Antiferromagnetic metal phases in double perovskites having strong antisite defect concentrations

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Recently an antiferromagnetic metal phase has been proposed in double perovskites materials like Sr$_2$FeMoO$_6$ (SFMO), when electron doped. This material has been found to change from half-metallic ferromagnet to antiferromagnetic metal (AFM) upon La-overdoping. The original proposition of such an AFM phase was made for clean samples, but the experimental realization of La-overdoped SFMO has been found to contain a substantial fraction of antisite defects. A phase segregation into alternate Fe and Mo rich regions was observed. In this paper we propose a possible scenario in which this type of strong antisite concentration can still result in an antiferromagnetic metal phase, by a novel hopping driven mechanism. Using variational calculations, we find that proliferation of such phase segregated domain regions can also result in the stabilization of an A-type AFM over the G-type AFM based on kinetic energy considerations.

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I. INTRODUCTION

Double perovskites, with the general formula $A_2BB'O_6$, $A=$ alkaline/rare-earth metals and $B/B'$=transition metals, are being studied extensively in recent years due to their half-metallic properties, and their importance in spintronic applications. A prominent member, Sr$_2$FeMoO$_6$, is ferromagnetic in the pure state with a $T_c$ as high as 410K. Substantial tunnelling magnetoresistance is also obtained in powdered samples of these compounds at low temperatures. There is a kind of defect which is possible in double perovskite materials called antisite defects in which a B-atom (Fe) and a B' atom (Mo) can interchange position, thereby bringing two B (Fe) atoms next to each other. Such defect regions tend to be antiferromagnetic and insulating, and decrease the overall magnetization. While tunneling across grain boundaries, rather than antisite regions dominates as the main mechanism for magnetoresistance, the magnitude of the magnetoresistance does get affected quite dramatically by the antisite defect concentration. Attempts have been made to electron dope this compound (SFMO) hoping to enhance the $T_c$ and hence the polarization at room temperature and thereby improve the magnetoresistance. While a slight increase in $T_c$ is indeed observed for low doping, but for overdoping ($x > 1$), the $T_c$ is found to decrease, as shown in $[1,2]$, and the ferromagnetism gets replaced by antiferromagnetic phases. These antiferromagnetic phases are however, metallic, and are stabilized over the ferromagnetic phase due to a kinetic energy-driven mechanism. This was derived using a model Hamiltonian in the clean limit without antisite defects, using analytical as well as numerical methods. Further confirmation was obtained using abinitio methods, by considering the Sr$_{2-x}$La$_x$FeMoO$_6$ series, for the overdoped case ($x > 1$). In the actual experimental preparation of this proposed series of materials, however, substantial concentration of antisite defects was found to be present. In fact, a microscopic phase segregation situation was encountered, where the sample phase segregated into alternate Fe-rich and Mo-rich regions, forming a patchy structure. In this paper, using a variational approach, we reconsider the stability of magnetic phases in presence of antisite defects, and in particular in the phase segregation scenario where alternate Fe-rich and Mo-rich regions are present. We find that antiferromagnetic metal phases are still stabilized kinetically for large regions of filling. The exact nature of the kinetically stabilized antiferromagnetic phase, however, changes from the clean limit to the alternate Fe-Mo rich phase segregated scenario. We confirm this change using numerical simulations based on exact diagonalization, where phase segregated Fe-Mo domains are allowed to proliferate over an otherwise clean sample. Our results are in consonance with those of an earlier study in presence of antisite defects using a different method, where it was found that antiferromagnetic phases do survive even in presence of antisite disorder. Although they considered correlated antisite disorder, they did not consider alternate Fe-Mo rich regions or phase segregation. We have obtained analytical results in the phase segregated limit, using a variational approach. The organization of the paper is as follows. In the next section, we shall briefly summarize the experimental results for the Sr$_{2-x}$La$_x$FeMoO$_6$ series (i.e., cation site substitution), and the role of antisite defects. Next, we discuss a Hamiltonian suitable for analyzing this problem including antisite defects. Then we proceed to a generic situation where Fe-rich and Mo-rich segments, using analytical variational methods. Then we proceed to consider a generic situation where Fe-rich and Mo-rich segments, using analytical variational methods. Then we consider the results. First we consider a fully phase segregated situation with alternate Fe-rich and Mo-rich segments, using analytical variational methods. Then we proceed to consider a generic situation where Fe-rich and Mo-rich segments, using analytical variational methods. Then we consider the results. First we consider a fully phase segregated situation with alternate Fe-rich and Mo-rich segments, using analytical variational methods. Then we proceed to consider a generic situation where Fe-rich and Mo-rich segments, using analytical variational methods. Then we consider the results. First we consider a fully phase segregated situation with alternate Fe-rich and Mo-rich segments, using analytical variational methods. 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II. EXPERIMENTAL DATA ON LA-DOPED SFMO: BRIEF SUMMARY

Experimental attempts at electron doping Sr2FeMoO6 by substituting Sr2+ with La3+ had been ongoing for a while. This results in the series of compounds Sr2−xLa2FeMoO6. While some of these authors have reported that the samples retained tetragonal symmetry (I4/mmm) upon electron doping from x=0 all the way up to x=1, others report a change to monoclinic symmetry (P21/n) upon doping beyond x=0.4. However, all the authors consent on the fact that the cell parameters increase upon doping, and the antisite defect concentration increases, thereby reducing the degree and extent of ordering. This can be understood by considering the behaviour of the saturation magnetization, and comparing with abinitio calculations. Such calculations indicate that the half-metallic behaviour persists from Sr2FeMoO6 till SrLaFeMoO6 (LSFMO), and the total moment changes from 4μB/f.u. to 3μB/f.u., i.e., a reduction in moment by 1μB/f.u. by doping with x=1, in the clean limit. This is due to the fact that a replacement of Sr2+ ion by La3+ ion due to La-doping results in the addition of an electron into the cell, and since LSFMO is half-metallic, the extra electron goes into the minority spin band, reducing the moment by exactly 1μB. The experimental reduction, on the other hand, is by 2μB/f.u., for example, clearly indicating the increase in concentration of antisite defects, along with the electron doping effect. Such increase in antisite defect concentration has been confirmed in almost all the studies, even leading to a concentration level of 0.5 in some cases for x > 0.8, where a phase separation scenario is possible.

Recently, there has been a study of La-overdoping of Sr2FeMoO6, where the regime above x > 1 is investigated. As before, increase in antisite disorder with increasing doping is observed. However, the sample is found to phase segregate into alternate Sr,Mo-rich and La,Fe-rich short range patches, which is confirmed by X-ray spectra analysis. The number of Mo-O-Mo connections, which should be 0 for a perfectly ordered arrangement, 3 for a random situation, and 6 for a phase segregation scenario, was found to be more than 3, while the samples crystallized to a space group of P21/n, indicating a patchy structure as mentioned before. Interestingly, even with this heavy concentration of antisite disorder, the samples remained metallic, although there was a transition from ferromagnetic to antiferromagnetic phase, as evidenced from magnetization hysteresis data. Thus, a rare antiferromagnetic metallic phase appears to be stabilized for an overdoped, phase-segregated sample of SFMO. In this paper we provide a plausible explanation to such a situation using model Hamiltonian methods. While a crossover from ferromagnetic metal phase to an antiferromagnetic metal phase has already been predicted in the clean limit without antisites, in this paper we consider the case with antisite defects, in particular a phase segregation scenario, and justify how this crossover can continue to hold even in this scenario.

III. HAMILTONIAN

A Hamiltonian suitable for considering general Fe-Mo configurations with antisite defects can be obtained in the following way, by considering a local binary variable ηi which is 1 or 0 depending on whether the site is Fe or Mo:

\[ H = \epsilon_{Fe} \sum_{i,\sigma} \eta_i f_i^{\dagger}_\sigma f_i^\sigma + \epsilon_{Mo} \sum_{i,\sigma} (1 - \eta_i) m_i^{\dagger} m_i^\sigma + t_{FF} \sum_{<ij>,\sigma} \eta_i \eta_j f_i^{\dagger}_\sigma f_j^\sigma + t_{MM} \sum_{<ij>,\sigma} (1 - \eta_i)(1 - \eta_j) m_i^{\dagger} m_j^\sigma + t_{FM} \sum_{<ij>,\sigma} (\eta_i + \eta_j - 2\eta_i \eta_j) f_i^{\dagger}_\sigma f_j^\sigma \eta_j f_i^\sigma + J_{AF} \sum_{<ij>} \eta_i \eta_j S_i \cdot S_j \]  

(1)

The f’s refer to the Fe sites and the m’s to the Mo sites. t_{FM}, t_{MM}, t_{FF} represent the nearest neighbor Fe-Mo, Mo-Mo and Fe-Fe hoppings respectively. σ is the spin index. The difference between the ionic levels, ∆ = ε_{Fe} - ε_{Mo}, defines the charge transfer energy. The S_i are ‘classical’ (large S) core spins at the B site, coupled to the itinerant B electrons through a coupling J >> t_{FM}. Each \{η_i\} realization corresponds to a configuration of antisite disorder; in particular, the ordered configuration (without antisite defects) corresponds to a checkerboard, or [π, π] configuration of η_i on a 2D lattice. The model then coincides with the two-sublattice Kondo lattice model which has been considered by several authors in the context of ordered double perovskites. If one considers the limit J → ∞, then the model given by Eq (1) simplifies to a model with “spinless” Fe degrees of freedom:

\[ H = t_{FM} \sum_{<ij>,\sigma} \eta_i \eta_j f_i^\dagger f_j + \epsilon_{Fe} \sum_{i,\sigma} \eta_i \eta_j f_i^{\dagger} f_i^\sigma \eta_j f_i^\sigma + \epsilon_{Mo} \sum_{i,\sigma} (1 - \eta_i) m_i^{\dagger} m_i^\sigma + J_{AF} \sum_{<ij>} \eta_i \eta_j S_i \cdot S_j \]  

(2)
In the ordered case, this model has been studied as a function of filling of the Fe and Mo degrees of freedom, using various analytical and numerical methods\(^\text{13}\). It was found that while a ferromagnetic phase was stable for low fillings \( n < 1 \), it became unstable to antiferromagnetic phases for larger filling \( n > 1 \). There appeared to be two main types of antiferromagnetic phases: A type (\( 0 - \pi \)) or AFM1, and G type (\( \pi - \pi \)) phases, or AFM2. A schematic of these three phases are shown in Fig 1.

IV. ALTERNATE PHASE SEGREGATED CASE

Samples of La-overdoped SFMO are found to order in a patchy structure\(^\text{15}\) where phase segregation occurs into alternate Fe-rich and Mo-rich regions. This leads to a substantial amount of antisite defects. The simplest model for this situation can be considered in 2D as follows. Let us consider strips of Fe and Mo atoms arranged alternately as shown in Fig 2 or in the bottom panel of Fig 4. This would mean alternate lines of antisite defects separated from each other by patches where Fe and Mo are nearest neighbour. Such a patchy structure can be used to effectively describe the samples of Sr\(_{2-x}\)La\(_x\)FeMoO\(_6\). This configuration can be thought to be realized from an ordered checkerboard configuration of Fe, Mo by proliferation of domain line-defects of Fe and Mo combined. Accordingly, the ferromagnetic, A type antiferromagnet and G type antiferromagnet can be realized in the the form shown in Fig 2. In this case, the dispersions in the three phases can be calculated as follows. In the fully ferromagnetic case, the dispersion is given by:

\[
\epsilon_k = \left[ \epsilon_{Fe} + \epsilon_{Mo} + 2(t_{FF} + t_{MM})\cos ky \right] \pm \sqrt{[(\epsilon_{Fe} + 2t_{FF}\cos ky) - (\epsilon_{Mo} + 2t_{MM}\cos ky)]^2 + 16t_{FM}^2\cos^2kx} \tag{3}
\]
If we put $t_{FF} = t_{MM} = 0$, then

$$
\epsilon_k = \frac{(\epsilon_F + \epsilon_M) \pm \sqrt{(\epsilon_F - \epsilon_M)^2 + 16t_{FM}^2 \cos^2 kx}}{2}$$

(4)

which is just the band structure of a 1D binary lattice, appropriate for the isolated Fe-Mo alternating chains in the x-direction (to the right). If $\epsilon_F = \epsilon_M = 0$, then $\epsilon_k = \pm 2t_{FM} \cos kx$, revealing the 1D character. If we put $t_{FM} = 0$, then we get, for $\epsilon_F = \epsilon_M = 0$, $\epsilon^\pm_k = 2t_{FF} \cos kx$ and $\epsilon^\mp_k = 2t_{MM} \cos kx$, once again 1D band structures, this time in the y direction, as expected.

For the antiferromagnetic cases, the dispersions are obtained in the following manner. For the A-type antiferromagnet, there are alternate ferromagnetic chains arranged antiferromagnetically. This can be obtained in the phase segregated limit by considering the fact that in the ordered phase (as shown in the central panel of Fig [1]), the up and down spins alternate on the Fe sites on any line along the x-direction, separated by an Mo site. Since this structure is preserved by a Fe-Mo line domain shift in the x-direction, the resulting phase is as shown in the central panel of Fig [2]. The dispersion is given by $\epsilon_k = \epsilon_M + 2t_{MM} \cos kx$ and

$$
\epsilon_k = \frac{[\epsilon_F + \epsilon_M + 2(t_{FF} + t_{MM}) \cos kx] \pm \sqrt{[(\epsilon_F + 2t_{FF} \cos kx) - (\epsilon_M + 2t_{MM} \cos kx)]^2 + 4t_{FM}^2}}{2}$$

(5)

If we consider $t_{FF} = t_{MM} = 0$, and $\epsilon_F = \epsilon_M = 0$, then the dispersion simplifies to just three possible values: 0, $\pm \sqrt{2t_{FM}}$ appropriate for a tratomic molecule, as expected for an Mo-Fe-Mo trimer. If $t_{FM} = 0$, then it gives the 1D dispersions $\epsilon_F + 2t_{FF} \cos kx$ and $\epsilon_M + 2t_{MM} \cos kx$, corresponding to 1D Fe chains and Mo chains in the y-direction, as expected.

The G-type antiferromagnet, which corresponds to the $\pi - \pi$ antiferromagnet for the ordered lattice, can be realized in this antisite disordered case by considering the fact that along a line in the x-direction, in the ordered phase, the Iron spins all remain parallel (see right panel of Fig [1]). Since this is once again preserved during a Fe-Mo line domain shift in the x-direction, hence the spin configuration that is realized is as shown in the right panel of Fig [2]. Here the Iron spins are parallel along the x-direction, while they alternate antiparallel along the y-direction. In this case, the dispersion is obtained as the roots of a cubic equation:

$$(\epsilon_F - \epsilon_k)(\epsilon_M - \epsilon_k)^2 - (\epsilon_F - \epsilon_k)t_{MM}^2(2 + 2 \cos^2 kx) - t_{FM}(2 + 2 \cos kx)(\epsilon_M - \epsilon_k) = 0$$

(6)

The limits can be obtained exactly. For example if $t_{MM} = 0$, $\epsilon_k = \epsilon_M$ (the isolated Mo level) and

$$
\epsilon_k = \frac{(\epsilon_F + \epsilon_M) \pm \sqrt{(\epsilon_F - \epsilon_M)^2 + 16t_{FM}^2 \cos^2 kx/2}}{2}
$$

(7)

If we put $\epsilon_F = \epsilon_M = 0$, this emerges as a 1D band structure $\epsilon_k = \pm 2t_{FM} \cos kx/2$, as the structure reduces to isolated binary Fe-Mo chains in the x-direction. If, on the other hand, we put $t_{FM} = 0$, then the band structure reduces to $\epsilon_k = \epsilon_F$, the isolated Fe level, and the 1D bands $\epsilon_k = \epsilon_M \pm 2t_{MM} \cos kx/2$ in the y-direction, as expected.

V. RESULTS

The DOS for the three phases (ferro, A-type AFM, G-type AFM) as a function of energy are presented in Fig [3].
potential where there is a gap in the DOS, arising from the charge transfer energy $\Delta = \epsilon_{Fe} - \epsilon_{Mo}$, which we have deliberately considered to be finite. This small portion of filling would represent the only insulating behaviour. The dominant region of filling, for large enough filling, continues to be antiferromagnetic metallic, thereby underlining that the same kinetic energy driven mechanism which works for the ordered phase continues to stabilize this AFM phase even in the presence of antisite defects, in a phase segregated scenario.

Interestingly, though, the remnant of the G-type antiferromagnet, most stable for large filling in the ordered phase, is not found to be stabilized kinetically in any part of the filling in this phase segregated case.

In order to investigate how the kinetic energy driven stabilization behaviour changes from the ordered phase to the phase segregated phase with antisite defects, we have also considered intermediate phases with a combined Fe-Mo domain structure which is linear in the y direction (Fig 4). Using Exact Diagonalization calculations in real space, we have obtained the energies of the three phases, variationally, as a function of filling. Parameters used are $t_{FM} = 1, t_{MM} = 0.75, t_{FF} = 0.5$ and $\Delta = 0.5$. We considered intermediate configurations with 2, 4, 6 and 8 domains in a $16 \times 16$ lattice. This symbolizes propagation of the linear domains in the x direction. It is observed (Fig 5) that the antiferromagnetic phases slowly interchange their stability behaviour as the domains propagate through the lattice. There is a smooth transition from stabilization of the G-type phase in the low domain case to the stabilization of the A-type phase in the case with large number of domains. Thus a smooth interpolation is obtained from the ordered phase to the phase segregated phase, proving the scenario proposed earlier, and showing the continued kinetic energy induced stabilization of an antiferromagnetic metal phase for large filling; only the character of the antiferromagnetic phase changes. Although the G type phase is no longer stabilized kinetically, the superexchange, being nearest neighbour for the phase segregated case, and antiferromagnetic, can stabilize it, and bring its energy close to that of the A-type phase, even possibly surpassing it at some filling. Such a scenario can however, occur only for a small region of filling, as the G-type phase has the lowest bandwidth. Even then, the ground state continues to be an antiferromagnetic metal at high filling; either A type or G type, depending in the filling. It is interesting to note that even from kinetic energy considerations, the energy difference between the ferro and the ground state antiferromagnetic phase is much larger for the ordered case rather than in the phase segregated limit, as can be understood by comparing the figures for 2 domains and 8 domains. This can provide a plausible explanation to the signature of phase coexistence observed in the actual experiment using the phase segregated samples.

**VI. SUMMARY AND OUTLOOK**

We have considered the simplest model of phase segregation of B-site (Fe) and B′ site (Mo) in double perovskite Sr$_2$FeMoO$_6$, leading to antisite regions. Using variational
Figure 5: Energy vs filling for the three phases, compared for configurations with 2, 4, 6 and 8 domain Fe-Mo antisite defects.

methods, we have shown that an antiferromagnetic metal phase can still be stabilized in large regions of filling. The nature of the antiferromagnetic phase that is kinetically stabilized, is however, found to change as the system goes from ordered to phase segregated. Using extensive simulations in the intermediate phases involving antisite domains, we have verified that this transition is smooth, and the system remains an antiferromagnetic metal throughout for large regions of the filling, only the nature of the antiferromagnet changes from the ordered to the phase segregated limit.

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