

tion theory that, if f is bound to the wall or reflectionless,

$$\int_{-\infty}^{\infty} f_0^\dagger L_1 f_0 ds_1 + \Omega_1 \int_{-\infty}^{\infty} f_0^\dagger \sigma_x f_0 ds_1 = 0. \quad (\text{B3})$$

Now in the bound case, (13b) for $s=0$, f_0 is even in s_1 and L_1 is odd in s_1 , so that $\Omega_1=0$. In the spin-wave case, $f_0=f_0' e^{ik_1 s_1}$, the form of the envelope function is such that only the term which re-

sults from differentiation of $e^{ik_1 s_1}$ contributes, and therefore

$$\Omega_1 = i \frac{\int_{-\infty}^{\infty} f_0^\dagger (\partial/\partial s_1) \sigma_x f_0 ds_1}{\int_{-\infty}^{\infty} f_0^\dagger \sigma_x f_0 ds_1} = -\kappa_1. \quad (\text{B4})$$

Given the eigenvalues the eigenfunctions may be verified by direct substitution.

- ¹A. A. Thiele, Bell System Tech. J. 50, 725 (1971).
²F. B. Hagedorn, in *Proceedings of the Seventeenth Annual Conference on Magnetism and Magnetic Materials*, Chicago, 1971, edited by C. D. Graham, Jr. and J. J. Rhyne (AIP, New York, 1972), p. 72.
³J. C. Slonczewski, Intern. J. Magnetism 2, 85 (1972).
⁴L. R. Walker (unpublished); described by J. F. Dillon [in *A Treatise on Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. III, p. 450]; see also Ref. 2 and E. Schlömann, in Ref. 2, p. 160; J. C. Slonczewski, in Ref. 2, pp. 170, 175.
⁵J. M. Winter, Phys. Rev. 124, 452 (1961).
⁶J. F. Janak, Phys. Rev. 134, A411 (1964).
⁷F. C. Butron, Compt. Rend. 252, 3955 (1961).
⁸Te. A. Turov, A. P. Tankeyev, and M. I. Kurkin, Fiz. Metal. Metalloved. 28, 385 (1969).
⁹M. M. Farztdinov and Ye. A. Turov, Fiz. Metal. Metalloved. 29, 11 (1970).
¹⁰A. A. Thiele, Bell System Tech. J. 48, 3287 (1969).
¹¹F. B. Hagedorn and E. M. Gyorgy, J. Appl. Phys. 37, 282 (1961).
¹²F. B. Hagedorn and D. H. Smith (unpublished).
¹³A. H. Bobeck, I. Danylchuk, J. P. Remeika, L. G. Van Uitert, and E. M. Walters, in *Ferrites: Proceedings of the International Conference, Japan, 1970*, edited by Y. Hoshino, S. Iioa, and M. Sugimoto (University of Tokyo Press, Tokyo, 1971), p. 361.
¹⁴F. C. Rossol, Phys. Rev. Letters 24, 1021 (1970); A. H. Bobeck, R. F. Fischer, A. J. Perneski, J. P. Remeika, and L. G. VanUitert, IEEE Trans. Mag. 5, 544 (1969).
¹⁵L. K. Shick, J. W. Nielsen, A. H. Bobeck, A. J. Kurtzig, P. C. Michaelis, and J. P. Reekstin, Appl. Phys. Letters 18, 89 (1971).

Multiple Ordering in Magnetite

James R. Cullen*

Naval Ordnance Laboratory, Silver Spring, Maryland 20910

and

Earl R. Callen†

Department of Physics, The American University, Washington, D. C.

(Received 7 July 1972)

We present results of a self-consistent band calculation of the ground-state energy and charge orderings based on a tight-binding scheme in magnetite. The calculation is greatly simplified by making use of the large intra-atomic Coulomb interactions between electrons on the Fe ions, previous estimates of the crystal field splittings, and the magnetic ordering. We find that below a critical value (~ 2.2) of the ratio of interatomic Coulomb energy U to bandwidth w the lowest-energy state has no order. Between this critical value and 2.5, the preferred state is multiply ordered (three nonzero order parameters). For larger values of this ratio, the Verwey-symmetry state (one order parameter) is stable, but the value of the order parameter approaches 1 (ionic Verwey order) only in the limit of $U/w \rightarrow \infty$.

INTRODUCTION

For many years, the accepted description of the metal-insulator transition in magnetite was that proposed by Verwey,¹ i.e., that below the transition temperature the Fe^{3+} and Fe^{2+} ions on the B sites are ordered, the likely order being alternate (001) planes of Fe^{3+} and Fe^{2+} ions.

Recently,² we introduced an itinerant-electron one-dimensional model of the extra B -site electrons interacting with each other via interatomic Coulomb repulsions. The model exhibited a phase transition from a "disordered" metallic state above a critical temperature to an ordered insulator below. The charge ordering allowed fractional occupation of sites even at $T=0^\circ\text{K}$. This

ordering was calculated by self-consistently breaking the symmetry of the high-temperature phase, in which all sites have the same occupancy. The order parameter, or charge difference on alternate sites in the one-dimensional array, which could be likened to a [110] line in the real three-dimensional lattice, was proportional to the energy gap. Thus insulation and ordering were simply related.

Hall-effect,³ conductivity,⁴ and thermopower⁵ measurements all suggest that the band model is more appropriate to magnetite than the ionic-hopping scheme (although the conductivity is interpretable in either way), but a one-dimensional description is so simple as to miss many of the interesting features of magnetite, and of conductivity transitions in general. Neutron diffraction,⁶ electron diffraction,⁷ and Mössbauer spectroscopy⁸ all suggest a more complex three-dimensional charge ordering. We consequently extended consideration to the actual magnetite structure. In studies preliminary to the present work we showed that three-dimensional ordering can assist in formation of an energy gap,⁹ that the high density of states in the conduction band can explain the apparent semiconductorlike behavior of the conductivity¹⁰ in the disordered high-conductivity phase above the Verwey transition temperature T_V , and that multiple orderings—that is, fractional charges within the tetrahedra of B -site ions—led, within the Landau theory of phase transitions, to a first-order phase transition at T_V .¹¹

In those preliminary studies the interlocked integral equations for the order parameters were not solved self-consistently; this cannot be achieved analytically. Sokoloff¹² has challenged our assumption of three order parameters, asserting that computer calculations lead only to Verwey c -axis ordering. In this paper we describe the 0°K behavior of magnetite. We do not allow for all the possible symmetry breaking that can occur, but restrict ourselves to a manageable three-order-parameter theory. We show that for certain ranges of the ratio of interatomic Coulomb energy U to bandwidth w , only metallic band structure results; as U/w is increased, multiple-ordering states, with a semiconducting energy gap, lie lowest in energy, and at high U/w a single-order-parameter structure lies lowest. It was only this region of extraordinarily high Coulomb energy that Sokoloff investigated.

MODEL

The intra-atomic interactions between electrons on B -site ions is assumed to be large enough that Hund's rule is satisfied; i. e., the state of maximum total spin is realized. For ions with five

electrons, all of them are in a closed shell with spin $\frac{5}{2}$. The "extra" electron present in half the ions (using localized-electron terminology) then resides in a fivefold-degenerate d band of spin opposite to that of the closed shell. Next, crystal fields split the d levels. In the spinel structure the field at a B site is trigonal; the levels split into two doublets and a singlet lying lowest.¹³ Finite overlap of the wave functions of these d electrons broadens these singlet levels into bands, while interatomic Coulomb repulsion merely splits the levels. The Hamiltonian, then, for the d electrons in singlet states is

$$H = \sum_{\substack{i,\alpha \\ j,\beta}} \epsilon_{i\alpha,j\beta} a_{i\alpha}^\dagger a_{j\beta} + U_{i\alpha,j\beta} n_{i\alpha} n_{j\beta} . \quad (1)$$

Here i and j refer to fcc lattice sites; α and β refer to positions within a cell. For magnetite, there are four B -site ions in the unit cell. We treat the second term in (1) in the Hartree approximation,

$$n_{i\alpha} n_{j\beta} \rightarrow n_{i\alpha} \langle n_{j\beta} \rangle , \quad (2)$$

the angular brackets referring to the quantum and thermal average of the enclosed operator. We can now diagonalize (1) using (2), find the eigenvalues and eigenfunctions, and then go back and calculate $\langle n_{j\beta} \rangle$. In the one-dimensional calculation, with one atom per unit cell, α and β indices were dropped. $\langle n_i \rangle$ was assumed to depend on whether i was even or odd. The self-consistency condition on the difference $\langle n_{j+1} \rangle - \langle n_{j-1} \rangle$, or order parameter, can then be expressed in terms of an integral equation²

$$m = m \frac{U}{2N} \sum_k \frac{1 - 2f(E_k)}{E_k} , \quad (3)$$

with $E_k = [e_k^2 + (\frac{1}{2}Um)^2]^{1/2}$. This was written for the special case of identical electron and hole spectra. Thus e_k represents either type of excitation in the case $m=0$. E_k is the excitation energy for either carrier when $m \neq 0$. Note this about Eq. (3): For any U , no matter how small, there exists a solution $m \neq 0$. This solution is also the one for which the free energy is lowest. This characteristic of (3) makes the one-dimensional model highly suspect. It is known that such behavior is expected in three dimensions only for simple cubic or bcc lattices in the extreme tight-binding approximation.

As in Refs. 9 and 11 we now allow all four charge densities within the primitive cell to be different. However, we constrain the total charge (outside of the closed Fe^{3+} shells) to be that of two electrons (corresponding to the ionic description of two Fe^{3+} and two Fe^{2+} ions on B sites in each molecular unit). This leaves three order parameters to be determined; we choose to work

with the linear combinations

$$\begin{aligned} m_1 &= \frac{1}{2}(n_1 - n_2 + n_3 - n_4) , \\ m_2 &= \frac{1}{2}(n_1 + n_2 - n_3 - n_4) , \\ m_3 &= \frac{1}{2}(n_1 - n_2 - n_3 + n_4) , \\ n &= n_1 + n_2 + n_3 + n_4 = 2 , \end{aligned}$$

where, e.g., $n_1 = \langle n_\alpha, \alpha = 1 \rangle$.

The ordering chosen is the same in each cell. Electron⁷ and neutron⁶ diffraction experiments indicate that the actual ordering involves doubling of the unit cell along a cube edge. In terms of our theory, this means that the order varies from cell to cell and there exist at least two sets of m values. Calculation of such a large set of parameters self-consistently becomes unwieldy, even numerically. We introduce here just enough symmetry breaking to indicate how multiple ordering can arise, and under what conditions it defines a stable ground state.

We use the tight-binding approximation, so that the operators a^\dagger (a) create (annihilate) atomic states. The hopping energies are calculated in the near-neighbor approximation. There are six of these to any B site: three in the same cell, three outside. Then

$$\begin{aligned} E_{i\alpha, j\beta} &= w \text{ for } i\alpha, j\beta \text{ near neighbors} \\ &= 0 \text{ otherwise} . \end{aligned} \quad (4)$$

Equation (1) becomes, using (2),

$$H \approx w \sum_{i\alpha, j\beta} a_{i\alpha}^\dagger a_{j\beta} + \sum_\alpha E_\alpha \sum_i a_{i\alpha}^\dagger a_{i\alpha} , \quad (5)$$

where

$$E_\alpha = E_0 + \frac{3}{2} U n_\alpha - U n_\alpha . \quad (6)$$

Diagonalization of H can now be reduced to solving a 4×4 equation by Fourier-transforming the a 's:

$$C_{k\alpha}^\dagger = \frac{1}{N^{1/2}} \sum_i a_{i\alpha}^\dagger e^{i\mathbf{k} \cdot \mathbf{R}_{i\alpha}} . \quad (7)$$

The sum is over the B -site lattice. In the new representation

$$H = \sum_k \sum_{\alpha\beta} h_{\alpha\beta}(k) C_\alpha^\dagger(k) C_\beta(k) , \quad (8)$$

$$h_{\alpha\beta} = w \cos \vec{k} \cdot \vec{\tau}_{\alpha\beta} , \quad h_{\alpha\alpha} = E_\alpha . \quad (9)$$

The six vectors $\vec{\tau}_{\alpha\beta}$ connecting lattice points (α, β) are parallel to the primitive lattice vectors of the fcc lattice and one-half their magnitude. Writing

$$H \psi_{kn} = \lambda_{kn} \psi_{kn} ,$$

with

$$\psi_{kn} = \sum_\alpha b_{n,\alpha}(k) C_\alpha^\dagger(k) ,$$

the eigenvalue equation becomes

$$\sum_\alpha (E_\alpha - \lambda_n) b_{\alpha n} + \sum_{\alpha \neq \beta} h_{\alpha\beta} b_{\alpha n} . \quad (10)$$

A. Disordered Phase

In this case, all $m = 0$, $E_\alpha = E_0$, the atomic potential corrected for interatomic Coulomb repulsion. Equation (10) can then be handled algebraically, because the "potential" $h_{\alpha\beta}$ in (10) is separable. Writing $\vec{\tau}_{\alpha\beta} = \vec{\tau}_\alpha - \vec{\tau}_\beta$, and

$$\begin{aligned} h_{\alpha\beta} &= -w \cos \vec{k} \cdot \vec{\tau}_{\alpha\beta} \\ &= -w (\cos \vec{k} \cdot \vec{\tau}_\alpha \cos \vec{k} \cdot \vec{\tau}_\beta + \sin \vec{k} \cdot \vec{\tau}_\alpha \sin \vec{k} \cdot \vec{\tau}_\beta) \\ &\equiv -w (u_\alpha u_\beta + v_\alpha v_\beta) , \end{aligned}$$

Eq. (10) becomes

$$(E - \lambda - w) b_\alpha - w u_\alpha \sum_{\beta=1}^4 u_\beta b_\beta - w v_\alpha \sum_{\beta=1}^4 v_\beta b_\beta = 0 . \quad (11)$$

Multiply (11) first by u_α and sum on α . Then do the same using v_α . The resulting two equations are

$$\begin{aligned} (E - \lambda - w) B - w (\sum_\alpha u_\alpha^2) B - w (\sum_\alpha v_\alpha u_\alpha) B' &= 0 , \\ (E - \lambda - w) B' - w (\sum_\alpha v_\alpha^2) B' - w (\sum_\alpha v_\alpha u_\alpha) B &= 0 , \end{aligned}$$

with

$$B \equiv \sum_\alpha u_\alpha b_\alpha , \quad B' \equiv \sum_\alpha v_\alpha b_\alpha .$$

Solving these two simultaneous equations yields

$$\lambda_{\pm} = E_0 - w \pm w \left(1 + \frac{1}{4} \sum_{\alpha \neq \beta} \cos 2\vec{k} \cdot \vec{\tau}_{\alpha\beta} \right)^{1/2} .$$

The other two degenerate solutions are obtained by setting B, B' equal to zero:

$$\lambda = E + w .$$

The band structure in the nonordered state is characterized by two flat bands at $\lambda = E_0 + |w|$ and two bands of width w symmetric about $E_0 - |w|$. At $T = 0^\circ \text{K}$, these latter are full and the maximum of the full bands is at $k = 0$. (See Fig. 1.) At finite T , there are mobile holes in the valence band, whose number increases with T . Though there is, strictly speaking, no gap, the conductivity increases with T because the number of holes increases,¹⁰ in agreement with experiment for magnetite above the Verwey temperature.¹⁴

The ground-state energy in this case is just

$$E_{gs} = \frac{1}{2N} \sum_{n,k} \lambda_{k,n} = E_0 - w . \quad (12)$$

B. One Order Parameter

If $m_2 = m_3 = 0$, but $m_1 \neq 0$, the energy bands can be obtained analytically in certain symmetry directions. Since this order corresponds to a

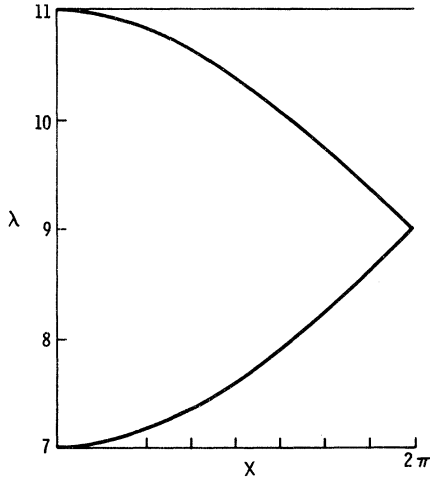


FIG. 1. Energy vs wave vector along [001], in the disordered phase. The lower two bands are full for pure magnetite. The upper two levels are independent of wave vector in any direction. All energies are in units such that $W=1$.

layered structure along the Z axis, say, the [001] bands will differ from those along [100] and [010]. Along [001],

$$\lambda = E - w \pm [(2w \cos \frac{1}{4} x)^2 + (\frac{1}{2} U m_1)^2]^{1/2}, \quad -2\pi \leq x \leq 2\pi$$

$$\lambda = E + w \pm \frac{1}{2} U m_1.$$

The two levels at $E + w$ have been split by $\pm \frac{1}{2} U m_1$; the wide bands have had their degeneracy at X ($x = \pm 2\pi$) removed (Fig. 2). Unless $\frac{1}{2} U m_1 > w$, the bands overlap. Along [100] or [010],

$$\lambda = E + w \cos \frac{1}{4} x \pm [(\frac{1}{2} U m_1)^2 + w^2(1 - \cos \frac{1}{4} x)^2]^{1/2},$$

$$\lambda = E - w \cos \frac{1}{4} x \pm [(\frac{1}{2} U m_1)^2 + w^2(1 + \cos \frac{1}{4} x)^2]^{1/2}.$$

In these directions there is a gap between valence and conduction bands [see Fig. 2(b)].

C. Multiple Ordering

Allowing m_3 and m_2 to be nonzero produces a coupling of the flat band $E + w - \frac{1}{2} U m_1$ with the upper wide band along [001]. This coupling tends to push the two bands apart, opening an insulating gap. Numerical calculation indicates that this gap is very small, an order of magnitude smaller than either $\frac{1}{2} U m_2$ or $\frac{1}{2} U m_3$. Whether or not this further symmetry lowering actually happens depends of course, on whether such a system lowers its free energy. For $T = 0^\circ\text{K}$ the free energy is

$$F = \frac{1}{2N} \sum_{k,n} \lambda_{k,n} f(\lambda_{k,n}) + \frac{1}{4} U(m_1^2 + m_2^2 + m_3^2). \quad (13)$$

The second term is the average of the inter-

action term which must be subtracted from the sum of the solutions of the Hartree-Fock equations (the first term), which includes the interaction twice. The plus sign occurs because the interaction energy is negative. f is the usual Fermi factor. Having obtained $\lambda_{k,n}$ from (10) for a given (m_1, m_2, m_3) , we do the sum indicated in (13) numerically, repeating the calculation for new (m_1, m_2, m_3) until a minimum of F in $(m_1,$

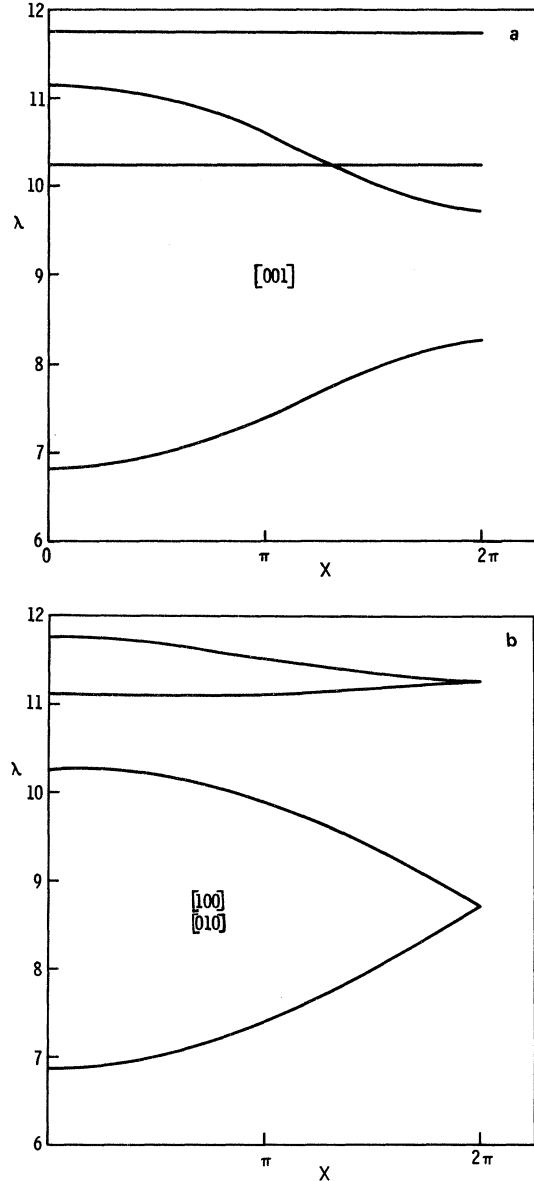


FIG. 2. (a) Energy vs wave vector along [001] for $(U/w)m_1 = 1.5$, $m_2 = m_3 = 0$. The Fermi energy equals 10.25; two bands are each partly full. (b) Energy vs wave number along [100] or [010] ($(U/w)m_1 = 1.5$, $m_2 = m_3 = 0$). In these directions, an insulating gap proportional to m_1 appears.

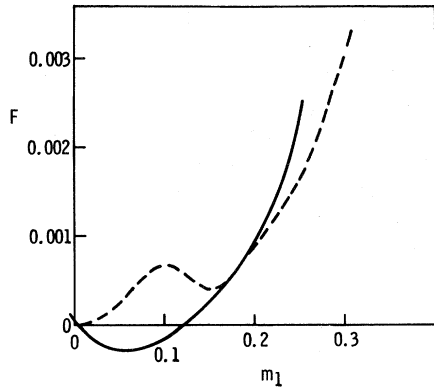


FIG. 3. Free energy (in units $W=1$) vs one order parameter, the other two held fixed. The full line is for $m_2=0.05$, $m_3=0.05$. The dashed line is for $m_2=m_3=0$. The free energy is measured relative to that of the disordered phase. $U/w=2.4$.

m_2, m_3) space is determined. We then change the value of the ratio of U to w and repeat the process.

D. Simple Model for One Order Parameter

Along the m_1 axis (or, equivalently, the m_2 or m_3 axes) we have noticed that the following simple formula holds remarkably well (to the fourth decimal) for small Um , and fairly well (1% accurate) at $Um \sim 1$:

$$F_A = - \left[\left(\frac{1}{2} Um_1 \right)^2 + w^2 \right]^{1/2} + \frac{1}{4} Um_1^2 + E_0 . \quad (14)$$

Equation (14) predicts that, for $U/w < 2$, the stable solution is $m_1=0$, i. e., no order. For larger U/w , the stable order is

$$m_1 = \pm \left[1 - (2w/U)^2 \right]^{1/2} . \quad (15)$$

m_1 increases as w/U decreases, reaching the ionic limit ($m=1$) only for $w/U=0$. The energy in the ground state is

$$F_A = E - \frac{1}{4} U - w^2/U, \quad U > 2w . \quad (16)$$

If we had adopted the ionic picture, arranged the wave functions in the Verwey order, and included the hopping energy as a perturbation, Eq. (16) would result, up to third order in the bandwidth. The last term in (16) is, on this picture, a measure of the zero-point fluctuations about the Verwey order.

In fact, however, numerical calculation of Eq. (13) shows that for $U/w \leq 2.2 \equiv r_c$ the lowest energy state is that for which all $m=0$. Between $U/w=2.2$ and 2.5 , multiply ordered states have lower energy. For example, at $U/w=2.4$, the stable state corresponds to $m_1=0.08$, $m_2 \approx m_3 \approx 0.05$. Figure 3 shows F vs m_1 both for $m_2 = 0.05$, $m_3 = 0.05$, and for $m_2 = m_3 = 0$. For U/w greater than 2.5 , the one-order-parameter state

is stable. Even above this value, however, there are multiply ordered states locally stable in $\{m\}$ space, with energy very close to that of the one-order-parameter state.¹⁵ As U/w is made larger, the difference in energy between the one-order-parameter state and the multiply ordered state becomes larger. The stable m_1 value is, of course, also getting larger. Figure 4 shows how the stable m_1 value varies with U/w , and indicates the multiple-ordering region.

It is not hard to see why multiple ordering wins out in the region near the critical value of U/w . In this region, we know the stable values of m are small, and we assume that F may be expanded¹⁶ in powers of m_1, m_2, m_3 . F is, in any case, invariant under operations of the space group of Fe_3O_4 (O_h^7),¹⁷ and so the general form of the energy is

$$F \approx F_0 + A(m_1^2 + m_2^2 + m_3^2) + B m_1 m_2 m_3 + c \sum_{i=1}^3 m_i^4 + \dots . \quad (17)$$

F_0 is the energy in the state of no order. The third term on the right-hand side of (17) is allowed because the $\{m\}$ transform as the off-diagonal elements of a rank-2 tensor.¹¹ Now in the "critical" region, A is close to zero, being positive for U/w close to r_c and negative for U/w somewhat greater than this (A need not change sign precisely at r_c). Then the B term dominates, and this term is negative in some region of $\{m\}$ space, independent of the sign of B , since the m 's can be of either sign. F will be less than F_0 in this region. The idea simply is that, wherever the stable m_1 is expected to be small, as calculated, for instance, using (15), multiple ordering

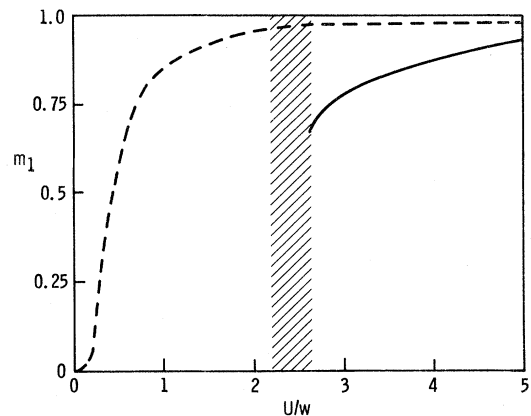


FIG. 4. Self-consistent order parameter m_1 vs U/w . Below $U/w=2.2$, there is no order. In the shaded regions, there is multiple ordering. The dashed curve shows the order parameter vs U/w for the one-dimensional model.

is either a more stable arrangement or at least very close in energy to the one-order-parameter state.¹⁸

As we pointed out in the discussion preceding Eq. (13), we expected the one-order-parameter state to be unstable for $(U/w)m_1 < 2$. This is only partly borne out by the calculations. At $U/w = 2.7$, for example, the stable state is the one-order-parameter state $m_1 = 0.7$; so $(U/w)m_1 = 1.89$. The ground state for this value of r is thus semimetallic. In this respect our results are similar to the Hartree-Fock calculations of the Hubbard Hamiltonian,¹⁹ which indicate a region of U/w where there is order (antiferromagnetism) but no insulation.

CONCLUSION

We have been able to show that there is a region of U/w where multiple-ordering states can be stable, which pins down the possible values that this ratio can take. Taking more orderings into account might widen this region slightly, but nonetheless the following picture emerges: Starting from small U/w , we have a disordered state, followed by multiply ordered states with a narrow band gap, followed by an ordered metallic state and, finally, for $U/w \gtrsim 3$, an ordered insulator. Multiple ordering explains the extra lines

seen in the Mössbauer results of Hargrove and Kündig⁸ and the NMR results of Rubinstein²⁰ (see also Rubinstein and Forester²¹). It also partly explains the neutron⁶ and electron⁷ diffraction patterns, i. e., the appearance of extra structure. c -axis doubling, which we have not included here, is of course necessary to obtain the observed $h, k, l \pm \frac{1}{2}$ lines.

The actual values of the order parameters vary with U/w in the shaded region of Fig. 4. The ground-state order is determined once U/w is given. These values will of course vary with temperature. They probably vary in such a way as to change the symmetry of the crystal below the Verwey temperature. This change could occur suddenly, that is, giving rise to an extra phase change before the disordered phase is reached at T_V . Such a phase change would be accompanied by the usual signs—for instance, a peak in the specific heat. A sharp peak in the specific heat of a synthetic crystal of magnetite at 114 °K has been reported.²² In the light of the preceding discussion, we interpret this as a phase change brought about by a rotation of the order-parameter tensor, just as in many magnetic systems, where the direction of spontaneous magnetization will undergo a shift at a temperature less than the Néel temperature.

*Work supported by the Naval Ordnance Laboratory Independent Research Fund.

†Work supported in part by NASA Grant No. NGR-09-003-014.

¹E. J. W. Verwey and P. W. Haayman, *Physica* **8**, 979 (1941); E. J. W. Verwey and E. L. Hailmann, *J. Chem. Phys.* **15**, 174 (1947); E. J. W. Verwey, P. W. Haayman, and F. C. Romeijn, *ibid.* **15**, 181 (1947).

²J. R. Cullen and E. R. Callen, *J. Appl. Phys.* **41**, 879 (1970).

³W. J. Siemons, *IBM J. Res. Develop.* **14**, 245 (1970).

⁴B. A. Calhoun, *Phys. Rev.* **94**, 1577 (1954).

⁵C. Constantin and M. Rosenberg, *Solid State Commun.* **10**, 675 (1972); P. Thayer (private communication).

⁶E. J. Samuelson, E. J. Bleeker, L. Dobrzynski, and T. Riste, *J. Appl. Phys.* **39**, 1114 (1969).

⁷T. Yamada, K. Suzuki, and S. Chikazumi, *Appl. Phys. Letters* **13**, 172 (1968).

⁸R. S. Hargrove and W. Kündig, *Solid State Commun.* **8**, 303 (1970).

⁹This form of the model was first presented in J. R. Cullen and E. R. Callen, *Phys. Rev. Letters* **26**, 236 (1971). Unfortunately, the bands in the disordered phase were given incorrectly there.

¹⁰J. R. Cullen, E. R. Callen, and B. Choudhury, *Phys. Letters* **38A**, 113 (1972); in *Magnetism and Magnetic Materials*, 1971, edited by C. D. Graham, Jr. and J. J.

Rhyne (AIP, New York, 1972), p. 295.

¹¹J. R. Cullen and E. R. Callen, *Solid State Commun.* **9**, 1041 (1971).

¹²J. B. Sokoloff, *Phys. Rev. B* (to be published).

¹³K. Yosida and M. Tachiki, *Progr. Theoret. Phys.* (Kyoto) **17**, 331 (1957).

¹⁴See, for example, Ref. 1.

¹⁵This is why, in this region, it is difficult to determine the equilibrium $\{m\}$ by simply looking for self-consistent solutions of (10).

¹⁶Such expansion is not possible, for example, in the one-dimensional model, where m_1 is a nonanalytic function of U/w .

¹⁷This argument is similar to that for the free energy in the region near the Verwey temperature (Landau theory of phase transitions) as applied to magnetite in J. R. Cullen and E. R. Callen, *Solid State Commun.* **9**, 1041 (1971).

¹⁸This last statement is true, of course, even if the preceding argument breaks down because the free energy is not expandable in powers of the order parameters.

¹⁹M. Cyrot, *Phil. Mag.* **25**, 1031 (1972).

²⁰M. Rubinstein, *Bull. Am. Phys. Soc.* **16**, 425 (1971).

²¹M. Rubinstein and D. W. Forester, *Solid State Commun.* **9**, 1675 (1971).

²²B. J. Evans and E. F. Westrum, Jr., *Phys. Rev. B* **5**, 3791 (1972).