

Energetic stabilization of the Mizoguchi structure for magnetite by band-structure effects

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We show that the Mizoguchi structure is energetically stabilized over the Verwey structure for magnetite by electron hopping on the B sublattice. We use the one-band Cullen-Callen model Hamiltonian for the electronic band structure taking the nearest-neighbor and the second-neighbor Coulomb interactions, U_1 and U_2 , into account. There is a competition between the Coulomb and the band-structure energies. The Coulomb energy tends to favor the Verwey structure while the band-structure energy tends to favor the Mizoguchi structure. We find that for $U_1 \lesssim 0.25$ eV, the kinetic-energy (band-structure energy) term dominates making the Mizoguchi structure energetically favorable over the Verwey structure. For a larger value of U_1 , the band-structure effect alone is insufficient, making it necessary to invoke other mechanisms such as the electron-phonon coupling earlier proposed by other authors, to stabilize the Mizoguchi structure. The energy of a single “reversed-ring” excitation in the Mizoguchi structure is calculated to be of the order of a few meV. The small energy is consistent with Cullen’s explanation of the absence of cell doubling in the C_a plane as observed in diffraction experiments. The Mizoguchi order is unstable with respect to the formation of reversed-ring excitations if only U_1 is present, but is stabilized by a small value of U_2 .

I. INTRODUCTION

The atomic charge ordering in magnetite below the Verwey transition temperature has been the subject of intense study for quite some time.¹ Of issue is the question concerning how the Fe^{2+} and the Fe^{3+} ions order on the B sublattice below the Verwey temperature of $T_v \approx 120$ K. It has long been recognized that the Coulomb repulsion between the Fe^{2+} ions, which may be viewed as “extra” electrons moving on the background of the Fe^{3+} ions, constitutes an important term in the total energy. A long time ago Anderson² pointed out the remarkable property of this sublattice, that the short-range [nearest-neighbor (NN)] part of the Coulomb interaction is minimized by $\sim (\frac{3}{2})^{N/2}$ different configurations where N is the number of B sites. Only a few of these configurations have long-range order (LRO) as well. Anderson interpreted the Verwey transition as a loss of the LRO of the “extra” electrons on the B sublattice above T_v while the short-range order (SRO) is maintained across the transition. Experiments indeed indicate the presence of LRO at temperatures below T_v , but the exact nature of this long-range order is still not completely clear.

The original model for the LRO proposed by Verwey³ consisted of alternate (001) planes of Fe^{2+} and Fe^{3+} ions on the B sublattice as indicated in Fig. 1. This model, however, ran into direct conflict with results of electron⁴ and neutron⁵ diffraction and furthermore was shown to be energetically unstable from theoretical analysis.⁶ In 1975, Yamada⁷ proposed the first model of B -site charge ordering consistent with the diffraction experiments. The model, however, did not allow the ordering of Fe^{2+} and Fe^{3+} ions on half of the (001) planes.

A more complete picture of charge ordering was proposed by Mizoguchi⁸ on the basis of an analysis of the NMR spectra below the Verwey temperature. The Mizoguchi

structure was accepted as the one that best describes the available experimental data. Even though, like the Verwey structure, the Mizoguchi structure does have the “Anderson property,” viz., that every Fe^{2+} ion is surrounded by two similar ions so as to minimize the short-range Coulomb energy, the Mizoguchi structure was quickly recognized to have a higher second-neighbor Coulomb energy as compared to the Verwey structure.⁹ However, since the Mizoguchi structure was based on a thorough analysis of the NMR data, it was proposed that a strong electron-phonon coupling mechanism could compensate for its large Coulomb energy.^{7,10,11}

In this paper we show that the kinetic-energy term involving hopping of the “extra” electrons on the B sublattice helps stabilize the Mizoguchi structure. In fact, if

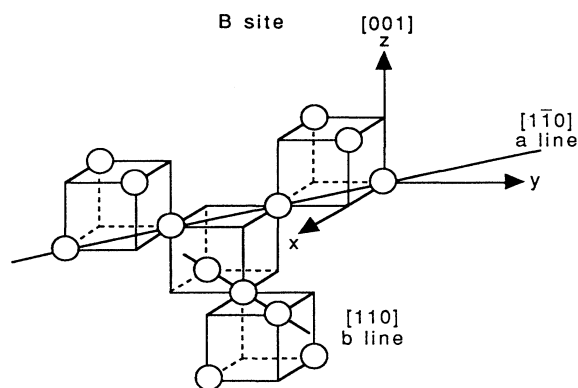


FIG. 1. Atomic arrangement of the iron atoms on the B sublattice of the spinel structure. There are two types of (001) planes: the a lines lie on which the C_b planes on which the b lines lie. The Verwey structure consists of alternate (001) planes of Fe^{2+} and Fe^{3+} ions.

the NN Coulomb repulsion $U_1 \lesssim 0.25$ eV, the kinetic-energy term is large enough to stabilize the Mizoguchi structure and an electron-phonon mechanism (lattice distortion) need not be invoked. Furthermore, we examine the energy cost to form a “reversed ring” in the Mizoguchi structure originally proposed by Cullen to explain certain aspects of the diffraction data.

II. THE MIZOGUCHI STRUCTURE

Magnetite, with the chemical formula Fe_3O_4 , forms in the spinel structure. The large oxygen atoms form a close-packed, face-centered-cubic structure with the smaller iron atoms occupying the interstitial positions. The iron atoms are arranged on two distinct, *A* and *B*, sublattices.

Recent band calculations^{12,13} have shown that, consistent with traditional wisdom, the relevant atoms involved in the Verwey transition are the *B*-sublattice Fe atoms as the electron bands arising out of the rest of the atoms lie sufficiently far from the Fermi energy. The band calculations, furthermore, have shown the remarkable feature of magnetite that the majority spin bands are semiconducting while the minority spin bands are metallic. This gives rise to a spinless model Hamiltonian. The problem finally reduces to motion of electrons in a spinless t_{1g} band on the *B* sublattice consisting of xy , yz , and zx orbitals on each Fe atom. Since the electron count is such that there is only half an electron per *B* site occupying the t_{1g} band, the *B* sublattice contains an equal mixture of Fe^{3+} and Fe^{2+} ions. The Fe^{2+} ions are produced by the presence of an “extra” electron on the background of Fe^{3+} ions. Below the Verwey transition temperature these Fe^{2+} and Fe^{3+} ions form an ordered structure.

The Verwey structure can be visualized from Fig. 1 where we have shown just the *B* sublattice. It consists of a series of alternating (001) planes on which Fe ions are arranged on lines along either the $[1\bar{1}0]$ or the $[110]$ direction. These are called, respectively, the *a* lines and the *b* lines, while the planes containing them are called the C_a or the C_b planes. In the Verwey structure all C_a planes consist of one type of ion (Fe^{2+} or Fe^{3+}) while the C_b planes consist of the other. Thus, the structure consists of alternating (001) planes of Fe^{2+} and Fe^{3+} ions.

Contrary to this, in the Mizoguchi structure each of the C_a and the C_b planes consists of an equal mixture of ions as indicated in Fig. 2. The atomic arrangement on these planes was originally obtained by a detailed analysis of the NMR data⁸ and is consistent with the recent scanning-tunneling-microscopy (STM) image.¹⁴ These planes are to be sequentially stacked along the *c* direction ($[001]$ direction) in a fashion compatible with the Anderson property.

Mizoguchi found essentially three different ways of stacking that gives rise to an ideal superstructure. The unit cell of the superstructure consists of 64 atoms with eight atoms each on four C_a planes and four C_b planes. Starting from one C_a plane, the other three C_a planes in the unit cell are assembled by shifting them by a distance of $a_0/2$ in the *c* direction and simultaneously displacing them along the xy plane. With respect to the original

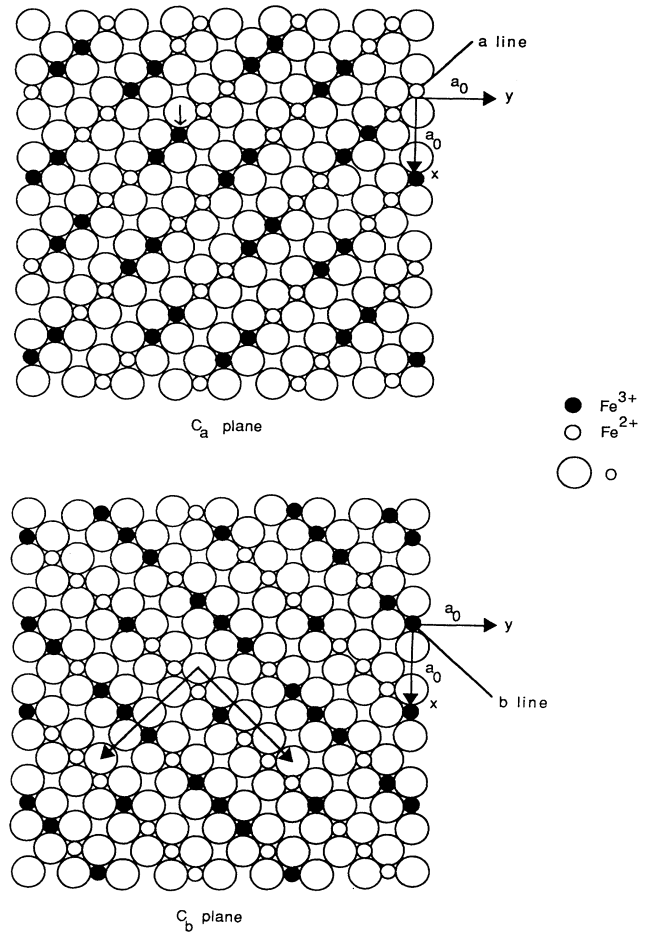


FIG. 2. Arrangement of Fe^{2+} and Fe^{3+} ions in the Mizoguchi structure for magnetite. The cubic lattice constant in the spinel structure is denoted by “ a_0 .” The lattice translation vectors for the planes are indicated on the C_b plane. The atom on the C_a plane indicated by the short arrow is positioned along the *c* direction with respect to the oxygen atom at origin on the C_b plane. The Mizoguchi structure is generated from these two planes as discussed in the text.

plane, the successive planes are displaced by the following amounts in the three different structures: (a) Mizoguchi (I): $(a_0/2)\hat{x}$, $a_0\hat{x}$, and $(3a_0/2)\hat{x}$; (b) Mizoguchi (II): $(a_0/2)\hat{x}$, $(a_0/2)\hat{x} - (a_0/2)\hat{y}$, and $a_0\hat{x} - (a_0/2)\hat{y}$; and (c) Mizoguchi (III): $(a_0/2)\hat{x}$, $a_0\hat{x}$, and $a_0\hat{x} - (a_0/2)\hat{y}$. Here a_0 is the cubic lattice constant of the spinel structure and the unit vectors denote the cube axes. For each structure the C_b planes are sandwiched between pairs of C_a planes in accordance with the Anderson property which uniquely determines their positions.

III. BAND-STRUCTURE EFFECTS

Essential to the understanding of the charge ordering in magnetite is the Anderson property. The large nearest-neighbor Coulomb repulsion term forces electrons to occupy two of the four sites on each tetrahedron on the *B* sublattice (perfect SRO). However, the number

of such configurations being large, the LRO is not stabilized because of a finite entropy term associated with the large number of configurations exhibiting perfect SRO. Any small interaction lifts the degeneracy and leads to an LRO state. For example, the second NN Coulomb repulsion U_2 stabilizes the Verwey structure in the absence of electron hopping. If U_2 is considered in addition to U_1 , then the Mizoguchi structure has the higher Coulomb energy as discussed below.

Keeping only the first and the second nearest-neighbor Coulomb interactions and taking double-counting into account, Table I indicates that the Verwey structure has the lowest energy of $U_1 + 2U_2$ per Fe^{2+} atom (i.e., per “extra” electron) while each of the three Mizoguchi structures has an energy of $U_1 + 3.5U_2$. By performing an Ewald summation, Sokoloff¹⁰ has shown that the Verwey structure still has the lowest Coulomb energy even if the Coulomb interactions beyond the second neighbors are retained. The structure observed in the experiment, however, is not the Verwey structure and therefore terms beyond the Coulomb interaction must be important leading Yamada,⁷ Sokoloff,¹⁰ and Ihle and Lorentz¹¹ to propose an electron-phonon coupling mechanism to reduce the energy of the Mizoguchi structure over that of the Verwey structure. We now show that the electron hopping on the B sublattice (band-structure effects) helps stabilize the Mizoguchi structure to the extent that the electron-phonon coupling is not necessary for the stabilization if U_1 is not too big.

To study the band-structure effects we adopt here a simple one-band effective Hamiltonian first proposed by Cullen and Callen:¹⁵

$$H = -t \sum_{ij} a_i^\dagger a_j + \sum_{ij} U_{ij} n_i n_j. \quad (1)$$

Here a_i^\dagger (a_i) are the creation (annihilation) operators of the “extra” electron on the B sublattice and n_i, n_j are the number operators with i, j being the site indices. The Hamiltonian (1) consists of a tight-binding nearest-neighbor hopping term, t , plus a Coulomb interaction term between the “extra” electrons. We include the first and the second NN Coulomb interactions, U_1 and U_2 , in our calculation. The coulomb repulsion between two electrons on the same site is large and this is, in fact, a justification for using the one-band model. The on-site Coulomb repulsion does not, of course, enter into the

spinless one-band model since each site can hold just one electron. With only U_1 and U_2 included in the Hamiltonian, there are two free parameters, viz., U_1/t and U_2/t . In the one-band model, the bandwidth for the B sublattice is $8t$.^{16,17} This bandwidth calculated from density-functional theory is about 1.55 eV,^{12,13} which results in a value of $t \approx 0.20$ eV for the effective hopping integral in the one-band model.¹⁸ Since the magnitudes of the Coulomb parameters, especially of U_2 , are less certain, in the initial discussions we treat them as free parameters. The Cullen-Callen Hamiltonian (1) has been studied by many authors and seems to be able to capture the gross features of the Verwey transition. However, a three-band spinless model Hamiltonian describes more accurately the motion of the “extra” electrons on the B sublattice and should be used for a better description of the electronic band structure.¹²

In the Hartree approximation the total energy is obtained by calculating the band-structure energy and the Coulomb energy:

$$E = \sum_i^{\epsilon_F} \epsilon_i - \frac{1}{2} \sum_{ij} U_{ij} \langle n_i \rangle \langle n_j \rangle, \quad (2)$$

where ϵ_i is the one-electron band-structure energy and the second term is subtracted so as to compensate for the double counting of the Coulomb energy in the band-structure term. The unit cell of the Mizoguchi structure consists of 64 atoms. The band energy was calculated by diagonalizing a 64×64 Hamiltonian matrix at each k point in the Brillouin zone. The band summation in (2) was performed with 125 k points in the full Brillouin zone. Test calculations that employed a larger number of k points or even just the single Γ point yielded substantially the same results.

Before discussing the results of the full calculation, we first present a simple two-level model to illustrate the band-structure effects on the total energy. In the Verwey structure, the on-site energy of an electron is either $2U_1 + 4U_2$ for an Fe^{2+} site (the Fe^{2+} site has two NN and four second NN Fe^{2+} sites) or $4U_1 + 8U_2$ for an Fe^{3+} site. The key physics may be described by considering just two isolated levels with the above energies, which are coupled to each other. This is represented in an energy level diagram in Fig. 3. On the other hand, it turns out that the on-site energy of an electron in the Mizoguchi structure can take four different values: $2U_1 + 6U_2$, $2U_1 + 8U_2$, $4U_1 + 4U_2$, and $4U_1 + 6U_2$. Since it is physically relevant to assume U_1 to be significantly larger than U_2 , we construct a two-level model for the Mizoguchi structure by taking the average of the lower two and the higher two levels in that structure. Since half the B sites are occupied by an electron and half unoccupied, in the two-level model only the lower level will be occupied. Its energy will, however, be reduced because of coupling to the higher level. The coupling parameter t_{eff} in the two-level model will, in general, be larger in magnitude than the hopping integral in (1), because in reality *each* lower level will be coupled to *several* higher levels by the matrix element t .

The energy reduction of the lower level caused by the

TABLE I. Average number of Fe^{2+} near-neighbors surrounding an Fe^{2+} ion in various structural models for magnetite.

Near neighbor	d^a	Number of near neighbors				
		Verwey	Mizoguchi			Mizoguchi (I) with
			I	II	III	one “reversed ring”/cell
1st	0.354	2	2	2	2	2
2nd	0.612	4	7	7	7	6.875
3rd	0.707	12	5	5	5	5.25
4th	0.791	4	6	7	6.5	6.25

^a d is the near-neighbor distance in units of a_0 , the cubic lattice constant.

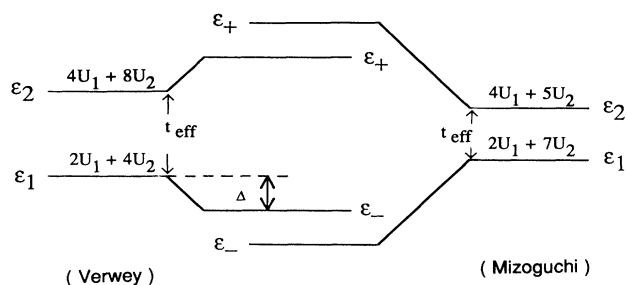


FIG. 3. A two-level model for the structural energy difference between the Verwey and the Mizoguchi structures. The lower-energy state is occupied while the higher state is empty. With the right electron interaction parameters, the hybridization energy in the Mizoguchi structure is large enough to compensate for its relatively larger Coulomb energy making the Mizoguchi structure the more stable.

coupling is then obtained by diagonalizing a 2×2 Hamiltonian for the coupled system:

$$\Delta \equiv \varepsilon_+ - \varepsilon_- = -\frac{\varepsilon_2 - \varepsilon_1}{2} + \frac{1}{2} \sqrt{(\varepsilon_2 - \varepsilon_1)^2 + 4t_{\text{eff}}^2} \quad (3)$$

in terms of the energies of the uncoupled levels, ε_1 and ε_2 , and the coupling matrix element t_{eff} . Thus, the total energies per electron in the Verwey and the Mizoguchi structures are given by

$$E = 2(U_1 + 2U_2) - \sqrt{(U_1 + 2U_2)^2 + t_{\text{eff}}^2} \quad (\text{Verwey}), \quad (4a)$$

$$E = 2U_1 + 2.5U_2 - \sqrt{(U_1 - U_2)^2 + t_{\text{eff}}^2} \quad (\text{Mizoguchi}). \quad (4b)$$

These expressions follow from (2) and (3), where double counting of the Coulomb energy has been accounted for. Equation (4) shows that the band-structure energy reduction is different for the two structures. As illustrated in Fig. 3, the coupling is more effective for the Mizoguchi structure since the energy separation between the two levels is *lower* as compared to the Verwey structure. In fact, if the hopping term t_{eff} is sufficiently large, then the larger Coulomb energy in the Mizoguchi structure is compensated by the band-structure gain. Figure 4 summarizes the effect of the band-structure term in stabilizing the Mizoguchi structure in the simple, two-level model.

The qualitative results of the two-level model are confirmed by the results of the full calculation where the appropriate coupling between the 64 atomic orbitals in the unit cell are retained within the one-band Hamiltonian (1). Figure 5 illustrates the effect of the kinetic-energy term on the total energy. In the absence of hopping, $t=0$, the Verwey structure has the lower energy by the amount $\Delta E = 1.5U_2$ compared to that of the Mizoguchi structure as anticipated from the Coulomb energy. As the magnitude of the nearest-neighbor hopping is increased, eventually the magnitude of the kinetic-energy gain for the Mizoguchi structure outweighs the Coulomb

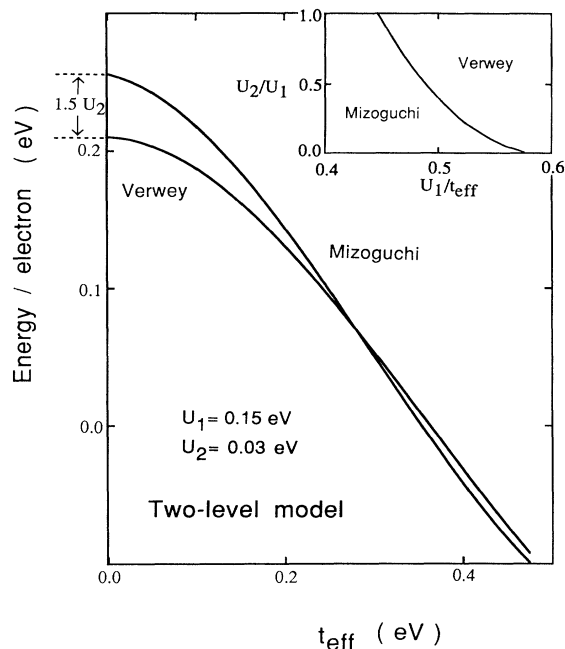


FIG. 4. Structural energy differences between the Verwey and the Mizoguchi structures in the two-level model indicating the role of the kinetic-energy term in stabilizing the Mizoguchi structure. The inset shows the region of stability of the Mizoguchi structure in the two-level model.

cost thereby stabilizing it over the Verwey structure.

The magnitude of the NN Coulomb repulsion as estimated from the “constrained” density-functional theory (DFT) calculation is $U_1 = 0.3-0.4$ eV.¹² The magnitude of U_2 is somewhat less certain. Unlike U_1 it is not amenable to “constrained” DFT calculation since the energy differences involved are extremely small. Different authors cite different values for U_2 : 0.004 eV ($kT_V \sim U_2$) (Ref. 11), 0.02 eV (Ref. 1), and 0.05–0.1 eV (Ref. 12).

The range of electron interaction parameters in which the Mizoguchi structure is stabilized is indicated in the phase diagram, Fig. 6. It should be mentioned here that the transition between the two completely ionic Verwey and Mizoguchi structures is not sharp as indicated from Fig. 6, but rather it takes place over a range of value of U_1/t . The analogous transition region between the disordered phase and the ordered Verwey phase is discussed in Ref. 16. We see that within our model, the band-structure term can stabilize the Mizoguchi structure for the value of $U_1/t \lesssim 1.2$. If we take the value of $t = 0.20$ eV appropriate for the one-band model for magnetite, then a value of $U_1 \lesssim 0.25$ eV is needed for the stabilization of the Mizoguchi structure. Thus, the calculated local-density approximation (LDA) value of $U_1 = 0.3-0.4$ eV for magnetite is somewhat too large to stabilize the Mizoguchi structure by band-structure effects alone. For such a large value of U_1 the band-structure effect has to be supplemented by other mechanisms, e.g., the electron-phonon coupling mechanism proposed by Yamada,⁷ Sokoloff,¹⁰ and Ihle and Lorentz,¹¹ in order to make the Mizoguchi structure stable.

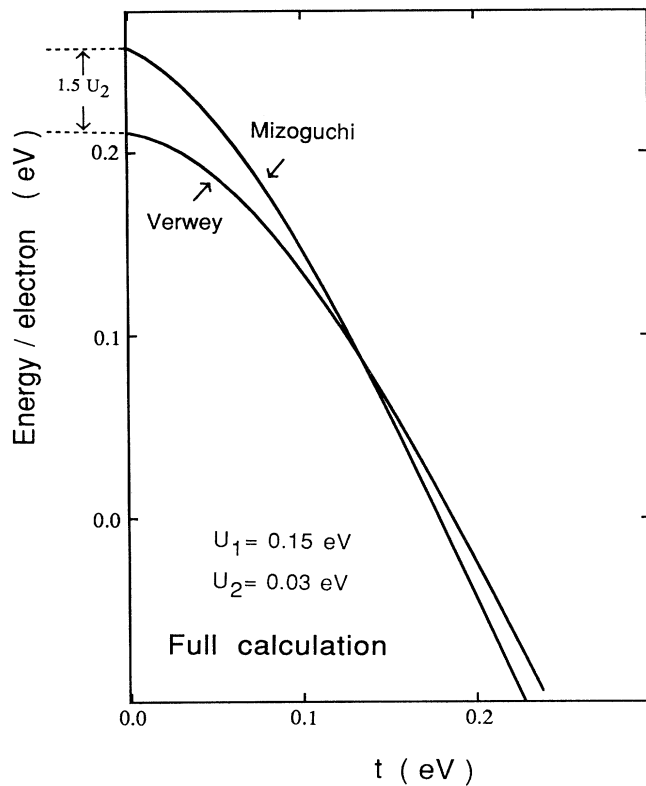


FIG. 5. Structural energy differences between the Verwey and the Mizoguchi structures, obtained from the full calculation, as a function of the strength of the tight-binding hopping parameter t . For smaller values of t , the Coulomb energy cost is too high for the Mizoguchi structure. Beyond a critical value of t , however, the kinetic-energy gain is large enough that the Mizoguchi structure has the lower energy.

We have also calculated the total energies for the three different Mizoguchi structures within the one-band model. There is no difference between the three models if only the nearest-neighbor hopping integral is retained in the one-band Hamiltonian. Even when we retain a

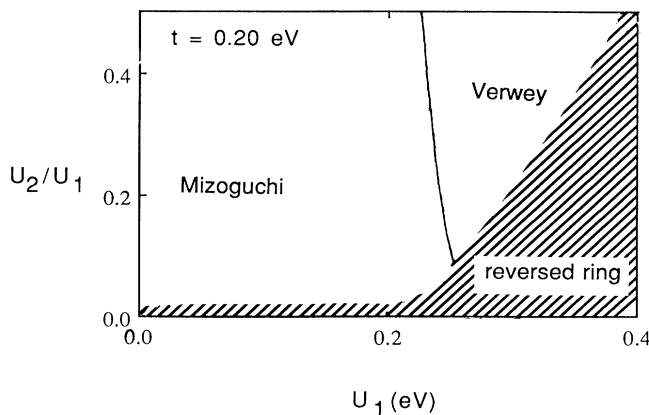


FIG. 6. Region of stability of the Mizoguchi structure. The hatched area indicates the regime in which the Mizoguchi structure is unstable to the formation of the "reversed rings."

second-near-neighbor hopping interaction, the resulting energy differences are so small that one cannot differentiate between the three structures. With such subtle energy differences one has to take into account all atoms in the crystal including oxygen atoms to determine which of the three structures has the lowest energy; e.g., a full density-functional calculation within the local-spin-density approximation may be of value here.

IV. "REVERSED RING" EXCITATIONS IN THE MIZOGUCHI STRUCTURE

We have also examined the energy required to produce a "reversed ring" (Fig. 7) as suggested by Cullen⁹ to account for the absence of c -axis doubling on the C_a planes as indicated by neutron diffraction. The Mizoguchi structure consists of hexagons made up of alternate Fe^{2+} and Fe^{3+} ions. If the electron arrangement on a hexagon is reversed (i.e., the Fe^{2+} and the Fe^{3+} ions are interchanged), then the Anderson property is still satisfied. That is, each Fe^{2+} ion continues to be surrounded by two NN Fe^{2+} ions, so that the short-range Coulomb energy is not affected by the presence of the "reversed ring" excitations. In fact, as indicated from the average number of near neighbors in Table I, there is very little change in the Coulomb energy even when terms beyond the NN are retained. Of course, in addition to the Coulomb energy, one has to examine the change in the kinetic-energy term introduced by the presence of the "reversed ring." Cullen hypothesized that the energy cost for such a "reversed ring" state could be low, and since the rings can migrate the resultant kinetic-energy reduction and the decrease in entropy would lead to the presence of such "reversed rings" at any finite temperature. Since all ions on the C_a plane participate in the hexagon rings while only a quarter of the ions on the C_b plane do so, presence of the "reversed rings" would lead to the absence of the c -axis doubling on the C_a planes but not on the C_b planes.

We have calculated the energy required to produce a single "reversed ring" in the one-band model. For this we compared the total energy of the Mizoguchi (I) structure with the energy of the same structure but with a "reversed ring" in each unit cell. To make the calculations

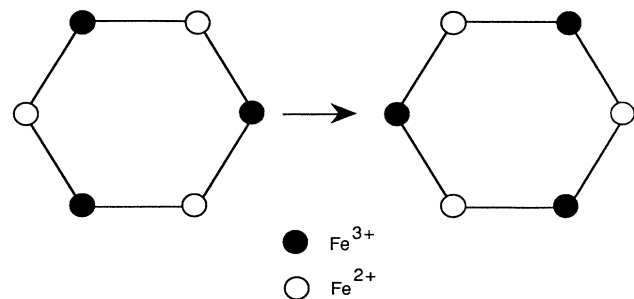


FIG. 7. A "reversed ring" in the Mizoguchi structure formed by interchanging the Fe^{2+} and Fe^{3+} ions on a hexagon ring. In magnetite, it costs a small but finite energy to create such a "reversed ring."

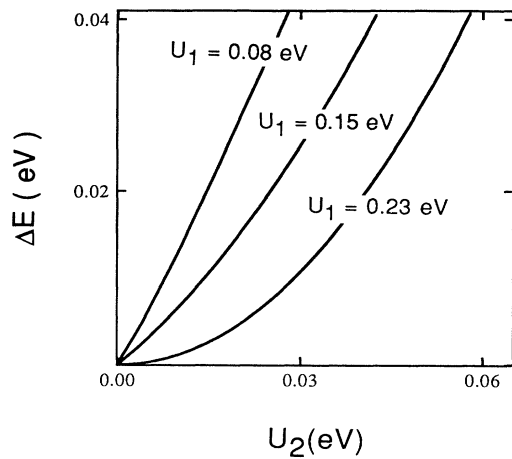


FIG. 8. The calculated energy cost, ΔE , to form a single “reversed ring” in the Mizoguchi structure.

manageable we have neglected the small interaction between the “reversed rings” in different cells. This is reasonable since a “reversed ring” corresponds to charge reversal on only six of the atoms out of a total of 64 atoms in the unit cell.

The energy needed to excite a “reversed ring” for several values of U_1 has been shown in Fig. 8. First of all, we notice that if the second NN Coulomb interaction is ignored, $U_2 = 0$, then it does not cost any energy to excite a “reversed ring” irrespective of the magnitude of U_1 . In that event entropic considerations require that a large number of “reversed rings” are indeed present in the structure and thus the long-range order is destroyed. A finite magnitude of U_2 is therefore necessary to stabilize the Mizoguchi state. This conclusion is analogous to Cullen’s result for the Verwey order that the Verwey order is unstable if only nearest-neighbor Coulomb interaction is retained.⁶ For finite values of U_2 , Fig. 8 shows that the energy needed to create a “reversed ring” is indeed positive in the range of electron parameters in which the Mizoguchi structure is stable. It is only for large values of $U_1 \gtrsim 0.25$ eV that the energy is lowered by the formation of a “reversed ring” state if the value of U_2

is not too large. The parameter range for which the Mizoguchi structure is unstable with respect to formation of the “reversed rings” has been indicated in Fig. 6.

As seen from Fig. 8, the energy cost to create a “reversed ring” is typically of the order of several meV’s. Owing to interactions between the “reversed rings,” such excitations would have a spread of several meV’s in energy. Since they occur in the right range of energy, it is tempting to speculate that these excitations might in some way be responsible for the unusual low-temperature behavior of specific heat observed in the range of $T \lesssim 20$ K.¹⁹

V. CONCLUSION

In conclusion, we have shown that even though the Mizoguchi structure has the higher Coulomb energy as compared to the Verwey structure, it is stabilized by the band-structure effects if the nearest-neighbor Coulomb interaction energy is sufficiently small, $U_1 \lesssim 0.25$ eV. The magnitude of U_1 obtained from the local-density calculations is in the range 0.3–0.4 eV, which is somewhat larger than the above value. For such a large value of U_1 , the band-structure energy gain is by itself not enough to stabilize the Mizoguchi structure, but helps reduce the energy of the Mizoguchi structure so that other mechanisms, such as the electron-phonon mechanism proposed by earlier authors, can presumably stabilize the structure. Even for the case $U_1 \lesssim 0.25$ eV, the LRO present in the Mizoguchi structure is not stable if the nearest-neighbor Coulomb interaction only is retained; rather, a small but finite magnitude of U_2 is needed to stabilize the Mizoguchi structure against excitation of the “reversed rings.” The energy cost to create a “reversed ring” is estimated to be typically of the order of a few meV. The small energy indicates that the cell doubling in the C_a plane is destroyed below T_v as argued by Cullen consistent with experimental diffraction data.

ACKNOWLEDGMENTS

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¹⁸The average hopping integral in the three-band model (Ref.

12) obtained from the local-density calculation is about 0.13 eV. In the one-band model considered in this paper, the effective hopping integral is about 0.20 eV so as to reproduce the bandwidth of the relevant t_{1g} electron band. There should be no confusion between these two different effective

values of t for magnetite.

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