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Electronic Structure of Sr_2FeMoO_6

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We have analyzed the unusual electronic structure of Sr_2FeMoO_6 combining *ab initio* and model Hamiltonian approaches. Our results indicate that there are strong enhancements of the intra-atomic exchange strength at the Mo site as well as the antiferromagnetic coupling strength between Fe and Mo sites. We discuss the possibility of a negative effective Coulomb correlation strength (U_{eff}) at the Mo site due to these renormalized interaction strengths.

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Colossal magnetoresistance (CMR) in transition metal oxides [1] has attracted a great deal of attention in recent times [2] owing to their technological as well as fundamental importance. The systems based on doped manganites have been most exhaustively studied and their behaviors have been broadly understood in terms of the double-exchange mechanism [3,4], possibly modified by the presence of various kinds of polarons [5]. Recently, an ordered double perovskite oxide without any manganese, Sr_2FeMoO_6, has been shown [6] to have CMR at a low field even at room temperature. This spectacular magnetoresistance (MR) in Sr_2FeMoO_6 is intimately connected with a large magnetic T_c (≈450 K) of this compound. The essential physics of Sr_2FeMoO_6 is believed to be very similar to that of the manganites. However, this apparent similarity between the manganites and Sr_2FeMoO_6 is surprising, if not totally unexpected.

Mo is not a strongly correlated system and, consequently, a magnetic moment at the Mo site is a rarity, in contrast to Mn. In the ordered double perovskite Sr_2FeMoO_6, the transition metal sublattice sites are occupied alternately by Fe and Mo ions. Experimental evidence of ferrimagnetic order as well as band structure results establish an *antiferromagnetic* coupling between Mo and Fe atoms, in contrast to the *ferromagnetic* coupling in manganites. The large magnetic transition temperature in Sr_2FeMoO_6, however, points to a large interatomic exchange coupling strength, J, between Fe and Mo, comparable to that between the Mn-Mn pairs in the manganites, in spite of the normally expected nonmagnetic nature of Mo. Mo is usually nonmagnetic as the intra-atomic exchange strength, I, within the Mo 4d manifold is small, typically 0.1–0.2 eV, nearly an order of magnitude smaller than that in the 3d transition metal systems [7]. Additionally, the Mo 4d bandwidth tends to be substantially larger compared to the exchange splitting. However, the magnetic structure of this compound requires a strong spin splitting of the delocalized bands, leading to nearly complete spin polarization. This issue is moot in the present context, since the spectacular properties of this system—a high temperature *and* low-field MR—are critically dependent on the large T_c and the half-metallic ferromagnetic state. We investigate the origin of these apparent anomalies by combining state-of-the-art *ab initio* methods as well as realistic multiband many-body models for electronic structure calculations. Our results clearly establish an unusual renormalization of the intra-atomic exchange strength at the Mo sites, arising from Fe-Mo interactions; this causes the *effective* I to be much larger than the expected atomic value. We further evaluate J to show that it is indeed large, owing to the renormalization of I. Finally, we suggest the novel possibility of a negative effective Coulomb interaction strength, U_{eff} ($= U - I$), for the Mo sites due to the enhancement of I, with some preliminary experimental evidence for the same. Our results underline the unusual and unique aspects of the electronic structure of Sr_2FeMoO_6 that have not been appreciated so far.

We have computed the band dispersion of geometry optimized [6] Sr_2FeMoO_6 within the framework of the linear muffin-tin orbital (LMTO) method [8] using the generalized gradient approximation (GGA) for the exchange-correlation parts. Figures 1(a) and 1(b) show the orbital projected band dispersions of Sr_2FeMoO_6 for the majority and the minority spin channels; here the fatness of the bands in each panel is the weight of the indicated orbital in the wave function. The minority *down* spin bands cross the Fermi level, while the majority *up* spin bands exhibit a band gap of ~0.8 eV. The bands below −2 eV are predominantly of oxygen character, while bands crossing the Fermi level and ranging from −2 eV to about 2 eV have significant mixing between the Fe-d and Mo-d characters with some small admixture of oxygen p states. The presence of approximate cubic symmetry of the octahedral coordination of the oxygen atoms around the transition metal sites results in a splitting of the d levels into t_{2g} and e_g orbitals. For the minority spin channel, the Fe t_{2g} and Mo t_{2g} bands are partially filled, while Fe e_g and Mo e_g bands remain empty. The occupied part of the bands near the Fermi level in the majority spin channel [see Fig. 1(a)] are mainly composed of Fe d character which hybridizes with the oxygen p states. The narrow bands lying immediately above the Fermi level spanning an energy range of about 0.7 to 1.2 eV are predominantly from Mo t_{2g}

contribution, while the Mo e_g bands are further high up in energy. In order to estimate the electronic interaction strengths, we fitted the *ab initio* band dispersions, shown in Fig. 1, in terms of a tight-binding model containing d orbitals at the Fe and the Mo sites and the p orbitals at the oxygen sites. Such methods have been successful in obtaining realistic estimates of the interaction strengths including that for the intra-atomic exchange interactions [7,9]. This analysis yields a value of the intra-atomic exchange splitting strength at the Mo site to be 0.13 eV, estimated from the spin polarization of the Mo site energies; this estimate is consistent with our expectation of a small I at the Mo sites, but is in apparent contradiction to the enhanced T_c and strong polarization of the bands in $\mathrm{Sr_2FeMoO_6}$. It is intriguing at this stage to note that the up spin bands related to the Mo d states appear in the energy window centered at ~1 eV, while the down spin states appear near the Fermi level with a larger bandwidth suggesting a spin splitting of the Mo d band, considerably larger than the bare I. This clearly indicates that the bare I at the Mo site must be strongly renormalized giving rise to an enhanced I_{eff} leading to the pronounced spin polarization of the Mo d bands. In order to understand this renormalization process, as well as to estimate the effective I in contrast to the bare I at the Mo sites, it is necessary to integrate out the other degrees of freedom, such as the Fe d states, from the *ab initio* results, so that the few orbital description retains the effect of renormalizations as a change in the *effective* interaction strengths.

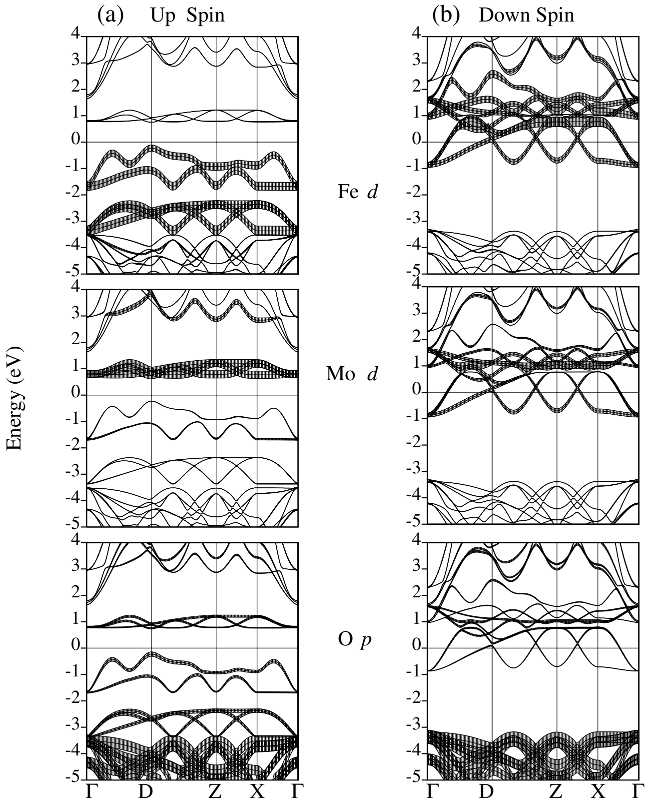

FIG. 1. LMTO band dispersions for $\mathrm{Sr_2FeMoO_6}$ along symmetry directions (see text).

Very recently, the third generation LMTO method [10] has been proved to be a powerful tool for deriving few orbital, orthogonal tight-binding Hamiltonians starting from the all orbital Hamiltonian representation used for the local density approximation or GGA self-consistency procedure, by integrating out other degrees of freedom.

In order to estimate the I_{eff} at the Mo sites, responsible for the large spin polarization of the bands, we have used this technique to derive the effective Mo t_{2g} Hamiltonian from the all orbital Hamiltonian. Figures 2(a) and 2(b) show the energy bands in *up* and *down* spin channels, respectively, obtained by diagonalizing the 3×3 Hamiltonian defined in the effective Mo t_{2g} basis. It is clear that this very powerful approach captures the dispersions of the Mo t_{2g} orbitals very effectively. The spin splitting of the on-site Mo t_{2g} energies can be directly read off from the diagonal terms of the real space representation of the Hamiltonian matrix [obtained by Fourier transformation of the down-folded Hamiltonian in k space, $H(k) \rightarrow H(R)$] and was found to be 0.8 eV. For fully polarized Mo t_{2g} electrons this is then the *ab initio* estimate of I_{eff}, while taking into account that the LMTO estimate for the magnetization $(N_\uparrow - N_\downarrow = 0.34\mu_B)$ increases the I_{eff} value to ~2.3 eV. This spectacular enhancement of the I_{eff} compared to the bare I of Mo is, in fact, easy to rationalize in terms of the details of the electronic interactions in such a double perovskite system. Within the band structure calculations performed for the nonmagnetic ground state we find the Mo $4d$ states to be located at higher energies compared to the Fe $3d$ states. By fitting the nonmagnetic band structure to a tight-binding model, this energy separation is found to be about 1.4 eV. Considering the ferrimagnetic arrangement of the Fe and Mo sites, the orbital energies are as shown in the left panel of Fig. 3 in the absence of any hopping interaction. The Fe^{3+} site has a larger exchange splitting compared to the crystal field splitting, while the situation is reversed for the Mo site. In the presence of hopping interactions, there is finite coupling between states of the

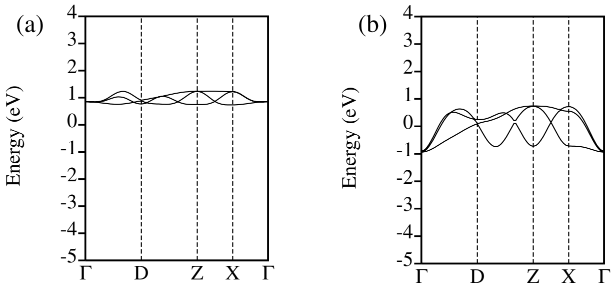

FIG. 2. The dispersions of the bands with t_{2g} symmetry at the Mo site for (a) up spin and (b) down spin. All other degrees of freedom have been integrated out as discussed in the text.

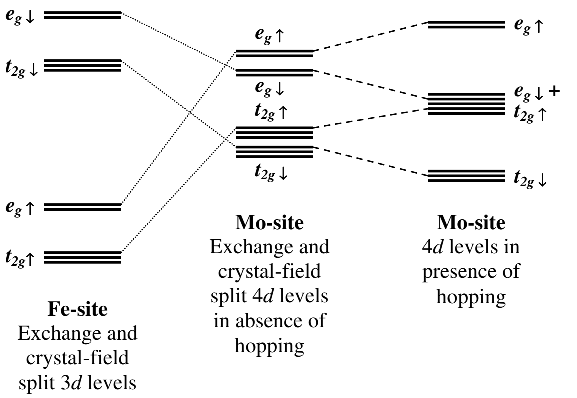

FIG. 3. Energy level diagram expected at the Fe (left panel) and Mo (central panel) sites from an ionic picture. The energy levels at Mo are modified in the presence of Fe-Mo hopping interactions as shown in the right panel.

same symmetry at the Fe and the Mo sites, leading to perturbations of the bare energy levels. It is then easily seen that the Mo $t_{2g_\uparrow}$ state will be pushed up and the Mo $t_{2g_\downarrow}$ state will be pushed farther down by hybridization with the corresponding Fe states, as shown in the figure. These opposite movements of the Mo up and down states increase the energy separation between these two states, thereby substantially increasing the effective exchange splitting at the Mo site. Thus, the renormalization of $I_{\rm eff}$ at the Mo site is driven by the large I at the Fe site and the substantial hopping interaction coupling the two sites. It is interesting to note, and also follows from the arguments given above, that the antiferromagnetic coupling between Fe and Mo is crucial for the enhanced $I_{\rm eff}$, and consequently, the T_c. A ferromagnetic arrangement, on the other hand, would result in a reduced T_c.

The above analysis as well as the estimate of $I_{\rm eff}$ are based on effectively single-particle theories. In order to verify that the present conclusions are not seriously affected by well-known limitations of such theories, we have also used many-body calculations to estimate $I_{\rm eff}$. In order to obtain a realistic description of the specific system, we fixed the hopping interactions between the various orbitals to those estimated from the tight-binding fit of the full *ab initio* calculations. Furthermore, we performed Hartree-Fock calculations for the multiband model for the lattice involving Fe and Mo d and oxygen p states and reproduced the half-metallic ferromagnetic state in order to obtain appropriate estimates for the charge transfer energies, intra-atomic Coulomb and bare exchange strengths. The parameters used are 0.65, 1.34, -2.33, and 1.47 eV for oxygen $pp\sigma$, oxygen-Mo $pd\pi$, oxygen-Fe $pd\sigma$, and $pd\pi$ hopping strengths; $U_{\rm Fe}$, $I_{\rm Fe}$, $U_{\rm Mo}$, $I_{\rm Mo}$, $\Delta_{\rm Fe}$, and $\Delta_{\rm Mo}$ were estimated to be 5.0, 0.8, 1.0, 0.2, 2.8, and 4.0 eV, respectively. Additional crystal field splittings between the t_{2g} and e_g orbitals at the Fe site and the Mo site were introduced.

For calculation of $I_{\rm eff}$, we consider a multiband Hubbard-like Hamiltonian for the finite cluster Fe-O-Mo-O-Fe. The Hamiltonian includes on-site energies, hopping interactions, and the on-site Coulomb interactions at Fe and Mo sites. The full Hilbert space for even such a small cluster has a dimension of $\sim 2 \times 10^9$; since such a large calculation is not tractable, we included the hopping interactions connecting only the transition metal t_{2g} orbitals to the oxygen p_π orbitals. This is a reasonable approximation, as the relevant charge dynamics involves only these orbitals with the e_g orbitals participating in Coulomb interactions. Moreover, we restrict ourselves to the $S_z = 9/2$ subspace in conformity with the experimentally observed antiferromagnetic arrangement of the transition metal moments. The renormalized $I_{\rm eff}$ can be estimated from this cluster by calculating $\delta E/\delta n_\uparrow - \delta E/\delta n_\downarrow$, where E is the total energy and $n_\uparrow$ and $n_\downarrow$ are the corresponding Mo occupancies. For the above set of parameter values, the $I_{\rm eff}$ is calculated to be 0.95 eV with integral charge (i.e., $\delta n = 1$) fluctuations, exhibiting a large enhancement from the bare I of 0.2 eV used in the calculation and in very good agreement with the estimate obtained from the *ab initio* results. Since this estimate depends on the choice of the parameter strengths, we have calculated $I_{\rm eff}$ with reasonable variations of the input parameters; we find that $I_{\rm eff}$ is always between 0.8 and 1.5 eV.

In order to calculate the J, coupling the Fe and the Mo sites antiferromagnetically, we perform Hartree-Fock calculations with the transition metal d-oxygen p multiband model with the parameter values specified earlier. We considered different magnetic ground states corresponding to different values of the spin-density wave vector q. Small rotations of the spin moments about the ground state gave us $J(q)$ [11]. We then mapped the results onto a nearest neighbor Heisenberg model and obtained a value of 18 meV for the coupling between Fe and Mo. A similar analysis [12] for the half-metallic 30% hole-doped $\rm LaMnO_3$ gave us 12.5 meV. Most importantly, we find that the J in $\rm Sr_2FeMoO_6$ is, in fact, somewhat larger than that in the manganites, explaining the enhanced magnetic transition temperature in the ordered double perovskite system compared to the hole doped manganites ($<$300 K). This enhanced value of J is, of course, intimately connected with the strong spin polarization of the Mo d states via the renormalized $I_{\rm eff}$ at the Mo sites.

It is to be noted that the exchange strength $I_{\rm eff}$ at the Mo site is comparable to or larger than the expected value of the direct Coulomb interaction strength, U, at the Mo site. This leads to the intriguing situation that the effective electron-electron repulsion strength, $U_{\rm eff} = U - I_{\rm eff}$, for Mo may become negative. If this were indeed to be true, there should be some measurable consequences in terms of the electronic properties. In order to verify this, we have performed core level x-ray photoemission study of the Mo 3d core level in $\rm Sr_2FeMoO_6$. The core level spectrum is shown in Fig. 4. For comparison, we also show

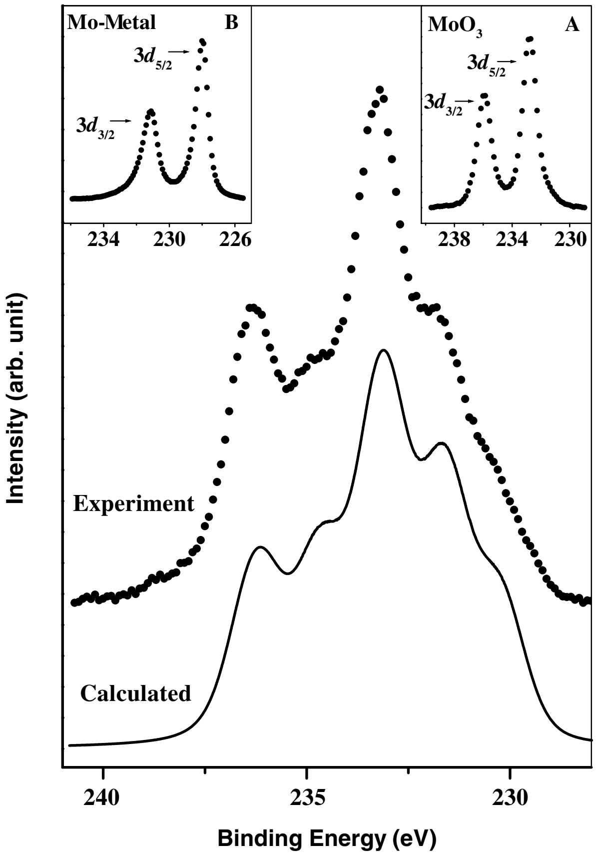

FIG. 4. The experimental (solid circles) and calculated (solid line) Mo 3d core level spectra for Sr$_2$FeMoO$_6$. The experimental spectra (solid circles) for MoO$_3$ and Mo-metal are also shown.

the Mo 3d spectra from two reference materials, Mo metal and MoO$_3$, in the insets 4(a) and 4(b). The insets clearly show that the core level spectra from reference Mo systems contain only a doublet feature arising from the spin-orbit splitting of the core level into 3$d_{5/2}$ and 3$d_{3/2}$ states. In sharp contrast, the Mo 3d spectrum from Sr$_2$FeMoO$_6$ shows multiple features, indicating an unusual electronic state of Mo in this compound. In order to explore whether the multiple feature within the main peak region of Mo 3d spectrum is a consequence of a negative U_{eff}, we have performed a core level calculation considering a cluster with four Mo atoms arranged at the corners of a square. Each atom had four orbitals, with a crystal field splitting of 0.9 eV between a triply degenerate set (t_{2g}-like) and a single e_g-like orbital. Hopping between t_{2g} orbitals was taken to be -0.4 eV, while that between the e_g-like orbitals was taken to be -0.5 eV. U_{eff} was taken to be -0.5 eV. The presence of the core hole was taken into account by a decrease in the on-site energies by the core-hole potential of 0.9 eV [13]. The resulting calculated spectrum is shown in the main figure as a solid line for comparison. The agreement between the experimental and the calculated spectra is remarkably good. It was also found that the calculated spectrum had invariably the simple double peak structure of Mo and MoO$_3$ for any parameter set as long as the U_{eff} was taken to be positive, indicating that the U_{eff} at the Mo sites is indeed negative in this system, driving an electronic phase separation.

Combining *ab initio* and model Hamiltonian calculations, we establish the presence of strongly enhanced I_{eff} and J, responsible for the unusual electronic and magnetic properties of Sr$_2$FeMoO$_6$. The enhanced I results in an effective negative U at the Mo site which results in a complex core level spectrum observed in our photoemission experiments.

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[1] R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).

[2] For a review, see *Collosal Magnetoresistive Oxides,* edited by Y. Tokura (Gordon and Breach, New York, 2000).

[3] C. Zener, Phys. Rev. **82**, 403 (1951).

[4] P.W. Anderson and H. Hasegawa, Phys. Rev. **100**, 67 (1955).

[5] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995); A. J. Millis, B. I. Shraiman, and R. Mueller, Phys. Rev. Lett. **77**, 175 (1996).

[6] K. I. Kobayashi *et al.,* Nature (London) **395**, 677 (1998); H. Asano *et al.,* Appl. Phys. Lett. **74**, 3696 (1999).

[7] Priya Mahadevan, N. Shanthi, and D. D. Sarma, J. Phys. Condens. Matter **9**, 3129 (1997).

[8] O. K. Andersen *et al.,* Phys. Rev. Lett. **53**, 2571 (1984).

[9] Priya Mahadevan, N. Shanthi, and D. D. Sarma, Phys. Rev B **54**, 11 199 (1996).

[10] O. K. Andersen *et al.,* in *Tight-Binding Approach to Computational Materials Science,* edited by L. Colombo, A. Gonis, and P. Turchi, MRS Symposia Proceedings No. 491 (Materials Research Society, Pittsburgh, 1998), pp. 3–34; O. K. Andersen *et al.,* cond-mat/9907064.

[11] S. V. Halilov *et al.,* Phys. Rev. B **58**, 293 (1998); *Quantum Theory of Solids* (John Wiley and Sons, New York, 1963).

[12] Priya Mahadevan, I. V. Solovyev, and K. Terakura, Phys. Rev. B **60**, 11 439 (1999).

[13] Usually the core-hole potential is taken to be 1.2 times U. In the present calculations, we found that varying the core-hole potential in the range 0.8–1.2 eV did not change the calculated spectrum significantly.