs. (3.10), (2.31), and (1.3) we can evaluate a as a function of J_2/J_3, and the zeroth approximation then implies ν_A continuous through the transition from A site resonance to Fe^{3+} resonance. However, the B-site resonance should shift in frequency and decrease in intensity in the transition to Fe^{2+} resonance.

D. Ferrimagnetic-Resonance *g* Factor

Ferrimagnetic resonance has been observed both below[6] and above[5] the Verwey temperature, in neither case confirming our expectations. At sufficiently low temperatures, where we would expect formula (3.14) to hold, we have, from (3.9) and (3.11)

$$g_{\text{eff}}=g_{B(2)}+(g_{B(3)}-g_A)(S_A/S_{B(2)}). \tag{5.5}$$

Even apart from the fact that $g_{B(3)}=g_A=2$, we expect a temperature-independent g factor, where the evidence[6] is that the g factor rises from 2.2 at 4.2°K to 2.28 at 33°K. Equation (4.7) leads to the same difficulty well above the transition. Boyd[8] has demonstrated that the empirical g_{eff}, NMR frequencies and magnetization are mutually badly inconsistent, but that if one ignores the ferrimagnetic resonance data and considers the electronic g factors to be temperature-independent, one obtains reasonable agreement between NMR data and the temperature-dependent magnetization. This observation, which is consistent with Eq. (5.5), suggests that some other unaccounted-for effect obscures the experimental g_{eff}.

E. Specific Heat

Here again we can diagnose only an "unaccounted-for effect." Kouvel[4] found that his very large low-temperature specific heat corresponded to an exchange constant only about 25% of that given in Eq. (1.4a), from molecular field theory and the Néel temperature. Pollack and Atkins[24] found the same result in many other ferrites: The specific heat can be described accurately by a spin-wave $T^{3/2}$ term and a lattice T^3 term, but while the lattice contribution is the correct size, the spin-wave contribution is 3 to 5 times larger than other estimates of the exchange constant would suggest.

This cannot be attributed to a shortcoming of molecular field theory, which, although inaccurate, is not that bad. With the exchange constant defined by Eq. (2.1), the molecular-field-theory Curie temperature is

$$kTc/J_{\text{MF}}=(z/3)S(S+1). \tag{5.6}$$

Rushbrooke and Wood[25] summarize the conclusions of accurate high-temperature expansions for cubic lattices by the empirical formula

$$kTc/J_{\text{RW}}=(5(z-1)/192)[11S(S+1)-1]. \tag{5.7}$$

Neglecting unity in comparison with $11S(S+1)$, we find

$$J_{\text{RW}}\cong(64z/55(z-1))J_{\text{MF}}, \tag{5.8}$$

and considering $z=(z_Az_B)^{1/2}=8.48$, we estimate the correct $\bar{J}$ by

$$\bar{J}\cong1.3\bar{J}_{\text{MF}}. \tag{5.9}$$

It will be noticed that, from the neutron-diffraction estimate of Eq. (5.1) and the molecular field result of Eq. (1.4a),

$$\bar{J}_{\text{WB}}\cong1.5\bar{J}_{\text{MF}} \tag{5.10}$$

which is of the correct size, considering that Eq. (5.7) is derived for ferromagnets.

Nor can the small intrasublattice exchange interaction be expected to account for a factor of 5 error in J_{AB}. Kenan, Glasser, and Milford[16] hoped to account for the enormous discrepancy by a treatment of the spin-wave energies which is accurate to higher orders in spin-wave momentum, as it was observed that derivations from k^2 occur even at very small momenta.[15] The hope was not fulfilled.

In this respect the present calculation is equally a failure. One might think that invocation of two exchange constants, J_2 and J_3, should allow resolution of the difficulty, with J_2 small to cause a large specific heat in the $B_{(2)}$ sublattice, and J_3 large to cause a high Néel temperature, and so it would in molecular field theory. But in spin-wave theory, at low temperatures only the acoustic modes are excited, all sublattices are locked together, and only a complicated sum of exchange constants matters.

Note added in proof. Two coincidental experimental investigations of magnetite have just been reported. Both confirm predictions of the present paper. T. Mizoguchi and M. Inoue [J. Phys. Soc. Japan **21**, 1310 (1966)] repeating NMR studies, find the A-site resonance continuous through the transition, the Fe^{3+} B-site resonance only slightly shifted, and the Fe^{2+} separated. H. A. Alperin, O. Steinsvoll, R. Nathans, and G. Shirane (to be published), using neutron diffraction find the lowest branch of the spin wave spectrum to be unaffected by electron ordering.

ACKNOWLEDGMENTS

The author expresses his gratitude to Professor Nagamiya, Professor Kanamori, and Professor Motizuki for their advice and companionship during a happy year at Osaka University, and to the U. S. Naval Ordnance Laboratory, which made this sojourn possible.

---

[24] S. R. Pollack and K. R. Atkins, Phys. Rev. **125**, 1248 (1962).

[25] G. S. Rushbrooke and P. J. Wood, Mol. Phys. **1**, 257 (1958).