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Charge-ordered insulating state of Fe_3O_4 from first-principles electronic structure calculations

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The charge-ordered insulating state of Fe_3O_4 below the Verwey transition temperature has been studied by the modified local density approximation with Coulomb interaction correction method. The charge ordering is found to be a stable solution with an energy gap value of 0.34 eV (the experimental value is 0.14 eV) in contrast to a uniform metallic state given by the standard local spin-density approximation. The calculated effective intersite Coulomb interaction is well screened ($V=0.18$ eV). It was shown that the change in electrostatic potential associated with the transition to a completely disordered state can close an energy gap leading to a metallic state. [S0163-1829(96)05328-3]

Magnetite (Fe_3O_4) is a mixed-valence 3*d* transition-metal compound. It crystallizes in the inverted cubic spinel structure in which tetrahedral *A* sites contain one-third of the Fe ions as Fe^{3+}, while octahedral *B* sites contain the remaining Fe ions, with equal numbers of Fe^{2+} and Fe^{3+} in *B*1 and *B*2 sites, respectively. Below 860 K, magnetite is ferrimagnetic with *A*-site magnetic moments aligned antiparallel to the *B*-site moments. At $T_V=122$ K Fe_3O_4 undergoes a first-order phase transition, the so-called Verwey transition,[1] in which dc conductivity abruptly increases by two orders of magnitude on heating through T_V. Verwey interpreted the transition as an order-disorder transformation of Fe ions on the *B* sites. Indeed, studies by electron and neutron diffraction and nuclear magnetic resonance[2–4] show that below T_V the *B*1 and *B*2 sites are structurally distinguishable in a distorted crystal structure. Photoemission measurements clearly show a gap $\simeq 0.14$ eV in the spectra.[5,6] However, band-structure calculations using the local spin-density approximation[7,8] (LSDA) gave only a metallic solution without charge ordering with partially filled bands (containing one electron per two *B* sites) originated from t_{2g} spin-down 3*d* orbitals of Fe ions in octahedral *B* sites.

The problem of charge ordering cannot be treated by the standard LSDA. The reason for that is a spurious self-interaction that is present in the LSDA. In contrast to the Hartree-Fock approximation, where self-interaction is explicitly excluded for every orbital, in the LSDA it is nearly canceled only in the total-energy integrals, but not in one-electron potentials that are orbital independent.

There are two cases where the LSDA gives qualitatively wrong results due to its ''average'' self-interaction correction. The first is the Mott-Hubbard insulator where the orbital dependence of the one-electron potential is essential for the description of splitting the electron spectrum between the occupied lower and unoccupied higher Hubbard bands. To do it on (at least) a mean-field approximation level one must introduce the on-site Coulomb interaction and add to the LSDA functional the difference between the Hartree-Fock approximation for the Coulomb interaction energy and the averaged form corresponding to the LSDA. That is the essence of the LDA+U method, which proved to be quite successful in treating systems with strong electron-electron correlations.[9,10]

Another example of failures of the LSDA is the description of charge ordering. For example, if there is one electron per two sites (as for Fe_3O_4), the state without charge ordering will correspond to the orbital population $\frac{1}{2}$ on every site. One electron per two sites means that the probability to have two electrons per site is negligible and the on-site Coulomb interaction, which is a driving force for Mott-Hubbard localization, is unimportant in this case. Instead the intersite Coulomb interaction plays a decisive role in lowering the total energy, when electrons are sitting on sites as far from each other as possible, which leads to a charge-ordered state. The intersite Coulomb interaction being purely electrostatic is well described by the LSDA. However, the spurious self-interaction still present in the LSDA leads to an increase in the Coulomb interaction when the distribution of the electron charge deviates from the uniform one. This effect can be illustrated in the following way. If one neglects the intersite Coulomb interaction, then the electron under consideration experiences the same potential of all sites independently of the occupancy of the particular site, as it does not interact with itself. However, as the LSDA potential is a functional of the electron density only, then increasing the electron density on one site and decreasing it on another one, with the development of the charge ordering, will lead to an increase of the potential on the first site and a decrease of it on the second one. In the process of self-consistent loops the charge distribution will return to the uniform one.

In order to cure this deficiency of the LSDA it is necessary to remove the spurious self-interaction. Formally

LDA+U does it, but this method was constructed for Mott insulators. For systems with charge ordering it must be modified. For Mott-Hubbard and charge-transfer insulators the main process to be taken into account is the virtual excitation of the electron to (or from) the *d* shell of the transition-metal ion (the addition or removal of a *d* electron). It is done by adding to the LSDA functional a mean-field expression for the Coulomb interaction energy between *d* electrons explicitly containing a self-interaction cancellation and by subtracting the averaged Coulomb interaction energy that is present in the LSDA. The corresponding Coulomb parameter U is calculated assuming a pseudocore approximation for *d* orbitals by switching off hybridization of *d* orbitals with all other orbitals and calculating the total energy as a function of the number of *d* electrons on a site in a supercell approximation.[11]

In contrast to that, for charge ordering in Fe_3O_4, the main virtual process is the hopping of the t_{2g} electron from one site to another with a negligible probability of meeting another t_{2g} electron on the same site due to a small number of these electrons. The change of the Coulomb energy in this process will be not due to the intrasite interaction U, but due to the intersite interaction V. Therefore, to describe such a process one must map the dependence of the Coulomb interaction energy on the number of t_{2g} electrons in the LSDA onto the model with on-site and intersite terms and then explicitly exclude the on-site self-interaction term.

If one defines n_i as the sum of the occupancies of t_{2g} orbitals $(n_{xy}+n_{yz}+n_{zx})$ for the minority spin direction on B site i, then the model that imitates the LSDA for the electrostatic energy associated with the t_{2g} electrons is

$$E[n_i]=\sum_i \left\{ \tfrac{1}{2}Un_i(n_i-1)+V\sum_j n_i n_j \right\}. \tag{1}$$

(The index j denotes neighbors of the site i.) The form of the on-site term is chosen so that in a fully ordered case, where one-half of the sites is completely occupied and the other half is empty, the self-interaction energy would vanish. In order to compute the value of the parameters U and V one must perform constraint calculation for the charge ordering where occupancies n_i on different sites are varied with the conserved total number of t_{2g} electrons. The simplest form of such a variation is to divide octahedral sites into two sublattices $B1$ and $B2$ with the number of electrons given by $n_i^{B1}=n_0+\delta n$ and $n_i^{B2}=n_0-\delta n$, respectively. Introducing Lagrange multipliers λ_{B1} and λ_{B2}, the functional becomes

$$E[n_i]+\sum_i \{\lambda_{B1}(n_i^{B1}-n_0-\delta n)+\lambda_{B2}(n_i^{B2}-n_0+\delta n)\}, \tag{2}$$

the variation of which with respect to δn gives

$$\frac{\delta E}{\delta n}+(\lambda_{B2}-\lambda_{B1})=0. \tag{3}$$

Lagrange multipliers λ have the meaning of external fields acting on t_{2g} electrons and the corresponding constraint LSDA calculations are performed with such fixed fields.

In the calculation of the intersite Coulomb interaction we took into account only nearest neighbors. It is known that the excitation energy gap in Fe_3O_4 is very small [0.14 eV (Ref. 5)] and therefore the dielectric screening must be very effective, being close to the metallic one, and the neglect of the long-range Coulomb interaction seems to be justified.

To determine two parameters U and V it is necessary to calculate two different types of charge ordering with essentially different sets of $B1$ and $B2$ sublattices. As the first type of charge ordering we chose the order suggested by Verwey *et al.*[1] It can be described as a lattice built with the neutral tetrahedra where every tetrahedron contains two atoms from the $B1$ sublattice and two atoms from the $B2$ sublattice. In this case every atom has two nearest neighbors of the same type and four neighbors belonging to the other sublattice and the first variation of the total-energy functional on δn is (if $\lambda_{B2}=-\lambda_{B1}=\lambda$)

$$(U-2V)\delta n=\lambda. \tag{4}$$

The second type of charge ordering corresponds to charged tetrahedra where one of them contains only $B1$-type and another only $B2$-type sublattices. In this case 75% of atoms have five nearest neighbors of the same type and one of the opposite type. Another 25% have equal numbers of neighbors of both types. The equation corresponding to this charge ordering is

$$(U+3V)\delta n=\lambda. \tag{5}$$

Having determined U and V parameters, we can define now a new functional without the self-interaction by subtracting the $\frac{1}{2}Un_i(n_i-1)$ term from the LSDA functional. The real on-site Coulomb interaction energy is small due to the small probability of two t_{2g} electrons to stay on the same site, but it is nevertheless nonzero and we take it into account by adding the corresponding term in the Hartree-Fock approximation

$$E=E_{\mathrm{LSDA}}-\tfrac{1}{2}\sum_i \left\{ Un_i(n_i-1)-\sum_{m,m'\neq m} Un_{i,m}n_{i,m'} \right\}, \tag{6}$$

where m,m' denote different t_{2g} orbitals for minority electrons of Fe ions on octahedral B sites. The corresponding orbital dependent potential $V_{i,m}$ is given by the variation of the new functional (6) with respect to the occupancy of the particular t_{2g} orbital $n_{i,m}$:

$$V_{i,m}=V_i^{\mathrm{LSDA}}+U(\tfrac{1}{2}-n_{i,m}). \tag{7}$$

The actual calculations were performed by using atomic-sphere approximation linear muffin-tin orbital method.[12] Constraint calculations with two types of charge ordering gave the following parameters: $U=4.51$ eV and $V=0.18$ eV. The small value of the intersite Coulomb interaction parameter V proves that, indeed, the screening of the Coulomb interaction in Fe_3O_4 is very effective and close to the metallic one.

Electronic-structure calculations with the functional (6) were performed for the Verwey type of charge ordering. In contrast to LSDA, where the stable solution is a metal with uniform distribution of the t_{2g} spin-down electrons on the octahedral sites, the self-interaction corrected functional (6)

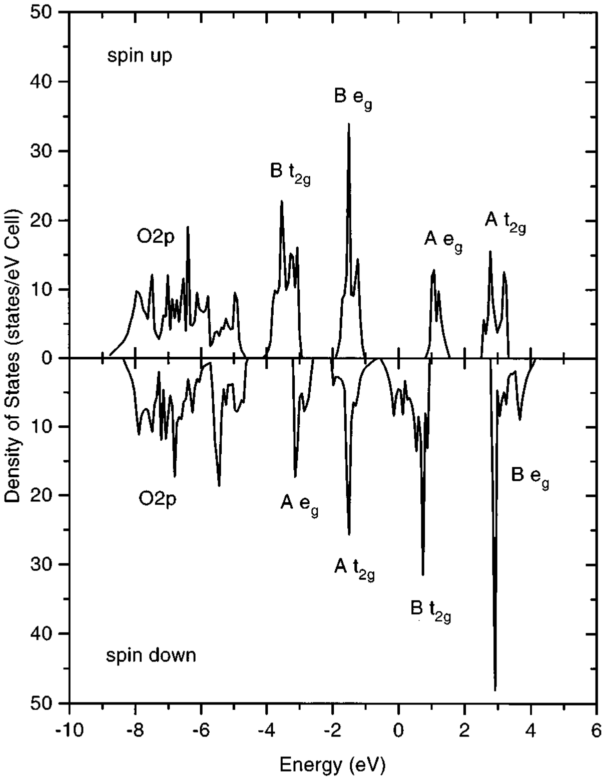

FIG. 1. Density of states for Fe_3O_4 in the LSDA calculation. *A*, tetrahedral coordinated Fe ions; *B* octahedral Fe ions.

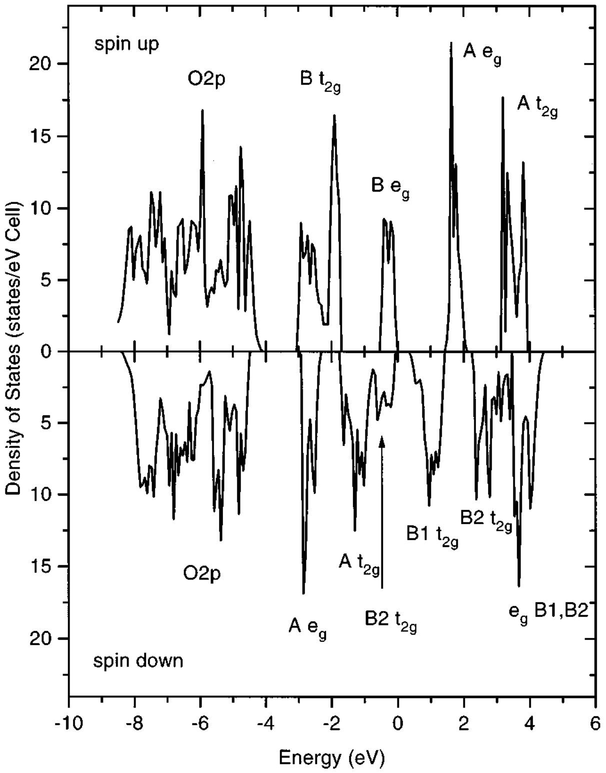

FIG. 2. Density of states for Fe_3O_4 in the calculation with functional (6) (LDA+U). *A*, tetrahedral coordinated Fe ions; *B*, octahedral Fe ions (*B*1 corresponds to Fe^{3+} and *B*2 to Fe^{2+} ions).

gave a charge-ordered insulator with an energy gap value of 0.34 eV [with the experimental value being 0.14 eV (Ref. 5)].

According to the ionic model, charge ordering means Fe^{3+} and Fe^{2+} ions on octahedral site sublattices *B*1 and *B*2 with configurations d^5 $(t^3_{2g\uparrow}e^2_{g\uparrow})$ and d^6 $(t^3_{2g\uparrow}e^2_{g\uparrow}t^1_{2g\downarrow})$ correspondingly. In our calculations, due to the strong covalence effects, the actual numbers of *d* electrons in atomic spheres were 5.91 and 6.23 with the charge difference 0.32 instead of the pure ionic value 1.0. (However, the difference in the occupancy of $t_{2g\downarrow}$ orbital for two sublattices is larger: 0.70.)

Figure 1 shows the densities of states (DOS) for Fe_3O_4 obtained in standard LSDA calculations and Fig. 2 the DOS calculated with the use of the functional (6). For the LSDA one can see the oxygen band between -8 and -4 eV and above it (for both a spin-up and a spin-down DOS) four bands of Fe 3*d* origin. For spin-up states the sequence is t_{2g} and e_g bands of iron in octahedral *B* sites and above it e_g and t_{2g} bands of iron in tetrahedral *A* sites. For spin-down states the order of the octahedral- and tetrahedral-site bands is reversed so that the first two *d* bands are e_g and t_{2g} bands of iron in tetrahedral sites (*A*) and above them are t_{2g} and e_g bands of iron in octahedral sites (*B*) with the Fermi energy lying in the t_{2g} band.

In the charge-ordered state the partially filled t_{2g} spin-down band of the octahedral (*B*) ions is split into three parts (Fig. 2): just below the Fermi energy is a subband corresponding to the occupied t_{2g} orbital of the *B*2 (Fe^{+2}) sublattice, then immediately above the Fermi energy t_{2g} orbitals band of the *B*1 (Fe^{+3}) sublattice, and above it the band formed by the empty orbitals of *B*2 (Fe^{+2}) ions and empty e_g bands of octahedral (*B*1 and *B*2) ions.

Our result shows that, indeed, after subtracting the spurious self-interaction present in the LSDA it is possible to obtain an insulating charge-ordered solution for Fe_3O_4. However, can our method describe the metal-insulator transition? Knowing the value of the intersite Coulomb interaction parameter *V*, it is possible to estimate the change in the potential acting on the t_{2g} electrons in going from a Verwey-type charge order to the completely disordered state. According to the argument leading to Eq. (4), the difference in the electrostatic potential for two sublattices in the Verwey-type charge order is equal to $\delta V = 4V\delta n_{t_{2g}}$. Our calculation gave $V=0.18$ eV and $\delta n_{t_{2g}}=0.70$, which results in $\delta V=0.50$ eV, which is definitely larger than the calculated energy gap value 0.34 eV. Therefore, completely destroying the charger order would close an energy gap and lead to a metallic state.

The actual experimental situation is much more complicated. As shown in Ref. 6, above $T_V=122$ K Fe_3O_4 is still an insulator, but with a smaller gap value. In Ref. 5 photoemission measurements are interpreted in another way: above T_V magnetite becomes metallic, but with a very small value of the density of states at the Fermi level, which becomes larger with increasing of temperature. That could be interpreted as a transition from one charge-ordered state to another charge-ordered state or maybe to a state with many different charge-ordered states having frustrated patterns and not showing macroscopic order, as proposed by Anderson.[13] We also note that the charge order below T_V is more complicated than the simple Verwey pattern, and that the phase transition is accompanied by a structure transformation from the spinel to a lower symmetry structure.[2] Calculations with more complicated crystal and charge-order structures are needed to obtain a quantitative description of the metal-insulator transition for Fe_3O_4. Nevertheless, the present work contains the basic ingredients in the charge ordering of Fe_3O_4 and the prescription can be applied to the real situation if it is known.

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