

Strong ferromagnetism and weak antiferromagnetism in double perovskites: Sr_2FeMO_6 ($M=\text{Mo}, \text{W},$ and Re)

Z. Fang,¹ K. Terakura,^{2,3} and J. Kanamori⁴

¹JRCAT, Angstrom Technology Partnership, Central 4, 1-1-1 Higashi, Tsukuba, Ibaraki 305-0046, Japan

²JRCAT, National Institute for Advanced Industrial Science and Technology (AIST), Central 4, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan

³Research Institute for Computational Sciences (RICS), AIST, Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-0046, Japan

⁴International Institute for Advanced Studies, 9-3 Kizugawadai, Kizu-cho, Soraku-gun, Kyoto 619-0225, Japan

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Double perovskites Sr_2FeMO_6 ($M=\text{Mo}$ and Re) exhibit significant colossal magnetoresistance even at room temperature due to the high Curie temperatures (419 and 401 K). However, such a high Curie temperature is puzzling, given the large separation between magnetic elements (Fe). Moreover, with $M=\text{W}$, the electronic and magnetic properties suddenly change to insulating and antiferromagnetic with the Néel temperature of only 16~37 K. Based on detailed electronic structure calculations, a mechanism is proposed which stabilizes the strong ferromagnetic state for $M=\text{Mo}$ and Re and is passivated for $M=\text{W}$.

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Intensive studies on the perovskite transition-metal oxides (TMO), particularly manganites, have revealed a variety of phenomena only for half a decade.¹ Among those phenomena, colossal magnetoresistance (CMR) has been attracting strong attention not only as a challenging subject of fundamental science but also as an important phenomenon for potential technological application. With regard to the latter aspect, materials with not only the half-metallic nature but also Curie temperature (T_c) much higher than room temperature is strongly desired in order to realize strong CMR effects at room temperature. It was demonstrated that some of the double perovskite TMO such as $\text{Sr}_2\text{FeMoO}_6$ (SFMO) and $\text{Sr}_2\text{FeReO}_6$ (SFRO) are suitable candidates.^{2,3} They are half metallic according to the band-structure calculations and their T_c 's are 419 and 401 K.

The present work deals with two fundamental problems in these double perovskite TMO by performing detailed electronic structure calculations. In both of SFMO and SFRO, the magnetic moments of Fe are aligned ferromagnetically and the induced moments on Mo and Re are coupled antiferromagnetically to Fe moments. Therefore these materials can be regarded as ferrimagnetic. However, we regard them as ferromagnetic (FM) because Mo and Re are intrinsically nonmagnetic in the sense that their magnetic polarization cannot be sustained spontaneously by the exchange potential on these atoms. Actually their negative moments (i.e., antiparallel to Fe moments) are induced by Fe moments through the $4d(5d)-3d$ hybridization. Now the first fundamental question is why the T_c is so high despite the fact that Fe atoms are very much separated with nonmagnetic elements (Mo, Re) sitting in between. We will point out that a FM stabilization mechanism proposed by Kanamori and Terakura⁴ operates in SFMO and SFRO. The same problem was treated recently also by Sarma *et al.* for SFMO.⁵ The second question concerns the striking difference of Sr_2FeWO_6 (SFWO) from SFMO and SFRO in the electronic and magnetic properties. SFWO is an antiferromagnetic (AF)

insulator and the Néel temperature is only 16~37 K.⁶ Why is the W case so different from the Mo and Re cases despite the fact that W is the $5d$ analogue of Mo and next to Re in the row of the Periodic Table?

We will show that the stronger $2p(\text{O})-5d(\text{W})$ hybridization compared with the $2p(\text{O})-4d(\text{Mo})$ hybridization is the main source of the difference between Mo and W pushing the $5d$ states higher in energy and passivating the FM stabilization mechanism in SFWO. Deeper $5d$ levels in the Re case compared with the W case cancel the effect of enhanced $p-d$ hybridization and restores the FM stabilization mechanism. Note, however, that the standard LSDA (local spin-density approximation) or GGA (generalized gradient approximation)⁷ cannot describe properly the ground state of SFWO. As Fe d states are strongly localized in these systems, the local Coulomb repulsion U_{eff} , which is semiempirically taken into account by the LDA+U method⁸ in the present work, plays crucially important roles.

We adopt the plane-wave pseudopotential method. The $3d$ states of Fe, $4d$ states of Mo, $5d$ states of W and Re, and $2p$ states of O are treated with the ultrasoft pseudopotentials⁹ and the other states by the optimized norm-conserving pseudopotentials.¹⁰ The cut-off energy for describing the wave functions is 30 Ry, while that for the augmentation charge is 200 Ry. The crystal structures of all the three systems are cubic with the nearest Fe- M distance given as 3.945, 3.975, and 3.945 Å for $M=\text{Mo}, \text{W},$ and Re , respectively.^{3,11} For the FM state, the number of \mathbf{k} points used in the \mathbf{k} -space integration is 19 in the irreducible Brillouin zone. For the AF state, two different configurations, AFI and AFII,¹² are considered. In the AFI (AFII) configuration, the magnetic moments are aligned ferromagnetically within the (001) ((111)) plane and alternate along the [001] ([111]) direction. The number of \mathbf{k} points in the AF configuration is chosen to be equivalent to that in the FM configuration. As for the electron-electron interaction, we adopt first the standard GGA (Ref. 7) and then the semiempirical

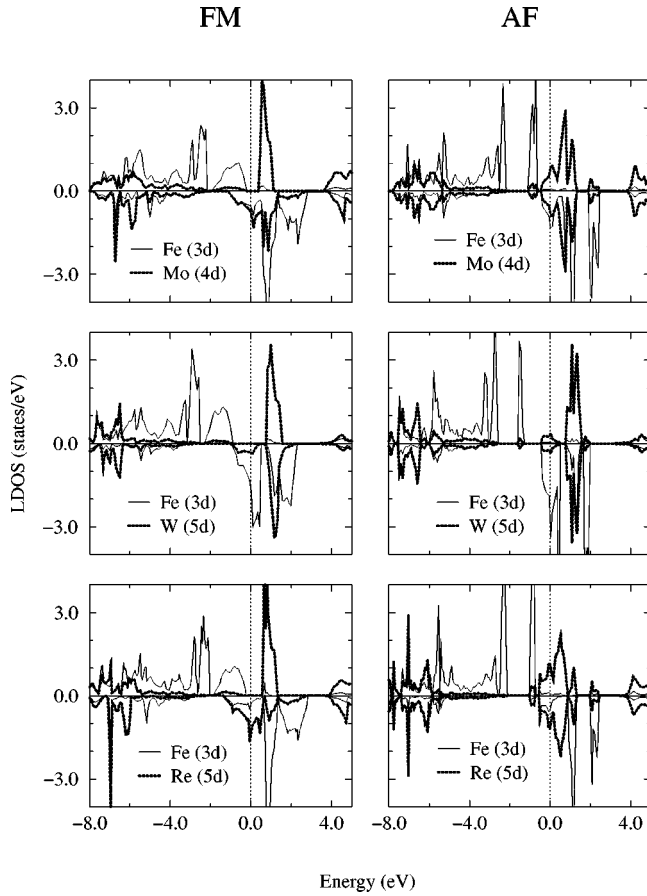


FIG. 1. The calculated local density of states (LDOS) for Sr_2FeMO_6 ($M=\text{Mo}, \text{W}, \text{and Re}$) in GGA. The left (right) panels are for the FM (AFII) states. The energy zero is taken at the Fermi level.

LDA+U method.⁸ The details of the implementation of the LDA+U method in the pseudopotential scheme can be found in our previous publication.¹³

Figure 1 shows a summary of the GGA calculations for three materials Sr_2FeMO_6 with $M=\text{Mo}, \text{W}, \text{and Re}$ in both FM and AF states. (Note that only the results for AFII are shown here for the AF states.) The thin solid lines denote the local density of states (LDOS) for Fe $3d$ orbitals and thick broken lines LDOS for $4d$ (Mo) or $5d$ (W, Re) states. The results for $M=\text{Mo}$ and Re in FM state are basically the same as those shown in the previous works.^{2,3} The oxygen p bands extend from -8 to about -4 eV, the Fe majority spin t_{2g} bands from about -4 to -2 eV, followed by the majority spin e_g bands extending up to near the Fermi level. In the majority spin state, the band just at and above the Fermi level is of t_{2g} character of M . In the minority spin state, t_{2g} states of Fe and M coexist around the Fermi level. The formal valence of the combination of FeM is $+8$, meaning that the number of d electrons per FeM is 6 for $M=\text{Mo}$ and W, and 7 for $M=\text{Re}$. In both FM and AF states, the majority spin bands of Fe are completely filled with five electrons and the minority spin bands accommodate one electron for $M=\text{Mo}$ and W, and two electrons for $M=\text{Re}$. These materials are predicted to be metallic in both FM and AF orders with

TABLE I. For each Sr_2FeMO_6 ($M=\text{Mo}, \text{W}, \text{and Re}$), the first row shows the total energies per Fe (in meV), and the second and the third rows list the magnetic moments (in μ_B) of Fe and M , respectively. Both the GGA and the LDA+U ($U_{\text{eff}}=4.0$ eV) results are given. The number in the bracket for $M=\text{W}$ is the total energy for the AFII state.

	GGA		LDA+U	
	FM	AFII	FM	AFII
$M=\text{Mo}$	0	84	0	58
	3.73	3.68	3.97	3.96
	-0.30	0	-0.39	0
	0	64 (145)	0	-30
$M=\text{W}$	3.65	3.63	3.87	3.68
	-0.14	0	-0.22	0
	0	103	0	52
$M=\text{Re}$	3.70	3.63	3.95	3.91
	-0.78	0	-0.86	0

GGA calculations. Particularly, they are half metallic in the FM order and this half metallicity is preserved even in the LDA+U calculation as shown later. In Table I, the total energies for AF states with reference to those for FM states are given for the three materials. The calculation for the AFII state for $M=\text{W}$ suggests that this magnetic order may have no chance of being realized in these materials. Therefore the AFII order will not be considered hereafter. Clearly, the FM state is significantly more stable than the AFII state in the GGA calculations for all three systems. The results in GGA are qualitatively consistent with experimental facts for SFMO and SFRO but inconsistent for SFWO, which is antiferromagnetic and insulating experimentally.⁶ Deferring the discussion on the stability of ferromagnetism for SFMO and SFRO for a while, we first discuss the problems of SFWO and how to solve them.

The LDOS for the AF state of SFWO has a very sharp peak of the Fe t_{2g} state origin just at the Fermi level. This suggests that the AFII state obtained in this stage may be unstable. Although the symmetry in the AFII state is reduced to D_{3d} , lift of degeneracy in t_{2g} orbitals is not strong enough to split the t_{2g} band. The situation is quite similar to FeO.¹⁴ In this case, the lattice is elongated along $\langle 111 \rangle$ direction (even with the GGA level treatment) and furthermore the local Coulomb repulsion (U_{eff}) strongly enhances the orbital polarization making the system insulating. On the analogy of FeO, we first studied effects of rhombohedral distortion of SFWO in GGA and found that such distortion either elongation or contraction along $\langle 111 \rangle$ direction simply increases the total energy. The cubic lattice for SFWO even in the AFII state is actually observed experimentally. As these analyses suggest that there is little chance of stabilizing the AF state for SFWO with the GGA level calculation, we applied the LDA+U method to these materials. Although the LDA+U method is semiempirical, it still provides us with some important insights into the problems. We set U_{eff} to be 4 eV and applied it only to the Fe d orbitals for the sake of simplicity. As was described in our previous paper, U_{eff} is nonzero in a rather limited region around the Fe nucleus and its actual

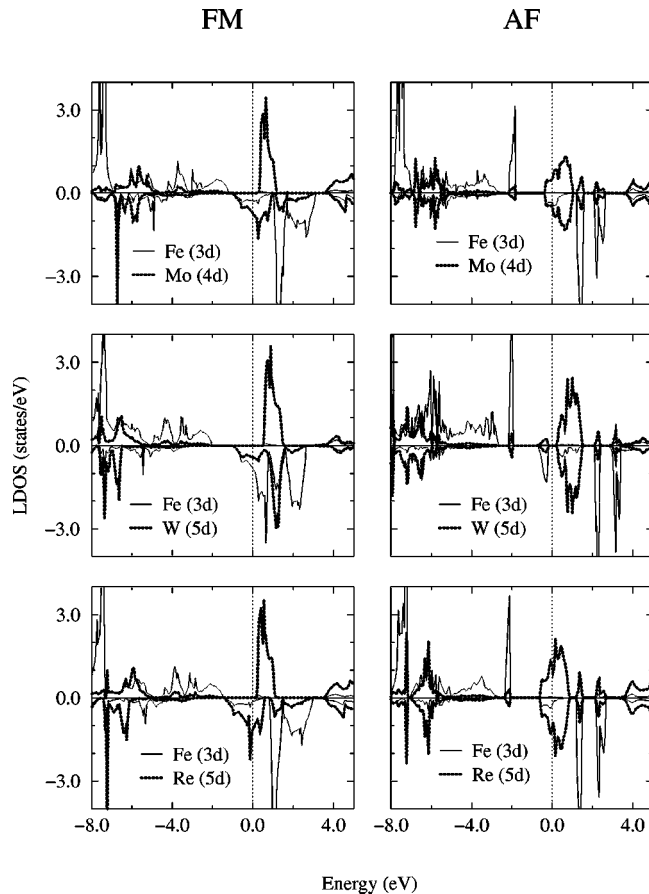


FIG. 2. The LDA+U version of Fig. 1.

value does not have definite meaning.¹³

Figure 2 shows the LDA+U version of Fig. 1, and Table I includes the corresponding total energies. The common characteristic feature in Fig. 2 is the enhancement in the exchange splitting of Fe. Nevertheless, the electronic structure remains qualitatively the same for SFMO and SFRO in both FM and AF states except the fact that the weight of Mo and Re d states increased significantly around the Fermi level. On the other hand, in SFWO, while the change in the FM state is minor, the AF state shows a dramatic change from Fig. 1 to Fig. 2. The t_{2g} band of Fe splits due to orbital polarization induced by U_{eff} and the occupied state in the minority spin state just below the Fermi level is of a_{1g} character. A band gap opens up and the AFII state becomes more stable than the FM state. The insulating nature of the ground state of SFWO is now correctly reproduced.¹⁵ The fact that the Néel temperature is only 16~37 K may suggest that the stabilization of the AFII state in the present calculation may be overestimated. However, the quantitative aspect can be tuned by U_{eff} .

Having shown the calculated results which are qualitatively consistent with experimental facts, we start discussions on the underlying mechanisms in relation to the two fundamental questions raised at the beginning of the present paper. The first one concerns the mechanism of the strong stabilization of the FM state for SFMO and SFRO. Recently Sarma *et al.* proposed an interesting explanation to the origin

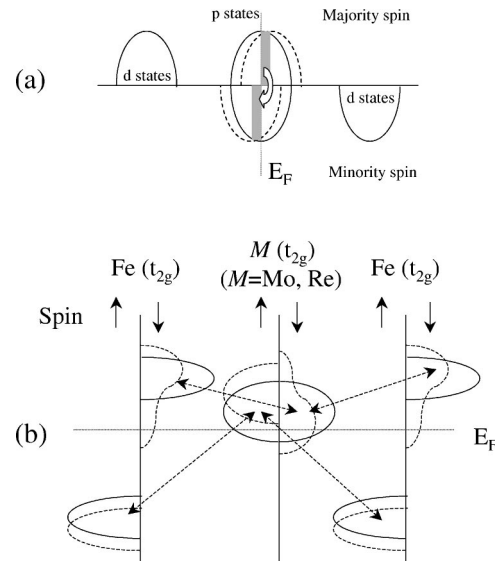


FIG. 3. A schematic illustration of a mechanism to stabilize the ferromagnetic state. The panel (a) demonstrates a typical case for the Kanamori and Terakura mechanisms, while (b) shows the case of Sr_2FeMO_6 ($M=\text{Mo}$ and Re). The hybridization paths are indicated by dashed lines with arrows. The solid (dashed) curves denote the bands without (with) hybridization.

of strong AF coupling between Fe and Mo in which they pointed out strong effective exchange enhancement at Mo due to the $3d(\text{Fe})\text{--}4d(\text{Mo})$ hybridization. Kanamori and Terakura⁴ proposed a more general idea for the mechanism where a nonmagnetic typical element located at the midpoint of neighboring high-spin $3d$ elements contributes to stabilization of the FM coupling of the $3d$ elements. Figure 3(a) is a schematic illustration explaining the mechanism. The states of the typical element located in between the majority and minority spin states of $3d$ elements are tentatively called p states. The key concept in this mechanism is the energy gain contributed by the negative spin polarization of the nonmagnetic element induced by the $p\text{--}d$ hybridization. Such spin polarization does not exist in the AF configuration and therefore there is no energy gain due to the spin-state relaxation at the typical element. In the present problem, the $4d$ states of Mo and $5d$ states of W and Re correspond to the p states in Fig. 3(a). The analogy is obvious in the majority spin state in the FM order. In the minority spin state, as the $4d$ (or $5d$) bands and the $3d$ bands are not well separated and the Fermi level lies in the $3d$ bands after including the hybridization, we need a careful analysis to distinguish the FM stabilization mechanism discussed above and the double exchange (DE).¹⁶ Figure 3(b) illustrates the situation corresponding to SFMO and SFRO where the $M t_{2g}$ bands are slightly below the Fe ones. We first treat the up and down spin states separately and then consider the electron transfer between two spin states. The standard DE mechanism takes account of the processes only in the first step. As for the hybridization between M ($=\text{Mo}$, W , Re) bands and the majority spin Fe bands, the total energy change caused by band shift due to the $3d\text{--}4d(5d)$ hybridization does not depend on the relative spin direction between the neighboring Fe atoms up to

the second order in the hybridization matrix element t . For example, the upward shift of the up spin M bands by $2t^2/\Delta$ in the FM state balances the upward shift of the both spin M bands by t^2/Δ in the AF state where Δ denotes the energy separation. Subtle features exist in the minority spin state. Not only the band shift but also band broadening have to be considered. It is obvious that the width of the minority spin bands will be wider in the FM state than in the AF state. As the Fermi level lies in the minority spin bands, the band broadening contributes to the stability of the FM state, like in the standard DE.¹⁷ In the present problem, we have an additional effect in the FM state coming from the electron transfer just like in Fig. 3(a). This electron transfer produces negative spin polarization at M atoms and contributes to further stabilization of the FM state. In contrast to SFMO and SFRO, the M t_{2g} bands in SFWO are slightly above the Fe ones. In this case, the M t_{2g} bands are basically empty and the electron transfer will not occur. Therefore the FM-stabilization mechanism of Fig. 3(a) is passivated for SFWO, while the DE mechanism may still be effective. Although Table I still shows small negative spin polarization at the W atom, this is due to the stronger $5d-3d$ hybridization in the minority spin state than in the majority spin state. We also speculate that the main reason of considerable relative stability of the FM order for SFWO in the GGA calculation is the rather unstable electronic configuration in the AFII order. Because of this, a change in the electronic structure in the AFII state from GGA to LDA+U reduces the energy of the AFII state dramatically.

The second question concerns the origin of the different behavior of W from other two elements Mo and Re. It is clear from the above arguments that in order to answer this question, we have to clarify the origin of the difference in the energy position of the minority spin t_{2g} bands. We assign the $p-d$ hybridization between oxygen and M to the main source of this difference. As the $5d$ orbital of W is more extended than the $4d$ orbital of Mo, the stronger $2p(\text{O})-5d(\text{W})$ hybridization pushes the $5d$ band, which is the $p-d$ antibonding state, higher in energy. This mechanism is supported by the fact that the $p-d$ bonding counter part is clearly deeper for SFWO than for SFMO (see Figs. 1 and 2). As Re has deeper $5d$ level than W to accommodate one more d electron, the energy scheme for SFRO becomes similar to that for SFMO.

In summary, we showed that the electronic structures and magnetic ordering in the ground state of Sr_2FeMO_6 ($M = \text{Mo}, \text{W}, \text{and Re}$) are properly reproduced by the LDA+U method. A mechanism was proposed to explain the high Curie temperature for $M = \text{Mo}$ and Re cases. An explanation was also given to the sudden changes in the electronic and magnetic properties in the $M = \text{W}$ case. The mechanism proposed by us⁴ is very useful to predict qualitatively the change in the magnetic states by changing constituent elements.

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