Electronic structure of the ferroelectromagnet YMnO$_3$

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Received 31 January 2000; accepted 17 April 2000

Communicated by J. Flouquet

Abstract

Using the self-consistent linear muffin-tin orbitals and atomic sphere approximation (LMTO-ASA) method, electronic structure calculations of the ferroelectromagnet YMnO$_3$ in the magnetic and nonmagnetic phases are performed in the local density approximation (LDA) of the density-functional theory. Total energy calculations reproduce the magnetic phase observed at low temperatures. Due to the Jahn–Teller distortion, antiferromagnetic insulating solution with a very small energy gap is also obtained. After including the strong electron–electron correlation effects in Mn 3d states by the on-site Coulomb interaction correction, the energy gap is increased to 1.1 eV and the density of states is greatly redistributed. The large component of oxygen 2p states at the top of the valence states shows that the insulator YMnO$_3$ has a charge-transfer character. © 2000 Published by Elsevier Science B.V. All rights reserved.

PACS: 71.20.Ps; 71.27.+a; 71.15.Mb; 75.50.Ee

1. Introduction

Recent discovery of the colossal magnetoresistance in doped LaMnO$_3$ near its magnetic transition temperature [1] provided renewed interest to the study of manganites. The yttrium and rare-earth manganites RMnO$_3$ usually have two structural phases [2,3]: The hexagonal phase for $R =$ Ho, Er, Tm, Yb, Lu or Y, which have a smaller ionic radius, and the orthorhombic phase for $R =$ La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy, which have a larger ionic radius. While the magnetic ordering can occur in both hexagonal and orthorhombic manganites, ferroelectric ordering occurs only in the hexagonal ones, which belong to the noncentrosymmetric $P6_3cm$ space group.

Due to coexistence of the ferroelectric and magnetic orderings at low temperatures, the hexagonal yttrium and rare-earth manganites are an interesting class of materials known as ferroelectromagnets. Indeed, the coupling phenomena between the ferroelectric and magnetic orderings have been recently observed in YMnO$_3$ [4], which displays a ferroelectric $T_f \approx 914$ K, but a rather low antiferromagnetic $T_M \approx 80$ K. This coupling can lead to the so-called magnetoelectric effect with an interesting potential use in devices, where the dielectric (magnetic) properties may be changed by the onset of the magnetic (elec-
where $E_{\text{LSDA}}$ stands for the energy functional in the LSDA, and parameters $U$ and $J$ are on-site Coulomb energy and exchange energy of the Mn 3d electrons, respectively. $n_{m\sigma}$ is the occupation number of a particular $d_{m\sigma}$ orbital at one site and $n^0_{m\sigma}$ is the average spin occupancy of d orbital for $\sigma$ spin. The corresponding one-electron potential is then given by:

$$V_{m\sigma} = V_{\text{LSDA}} + U \sum_{m} (n_{m\sigma} - n^0_{m\sigma})$$

$$+ (U - J) \sum_{m' \neq m} (n_{m'\sigma} - n^0_{m\sigma})$$

In the following LSDA + U calculation, the values of $U = 10.1 \text{ eV}$ and $J = 0.88 \text{ eV}$ are selected for the Mn 3d states in YMnO$_3$ (Ref. [16]).

The hexagonal structure of the ferroelectromagnet YMnO$_3$ contains layers of corner-sharing MnO$_5$ bipyramids with triangular base of nonequivalent O(3) and O(4) atoms, whereas the O(1) and O(2) are at the apexes. The Mn-O(1) and Mn-O(2) bonds are slightly tilted with respect to the $c$ axis. The Y(1) and Y(2) atoms lie between the bipyramidal layers. The unit cell has six formula units for both antiferromagnet and paramagnet. The lattice constants and atomic position parameters are summarized in the Table 1 [5;18]. The ratio of the atomic sphere radii is taken as 1.26:1.0:0.79:0.70 for Y, Mn, O, and empty spheres. The Y 5s5p4d, Mn 4s4p3d and O 2s2p orbitals are chosen as the valence states and the frozen-core approximation is used for the core electrons. The exchange-correlation potential is adopted in the form of von Barth–Hedin. Self-consistency is

<table>
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<th>Atom</th>
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<th>$y$</th>
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carried out on 216 special k-points in the irreducible Brillouin zone.

3. Results and discussions

The calculation of the electronic structure for the ferroelectromagnet YMnO$_3$ in the paramagnetic phase is performed first. The results for density of states (DOS) are plotted in Fig. 1. Because of lack of spin-splitting, the Mn $t_{2g}$ states are partially filled and the metallic solution for nonmagnetic (NM) state is obtained. The occupied O 2p bands are separated from the partially occupied Mn 3d bands in the range of $-7$ eV to $-3$ eV relative to the Fermi level. A large peak in density of states $N(E)$ falls precisely at Fermi energy $E_F$, suggesting a Stoner instability of the nonmagnetic state.

When the temperature is lowered, the Mn$^{3+}$ magnetic moments in the ferroelectromagnet YMnO$_3$ become antiferromagnetic (AFM) ordering while the crystal structure is unchanged. Like LaMnO$_3$, YMnO$_3$ has A-type antiferromagnetic long-range ordering, where there is ferromagnetic ordering in Mn(1000) planes and AFM ordering between the Mn(1000) planes. The present spin-polarized calculation yields an insulating solution with a very small gap (about 0.01 eV). Moreover the total-energy calculation shows that the AFM spin-polarization leads to an energy gain of 0.131 eV per formula unit relative to the NM case, confirming the YMnO$_3$ to be an AFM insulator as expected.

Fig. 2(a) and Fig. 3(a) show the band structure and the total and partial density of states (DOS), respectively, for AFM YMnO$_3$ based on the LSDA. In the valence bands, the Mn 3d bands occur above O 2p bands much like in LaMnO$_3$. The completely filled O 2p band is mainly distributed over a range of energy from $-3$ to $-8$ eV relative to the Fermi level despite a slight difference between the partial DOS of apex O(1),O(2) and planar O(3),O(4) due to their different O-Mn-O bond angles. The occupied majority Mn 3d bands are largely located at about 1.8 eV below the Fermi level and a little mixed with the O 2p band, but the minority Mn 3d bands are almost fully unoccupied up to 0.8 eV. Most of Y 4d bands are above 4.8 eV except a few band hybridized with O 2p orbital below $-3$ eV. In LaMnO$_3$, the octahedral MnO$_6$ results in the strong splitting of d states into triply degenerate $t_{2g}$ orbitals with lower energy and double degenerate $e_g$ orbitals with higher energy. In YMnO$_3$, the bipyramidal MnO$_5$ with the trigonal symmetry crystal field induces that the three $t_{2g}$ orbitals are further split into the nondegenerate $A_{1g}$ and double degenerate $E_g$ orbitals of the $D_{3d}$ group. In Fig. 4(a), the results for Mn 3d band are presented with the partial density of states projected to $t_{2g}$, $e_{g}^1$ and $e_{g}^2$ orbitals. For the $d^4$ configuration of Mn ion, the $t_{2g}$ manifold is essentially completely polarized with the exchange splitting $\approx 3$ eV. Due to the Jahn–Teller distortion, Mn $e_g$ band is split into $e_{g}^1$ and $e_{g}^2$ band, opening a very small energy gap between $e_{g}^1 \uparrow$ and $e_{g}^2 \uparrow$ band. Unlike in the LaMnO$_3$, the occupied $t_{2g}$ and $e_{g}^1$ bands are not well separated under the trigonal crystal field. The $e_{g}^1 \uparrow$ band is more dispersive with a width of $\approx 3$ eV distributed just below the Fermi level while the narrow $t_{2g} \uparrow$ band with a width of $\approx 1$ eV is located at about 2 eV below the Fermi level, and the occupation numbers in the $e_{g}^1 \uparrow$ and $t_{2g} \uparrow$ bands are 1.50...
Fig. 2. Energy band structure of the antiferromagnetic (AFM) state obtained from (a) the LSDA and (b) the LSDA + U. Fermi level is shifted to zero. High-symmetry points in the first Brillouin zone are: \( \Gamma = (0,0,0) \), \( M = (0,\frac{1}{2},0) \), \( K = (\frac{1}{2},\frac{1}{2},0) \), \( H = (\frac{1}{2},\frac{1}{2},\frac{1}{2}) \), \( A = (0,0,\frac{1}{2}) \). and 2.97, respectively. The extra electrons in the \( e_g^{\uparrow} \) band indicate its strong hybridization with the O 2p orbitals. Above Fermi level, the lowest conduction band has \( e_g^{\downarrow} \) character, and there is also the overlap of \( e_g^{\downarrow} \) and \( t_{2g}^{\downarrow} \) band in the energy range from 0.2 eV to 2.6 eV. The band width of \( t_{2g} \) orbitals is narrower than that of \( e_g \) orbital, indicating that \( t_{2g} \) orbitals are more localized than \( e_g \) orbital. Moreover, since the Mn(1000) planes with ferromagnetic ordering are separated by the Y planes along the \( z \) axis, the band along \( \Gamma - A \) is very flat, as shown in Fig. 2a.

It is well known that electron correlation effects are important for the transition metal compounds. Its effect on the electronic structure can be treated by the LSDA + U method, which is basically a combination of the Hartree–Fock approximation to the multiband Hubbard model with LSDA. Fig. 2(b) and 3(b) show the band structure and the DOS of YMnO\(_3\) calculated by LSDA + U, respectively. The projected DOS of \( t_{2g} \), \( e_g^1 \) and \( e_g^2 \) orbitals for Mn 3d band are also presented in Fig. 4(b). The unoccupied d bands shift up and the occupied d bands move down due to the strong on-site Coulomb repulsions, leading to an increased gap of 1.1 eV which is close to an optical gap of 1.55 eV observed experimentally [17]. The strong electron correlation significantly modifies the spectral weight of states. In particular, the center of Mn 3d band moves to below the O 2p band in contrast to the LSDA result. The occupied Mn 3d states are separated from the unoccupied ones by an energy of order \( U \). Due to the hybridization between the Mn 3d states and O 2p states, the partial DOS of the O 2p states are also redistributed. The large downshift of the occupied 3d band induces a significant enhancement of the oxygen component at the topmost valence band, which is composed of the O 2p states (about 70%) and the Mn 3d one (nearly 30%), and the lowest conduction band is still of the \( e_g^{\uparrow} \) character. Compared with the above LSDA result — that the topmost valence band contains an O 2p component about 8% the present LSDA + U result supports the proposal of a 2p–3d charge-transfer (CT) insulating character for the manganese oxides. Besides, the magnetic moment on Mn ion is 3.8 \( \mu_B \) in the LSDA and 3.9 \( \mu_B \) in the LSDA + U, which is close to the experimental value 3.1 \( \mu_B \) for YMnO\(_3\) [18] reduced by the quantum fluctuations.
Fig. 3. Total and projected densities of states (DOS) for the AFM state obtained from (a) the LSDA and (b) the LSDA + U. For the O 2p-projected DOS, the solid and dashed curves denote DOS of the O 2p, O 3 atom and the O 2p, O 4 atom, respectively. The vertical dashed line refers to the Fermi level.

Fig. 4. The projected densities of states (DOS) of Mn $t_{2g}$, $e_{g}^{+}$ and $e_{g}^{-}$ orbitals obtained from (a) the LSDA and (b) the LSDA + U. The solid (dashed) curve denotes the majority (minority) spin. The vertical dashed line refers to the Fermi level.

Although the valence-band photoemission spectrum measurement for YMnO$_3$ has not been made, our present LSDA + U band structure is consistent with spectra for LaMnO$_3$ or MnO which have a broad O 2p – Mn 3d double-peak structure with about 7 eV width [19,20]. The first structure detected at the binding energy of about 3 eV could be attributed to the emission of the O 2p electrons, in accord with the CT insulating character and corresponding to a final state dL (‘L’ stands for a ligand hole). The second detectable structure of spectrum would be assigned to the d$^4$ state with some contribution from the oxygen states in the range from $-8$...
to \(-5\) eV relative to \(E_F\), as shown in Fig. 3(b). Besides, compared with the optical second harmonic (SH) spectra of YMnO₃, in which two peaks are observed in the energy range of \(2\hbar\omega = 2.0\)–\(3.2\) eV, the LSDA + U result shows that the SH peaks are caused mainly by the transitions of O 2p to Mn \(e_g\) band, which is in accord with the recent calculations of the second-order nonlinear optical susceptibility by the real-space recursion method [21].

4. Conclusion

In summary, we have performed self-consistent electronic structure calculations for the ferroelectromagnet YMnO₃ in both antiferromagnetic and paramagnetic phases, based on the local density approximation. The antiferromagnetic insulating solution is reproduced as the ground state of YMnO₃ with distorted structure. Switching on the on-site Coulomb interaction of the localized d electrons, the LSDA + U calculation yields a \(2p\)–\(3d\) CT band gap of 1.1 eV, which is close to the experimental observation. In addition, the density of states is redistributed and comparable with the usual valence band spectrum of the transition metal Mn compound.

Acknowledgements

The authors thank support to this work from a grant for State Key Program of China, and also support from National Science Foundation of China through grant No. 19677202. The LDA calculation in this work has been done on the SGI origin-2000 Computer. One of the authors, Meichun Qian, is grateful to Xiangang Wan for his valuable discussions.

References