Charge and Orbital Order in Fe_3O_4

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Charge and orbital ordering in the low-temperature monoclinic structure of magnetite (Fe_3O_4) is investigated using the local spin density approximation with Coulomb interaction correction method. While the difference between t_{2g} minority occupancies of Fe_B^{2+} and Fe_B^{3+} cations is large and gives direct evidence for charge ordering, the screening is so effective that the total $3d$ charge disproportion is rather small. The charge order has a pronounced [001] modulation, which is incompatible with the Anderson criterion. The orbital order agrees with the Kugel-Khomskii theory.

The magnetic properties of magnetite, the famous lodestone, have fascinated mankind for several thousand years already [1]. Even today, in view of the possible technological importance of this material for spintronics [2], and because of the still not well understood low-temperature properties, magnetite remains at the focus of active research.

Magnetite is a mixed-valent system and is the parent compound for magnetic materials such as maghemite (γ-Fe_2O_3) and spinel ferrites. At room temperature it crystallizes in the inverted cubic spinel structure $Fd\bar{3}m$ with tetrahedral A sites occupied by Fe^{3+} cations, whereas octahedral B sites are occupied by an equal number of randomly distributed Fe^{2+} and Fe^{3+} cations. Magnetite is ferrimagnetic with an anomalous high critical temperature $T_c \sim 860$ K, the A-site magnetic moments being aligned antiparallel to the B-site moments. At room temperature Fe_3O_4 is a poor metal with an electronic conductivity of 4 mΩ cm. Upon further cooling a first-order metal-insulator (Verwey) transition occurs at $T_V \sim 120$ K where conductivity abruptly decreases by 2 orders of magnitude. According to Verwey this transition is caused by the ordering of Fe^{2+} cations on the B sublattice, with a simple charge arrangement of $(001)_c$ planes (indexed on the cubic cell) alternately occupied by $2+$ and $3+$ Fe_B cations (Verwey charge ordering model) [3,4]. This particular charge order (CO) obeys the so-called Anderson criterion [5] for minimal electrostatic repulsion leading to a short range CO pattern, namely, tetrahedra of B sites with an equal number of $2+$ and $3+$ cations. Since then a wide range of other CO models has been proposed which, however, all make use of the Anderson criterion [6,7].

Later experiments showed that the Verwey transition is accompanied by a structural distortion from cubic to the monoclinic structure which has not been fully resolved so far [7,8]. In the absence of a definitive, experimentally determined structure many theoretical models for the low-temperature (LT) phase of magnetite [9] have been proposed. They include purely electronic [10,11] and electron-phonon [12,13] models for CO, as well as a bond dimerized ground state without charge separation [14]. In particular all previous calculations within local density approximation [LDA($+U$)] were performed for undistorted cubic unit cell. In spite of the fact that the amplitudes of these distortions are quite small this approximation for the LT unit cell in LSDA $+ U$ calculations results inevitably in the Verwey CO. This problem is overcome in our work using recently refined crystal structure [15,16] in which the ground state with more complicated CO was found. This also confirms the Szotek *et al.* [17] conclusion that the Verwey CO is not the ground state for magnetite, which is based on self-interaction corrected local spin density calculations for the refined LT crystal structure.

In this Letter we report LSDA $+ U$ calculations [18,19] in the tight-binding linear muffin-tin orbital (TBLMTO) calculation scheme for Fe_3O_4 in the $P2/c$ structure [15,16]. Motivated by our results, we propose an order parameter, defined as the difference between t_{2g} minority spin occupancies of Fe_B^{2+} and Fe_B^{3+} cations. This order parameter is found to be quite large, although the total $3d$ charge difference between these cations, is small. It seems certain that magnetite is long-range ordered below T_V, in contrast to the intermediate valence regime proposed by García *et al.* [20–22].

Recently, the LT superstructure of magnetite was refined by Wright *et al.* [15,16]. The space group was confirmed to be monoclinic Cc, but the structure refinement was only possible in the $P2/c$ group. They proposed a $a_c/\sqrt{2} \times a_c/\sqrt{2} \times 2a_c$ subcell (a_c is the cell parameter of the undistorted cubic unit cell) with $P2/c$ space group symmetry and 8 formula units in the primitive unit cell. The additional $Pmca$ orthorhombic symmetry constrains were also applied. The refined cell parameters were $a = 5.94437(1)$ Å, $b = 5.92471(2)$ Å, $c = 16.77512(4)$ Å, and

    0031-9007/04/93(14)/146404(4)$22.50

$\beta = 90.236(1)°$. Structural evidence for CO below the transition in the refined crystal structure, based on estimations of the mean B-site-to-oxygen distance or bond valence sum (BVS) analyses, was also presented [15,16]. However, this refined structure analysis has recently been found to be controversial [21]. The lack of atomic long-range order and, as a result, an intermediate valence regime below the Verwey transition were proposed. Indeed, a difference between averaged Fe-O distances of compressed and expanded FeO_6 octahedra corresponds to the maximum limit of charge disproportion ($0.2\bar{e}$), which has the same order as the total sensitivity (including experimental errors) of the BVS method. This contradiction as well as the ambiguity of proposed CO schemes (two different CO classes were proposed: class-I in the $P2/c$ unit cell and class-II in the full Cc superstructure) is resolved in our electronic structure study.

We perform LSDA and LSDA + U calculations for Fe_3O_4 in the $P2/c$ structure. For simplicity we neglect small spin-orbit coupling (in previous calculations for cubic Fe_3O_4 spin-orbital splitting of the $3d$ band was found to be 2 orders of magnitude smaller than the crystal field splitting [23]). The LSDA calculations give only a half-metallic ferrimagnetic solution without CO. Partially filled bands at the Fermi level originate from the minority spin t_{2g} orbitals of Fe_B cations. The tetrahedral Fe_A cations do not participate in the formation of bands near the Fermi level, since their minority and majority spin $3d$ states are completely occupied and completely empty, respectively. Thus, the LSDA results qualitatively agree with previous band-structure calculations for the cubic phase [17,24–26]. Apparently, only crystal structure distortion from cubic to monoclinic phase is not sufficient to explain metal-insulator transition and charge ordering in magnetite. The electron-electron correlations, mainly in the $3d$ shell of Fe cations, play a significant role.

To proceed further we take into account the strong electronic correlations in Fe $3d$ shell using the LSDA + U method. In contrast to LSDA, even with U and J obtained from constrained calculations (4.5 and 1 eV, respectively), a charge ordered insulator with an energy gap of 0.03 eV was obtained. On the other hand, the calculation of U depends on theoretical approximations and, as a rule, the accuracy does not exceed 10%–20%. A reasonably good agreement between the calculated gap of 0.18 eV and the experimental value of 0.14 eV [27] was found using the U value of 5 eV, but it is important to note that CO and orbital order do not depend on the U value of 4.5–5.5 eV. As shown in Fig. 1, the gap is opened between occupied and unoccupied $t_{2g\downarrow}$ states of Fe_{B1}^{2+}, Fe_{B4}^{2+} and Fe_{B2}^{3+}, Fe_{B3}^{3+}, respectively (Fe_B sites are labeled according to the notation in Fig. 2 of Ref. [15] and Table II of Ref. [16]). The remaining unoccupied Fe_B states are pushed by strong Coulomb repulsion to the energies above 2 eV.
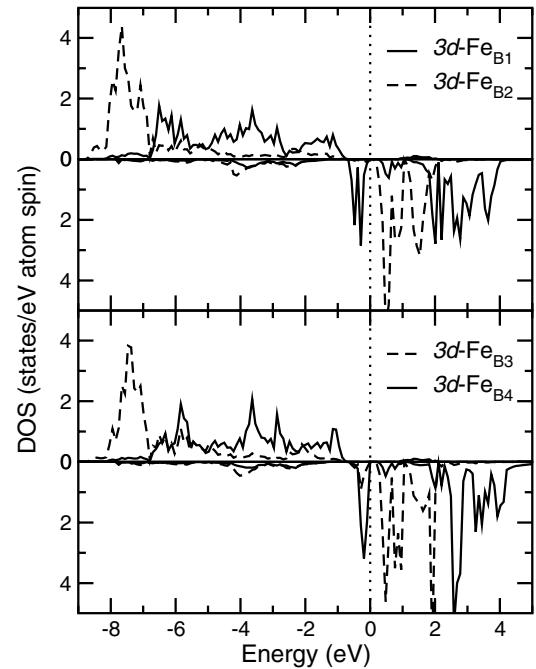

FIG. 1. Partial DOS obtained from the LSDA + U calculations with $U = 5$ and $J = 1$ eV for the low-temperature $P2/c$ phase of Fe_3O_4. The top of the valence band is shown by dotted lines.

The obtained CO coincides with the class-I CO, proposed earlier by Wright *et al.* [15,16], and is described by a dominant $[001]_c$ charge density wave which is characterized by alternate Fe_{B1}^{2+} and Fe_{B2}^{3+} planes separated by charge neutral planes consisting of chains formed by alternate Fe_{B3}^{3+} and Fe_{B4}^{2+} cations. An additional minor $[00\frac{1}{2}]_c$ modulation appears as a result of interchanged positions of Fe_{B3}^{3+} and Fe_{B4}^{2+} cations in the chains shifted by the vector $(0, 0, \frac{1}{2})$ [see Fig. 7(a) of Ref. [16]]. Thus, the LSDA + U calculations confirm violation of the Anderson criterion for Fe_3O_4 in the LT phase. In order to check the stability of the obtained CO solution we performed additional self-consistent LSDA + U calculations both for the $P2/c$ structure and the Cc supercell. In the first case the Verwey CO was used as the starting CO model, while in the second one we started from class-II CO, shown in Fig. 2 of Ref. [15]. However, it was found that these CO models are unstable and the obtained self-consistent solutions coincide with the stable one found previously, i.e., for a certain value of U the obtained CO does not depend on the initial charge arrangement. Obviously, we did not check all possible CO scenarios within the $P2/c$ unit cell or the Cc supercell, but our results consistently indicate that the obtained class-I CO solution is the ground state of Fe_3O_4 in the LT phase. It is important to note that LSDA + U calculations performed for an undistorted $P2/c$ supercell of $Fd\bar{3}m$ structure result in an insulating CO solution which is *compatible* with the Verwey CO model.

An analysis of occupation matrices of $3d$-Fe_B minority spin states confirms substantial charge disproportionation. As shown in Table I, one of the $t_{2g\downarrow}$ states of Fe_{B1}^{2+} and Fe_{B4}^{2+} cations is almost completely filled with the occupation numbers $n \approx 0.8$. On the other hand, the remaining two $t_{2g\downarrow}$ orbitals of the Fe^{2+} cations have a significantly smaller population of about 0.15. The occupation numbers of $t_{2g\downarrow}$ orbitals for Fe_{B2}^{3+} and Fe_{B3}^{3+} do not exceed 0.1, which gives the value of about 0.7 for the largest difference between Fe_B^{2+} and Fe_B^{3+} t_{2g} minority spin populations. The corresponding total $3d$ charges difference (0.23) and disproportionation of the total electron charges inside the atomic spheres of Fe_B^{2+} and Fe_B^{3+} cations (0.24) is in reasonably good agreement with the value of 0.2 estimated from the BVS analysis of monoclinic structure. This shows that the change of the $t_{2g\downarrow}$ occupations caused by the charge ordering is very effectively screened by the rearrangement of the other Fe electrons.

Significant contribution to the charge screening is provided by Fe_B e_g states. Although the bands originating from these states are located well above the energy gap, the e_g minority orbitals form relatively strong σ bonds with $2p$ states of the oxygen octahedron and, as a result, give appreciable contribution to the occupied part of the valence band. The above mentioned screening reduces the energy loss due to the development of CO incompatible with the Anderson criterion in the LT phase of Fe_3O_4. Hence, due to strong screening effects, the order parameter, introduced as the total $3d$ charge difference between $2+$ and $3+$ Fe_B cations, is ill defined. That explains why the BVS analysis does not give convincing proof of CO existence. Apparently, the well-defined order parameter is the difference of $t_{2g\downarrow}$ occupancies for Fe_B^{3+} and Fe_B^{2+} ions, which amounts to 70% of the ideal ionic CO model and clearly pronounces the existence of CO below the Verwey transition.

The self-consistent solution obtained from the LSDA $+ U$ calculations is not only charge but also orbitally ordered. The occupied minority spin t_{2g} state of Fe_{B1}^{2+} and Fe_{B4}^{2+} cations is predominantly of $d_{xz} \pm d_{yz}$ and $d_{x^2-y^2}$ character, respectively. This is illustrated by Fig. 2 which shows the angular distribution of the minority spin $3d$ Fe_B

electron density. Note, however, that the cubic harmonics are defined in the $P2/c$ frame which is rotated by an angle $\sim \pi/4$ with respect to the cubic one and the angular dependence of t_{2g} states in this frame is given by $d_{xz} \pm d_{yz}$ and $d_{x^2-y^2}$ combination of cubic harmonics. The obtained relative orientation of occupied Fe_B t_{2g} minority orbitals corresponds to the anti-ferro-orbital order, i.e., the orbitals on neighboring Fe^{2+} sites are orthogonal to each other. Since all Fe_B cations are ferromagnetically coupled, the obtained orbital order is consistent with the anti-ferro-orbital ferromagnetic state, which is the ground state of the degenerate Hubbard model according to the Kugel-Khomskii theory [29]. This orbital order leads to the corresponding distortions of FeO_6 octahedra. An analysis of interatomic distances in the monoclinic structure (Table II) shows that the average Fe_{B1}-O distance (2.087 Å) in the plane perpendicular to one of the diagonals of the distorted $Fe_{B1}O_6$ octahedron is considerably larger than average distances in the other two planes (2.063 and 2.067 Å). It turns out that the occupied Fe_{B1} t_{2g} minority spin orbital is the one oriented in the plane with the largest average Fe_{B1}-O distance. The same is also true for the Fe_{B4} ion but in this case the variation of
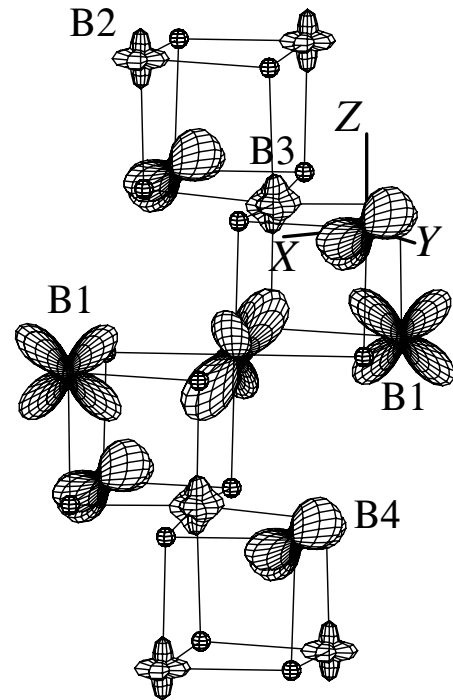

FIG. 2. The LSDA $+ U$ angular distribution of the minority spin $3d$ electron density of Fe_B cations for the low-temperature $P2/c$ phase of Fe_3O_4. The angular distribution is calculated according to $\rho(\theta, \phi) = \sum_{m,m'} n_{m,m'} Y_m^*(\theta, \phi) Y_{m'}(\theta, \phi)$, where $n_{m,m'}$ is the occupation matrix of d minority states for Fe_B atoms. $Y_m(\theta, \phi)$ are corresponding spherical harmonics. Oxygen atoms are shown by small spheres. The size of orbital corresponds to its occupancy.

TABLE I. Total and l-projected charges, magnetic moments, and occupation of the most populated t_{2g} minority orbitals calculated for inequivalent Fe_B ions in the low-temperature $P2/c$ phase of Fe_3O_4 [28].

Fe_B ion	q	q_s	q_p	q_d	$M (\mu_B)$	$t_{2g\downarrow}$ orbital	n
Fe_{B1}	6.04	0.17	0.19	5.69	3.50	$d_{xz} \mp d_{yz}$	0.76
Fe_{B2}	5.73	0.19	0.21	5.44	3.94		0.09
Fe_{B3}	5.91	0.19	0.21	5.51	3.81		0.09
Fe_{B4}	6.03	0.16	0.18	5.69	3.48	$d_{x^2-y^2}$	0.80

TABLE II. The averaged Fe_B-O distances in the plane of t_{2g} orbitals for $P2/c$ structure of Fe_3O_4 [28].

Fe_B atom	Orbital	d_{orb} (Å)	d_{av} (Å)
Fe_{B1a}	$d_{xz} + d_{yz}$	2.067	2.072
	$d_{xz} - d_{yz}$	2.087	
	$d_{x^2-y^2}$	2.063	
Fe_{B1b}	$d_{xz} + d_{yz}$	2.087	2.072
	$d_{xz} - d_{yz}$	2.067	
	$d_{x^2-y^2}$	2.063	
Fe_{B4}	$d_{xz} \pm d_{yz}$	2.067	2.069
	$d_{x^2-y^2}$	2.074	

the average Fe_{B4}-O distances is smaller (2.074 Å vs $2 \times$ 2.067 Å) and, as a consequence, the out-of-plane rotation of the occupied $t_{2g\downarrow}$ orbital is stronger.

As was shown earlier, the Verwey CO model possesses the minimum electrostatic repulsion energy among all possible CO models [7]. However, due to the existence of two perpendicular families of B-site chains (for instance $[110]_c$ and $[1\bar{1}0]_c$) correspondingly occupied by 2+ and 3+ Fe_B cations, the lattice "feels" significant stresses and tends to expand in the one ($[110]_c$) and to compress in the other ($[1\bar{1}0]_c$) direction. Therefore, the Verwey CO gives a significant "elastic" energy contribution to the total energy, and in spite of the lowest electrostatic energy, becomes less favorable than other arrangements. The competition of these two (elastic and electrostatic) contributions in the total energy appears to be responsible for the charge order, which is realized in the experimentally observed low-temperature monoclinic structure. In this CO scheme the alternating $(001)_c$ planes occupied by 2+ ("occupied" plane) and by 3+ ("empty" plane) Fe_B cations are separated by the "partially" occupied plane. This $(001)_c$ plane order makes the difference between $[110]_c$ and $[1\bar{1}0]_c$ directions less pronounced and significantly reduces the lattice stress and, as a result, reduces the elastic energy contribution in the total energy. We propose that this scenario is the primary cause for development of the class-I CO found below the Verwey transition.

In summary, in the present LSDA $+ U$ study of the LT $P2/c$ phase of Fe_3O_4 we found a charge and orbitally ordered insulator with an energy gap of 0.18 eV. The obtained charge ordered ground state is described by a dominant $[001]_c$ charge density wave with a minor $[00\frac{1}{2}]_c$ modulation. The CO coincides with the earlier proposed class-I CO [15,16] and confirms a violation of the Anderson criterion [5]. While the screening of the charge disproportion is so effective that the total $3d$ charge disproportion is rather small (0.23), the charge order is well pronounced with an order parameter defined as a difference of $t_{2g\downarrow}$ occupancies of 2+ and 3+ Fe_B cations (0.7). This agrees well with the result of BVS analysis for monoclinic structure (0.2). The orbital order is in agreement with the Kugel-Khomskii theory [29] and corresponds to the local distortions of oxygen octahedra surrounding Fe_B sites.

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[1] D. C. Mattis, *The Theory of Magnetism I* (Springer, Berlin, 1988).
[2] J. M. D. Coey *et al.*, Appl. Phys. Lett. **72**, 734 (1998).
[3] E. J. W. Verwey, Nature (London) **144**, 327 (1939).
[4] E. J. W. Verwey *et al.*, J. Chem. Phys. **15**, 181 (1947).
[5] P. W. Anderson, Phys. Rev. **102**, 1008 (1956).
[6] M. Mizoguchi, J. Phys. Soc. Jpn. **44**, 1501 (1978).
[7] J. M. Zuo, J. C. H. Spence, and W. Petuskey, Phys. Rev. B **42**, 8451 (1990).
[8] M. Iizumi *et al.*, Acta Crystallogr. Sect. B **38**, 2121 (1982).
[9] Several reviews of research on the Verwey transition up to 1980 are contained in the special issue of Philos. Mag. B **42** (1980).
[10] J. R. Cullen and E. R. Callen, Phys. Rev. Lett. **26**, 236 (1971).
[11] J. R. Cullen and E. R. Callen, Phys. Rev. B **7**, 397 (1973).
[12] N. F. Mott, Philos. Mag. B **42**, 327 (1980).
[13] Y. Yamada, Philos. Mag. B **42**, 377 (1980).
[14] H. Seo, M. Ogata, and H. Fukuyama, Phys. Rev. B **65**, 085107 (2002).
[15] J. P. Wright, J. P. Attfield, and P. G. Radaelli, Phys. Rev. Lett. **87**, 266401 (2001).
[16] J. P. Wright, J. P. Attfield, and P. G. Radaelli, Phys. Rev. B **66**, 214422 (2002).
[17] Z. Szotek *et al.*, Phys. Rev. B **68**, 054415 (2003).
[18] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).
[19] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, 5467 (1995).
[20] J. García *et al.*, Phys. Rev. B **63**, 054110 (2001).
[21] J. García *et al.*, cond-mat/0211407.
[22] J. García *et al.*, Phys. Rev. Lett. **85**, 578 (2000).
[23] V. N. Antonov *et al.*, Phys. Rev. B **64**, 134410 (2001).
[24] V. I. Anisimov *et al.*, Phys. Rev. B **54**, 4387 (1996).
[25] Z. Zhang and S. Satpathy, Phys. Rev. B **44**, 13319 (1991).
[26] A. Yanase and N. Hamada, J. Phys. Soc. Jpn. **68**, 1607 (1999).
[27] S. K. Park, T. Ishikawa, and Y. Tokura, Phys. Rev. B **58**, 3717 (1998).
[28] Here: $d_{xz} - d_{yz}$, $d_{xz} + d_{yz}$, and $d_{x^2-y^2}$ correspond to d_{xz}, d_{yz}, and d_{xy} orbitals t_{2g} in the local frame connected to an oxygen octahedron or in the $Fd\bar{3}m$ frame.
[29] K. I. Kugel and D. I. Khomskii, Sov. Phys. Solid State **17**, 285 (1975).