

Finding Universal Correlations between Cationic Disorder and Low Field Magnetoresistance in FeMo Double Perovskite Series

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We search for general patterns that explain the low field magnetoresistance at low temperatures in the system $A_{(2-x)}A'_x\text{FeMoO}_6$. The observed linear dependence of the low field magnetoresistance with the saturation magnetization for the series is related to the antisite disorder at the Fe and Mo sites. This is explained in terms of a spin dependent crossing of intragranular barriers originated from the presence of antiferromagnetic SrFeO_3 patches that naturally develop when antisite disorder occurs in the double perovskite. The presence of a moderate level of antisite disorder is at the very root of low field magnetoresistance although effects such as disorder distribution, connectivity, or morphology add their contribution.

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The role of half metals in the building up of the new art of magnetoelectronics is now well established [1]. Within this approach to electronics, electron transport is spin polarized and, therefore, can be achieved when an unbalance of the spin populations occurs at the Fermi level. A natural realization of such a system has been shown to be the double perovskite $\text{Sr}_2\text{FeMoO}_6$, for which the predicted and measured polarization of the conduction electrons is complete [2]. The majority spin band is gapped and the corresponding $3d^5$ spin up electrons localize in the Fe^{3+} ions while the conduction band is partially occupied by the $4d^1$ down spin electrons of Mo^{5+} ions. A large antiferromagnetic superexchange interaction between the $S = 5/2$ spins of Fe^{3+} and the $S = 1/2$ spins of Mo^{5+} induces a ferrimagnetic half metallic state with a large saturation moment of $4\mu_B$. The perfect alternating order of Fe and Mo ions in the octahedral sites promotes the equilibrium reaction $\text{Fe(III)} + \text{Mo(V)} = \text{Fe(II)} + \text{Mo(VI)}$ in which the itinerant minority spin electron is shared by both types of atoms. Since almost full polarization is reached well above room temperature, $\text{Sr}_2\text{FeMoO}_6$ is a promising fruitful system from an applied point of view.

Recently, the magnetotransport properties of this perovskite have been exhaustively re-examined in view of their potential applications in magnetic recording devices, for which large magnetoresistance at low fields is desirable. Tomioka *et al.* [3], from their measurements on a single crystal, confirm its half metallic and ferrimagnetic nature and proved the extrinsic origin of the magnetoresistance observed in polycrystalline samples [2,4]. Yin *et al.* [5], studying a $\text{Sr}_2\text{FeMoO}_6$ epitaxial film grown on a bicrystal boundary, further proposed that the low field magnetoresistance (LFMR) is due to electron spin dependent transfer across grain boundaries and not to an intragranular effect. The effect of grain boundaries on the LFMR of $\text{Ba}_2\text{FeMoO}_6$ has also been explored by Maignan *et al.* [6] and was found to increase with the degradation of the grain surfaces upon annealing. Grain size effects have been correlated to the observed enhancement of

the LFMR [7] when decreasing grain size into the nanometric scale.

One of the puzzling facts about these materials is the wide dispersion of values for the saturated magnetization for $\text{Sr}_2\text{FeMoO}_6$ samples reported in the literature. Ogale *et al.* [8] investigated this fact and explained the observed differences in terms of the various levels of antisite disorder at the Fe and Mo sites for the different samples. According to Sarma *et al.* [9], this antisite disorder would be related to the LFMR in such a way that the less disordered samples would exhibit higher LFMR ratios.

At this point it will therefore be apparent that the origin of an enhanced LFMR for some FeMo double perovskite samples is still controversial since effects as disparate as grain size, degraded surfaces, or cation ordering are invoked so as to explain the measured quantities. It is the purpose of the present Letter to clarify the current debate: aiming at concluding with a general pattern to explain the LFMR in these systems, we have explored a broad set of samples sharing only the common feature of being FeMo double perovskites. To do so we have covered a broad range of chemical compositions by exchanging the alkaline earth atoms A in the general formula $A_2\text{FeMoO}_6$ and by doping with an aliovalent cation such as La, ($A_{2-x}\text{La}_x\text{FeMoO}_6$). In addition, we have used different synthesis routes leading to different degrees of cationic antisite disorder, as well as morphologies for the same nominal compositions. Regarding the synthesis of our polycrystalline samples we have devised two routes. In both cases we start the reaction by the controlled reduction of previously decomposed citrate precursors as described in Ref. [10]. This step is the final one in the case of $\text{Ca}_2\text{FeMoO}_6$ and SrCaFeMoO_6 (rendering Fe/Mo ordering around 90%) and may be followed by a hot pressing stage under 20 kbar (hot press route) for the rest of the compounds, thus increasing their Fe/Mo ordering from 15% up to values near 93%. For our purpose, powder x-ray diffraction profiles can be interpreted within a cubic symmetry frame ($a = 8 \text{ \AA}$) in samples prepared following

either route. We have evaluated the antisite disorder by analyzing the intensity of the (111) superstructure peak in the x-ray diffractograms, and our results for this magnitude are consistent with our measurements of the saturated magnetization M_s following the link established both by Monte Carlo simulation [8] and experimentally [11]. X-ray diffraction and magnetization data evidence that doping with La seems to hamper the alternating ordering of the Fe and Mo sublattices, even if a high external pressure is applied during the synthesis.

A SQUID magnetometer was used for magnetization versus temperature measurements under a static field of 0.1 T. We also recorded the hysteresis cycles at 5 K so as to determine the saturated magnetic moment. Figure 1 shows the magnitude $(M/M_s)^2$ at a temperature of 5 K for a set of representative samples. As it can readily be seen, some degree of magnetic frustration is present in all the samples, even for those with the highest M_s . In the ensuing discussion we shall propose this frustration to be related to the antisite disorder and to be primarily localized in the surroundings of the antiferromagnetic (AF) Fe-O-Fe antisite patches, that via next near neighbor interactions impede the complete ferromagnetic (FM) ordering of the Fe^{3+} sublattice in the stoichiometric volume.

The electrical resistance and its magnetic field dependence at a temperature $T = 5$ K were measured under a magnetic field up to 9 T using a four probe method. Figure 2 shows the behavior of the measured $R(H)/R(0)$ versus the external applied field. Two different regimes can

be defined in the variation of the magnetoresistance with the applied magnetic field: the low field region ($H < 2$ T) with a steeper slope and the high field behavior with a less pronounced slope. Differences between samples translate into differences in LFMR rather than in the high field behavior. Now, for the sake of establishing universal correlations within this series of compounds we focus our attention on defining two slopes (in the low field region and in the high field regime), each one assuming a linear variation of the magnetoresistance with the applied field.

Figure 3 shows the behavior of the percentage of variation of the LFMR per unit applied field as a function of the saturated magnetization measured at the same temperature for a wide set of the Fe-Mo double perovskites, including also most of the data reported in the literature. The saturated moments at 5 K for all the samples as well as the coercive fields can be found in the caption of Fig. 3. The first result that we can extract from Fig. 3 is the existence of a neat increase of the LFMR with M_s and, even if there is an important dispersion in the data, a linear dependence can be extracted. The observed dependence is further linked to the Fe-Mo relative ordering in the superstructure as can readily be seen in Fig. 4. This result is most remarkable if we take into account the broad set of samples we are dealing with: the samples stem from a variety of precursors (conventional ceramic methods, citrate precursors); temperature and pressure synthesis conditions

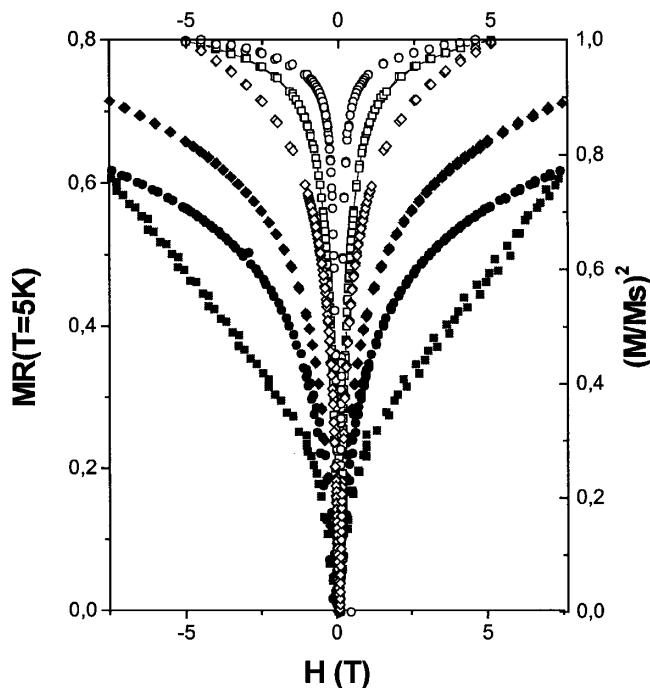


FIG. 1. Right axes: Measured $(M(H)/M_s)^2$ vs applied field for $\text{Ca}_2\text{FeMoO}_6$ (open squares), $\text{Sr}_2\text{FeMoO}_6$ (open lozenges), and $\text{Ba}_2\text{FeMoO}_6$ (open circles). Left axis: Magnetoresistance for the same set of samples. Symbols as above but solid.

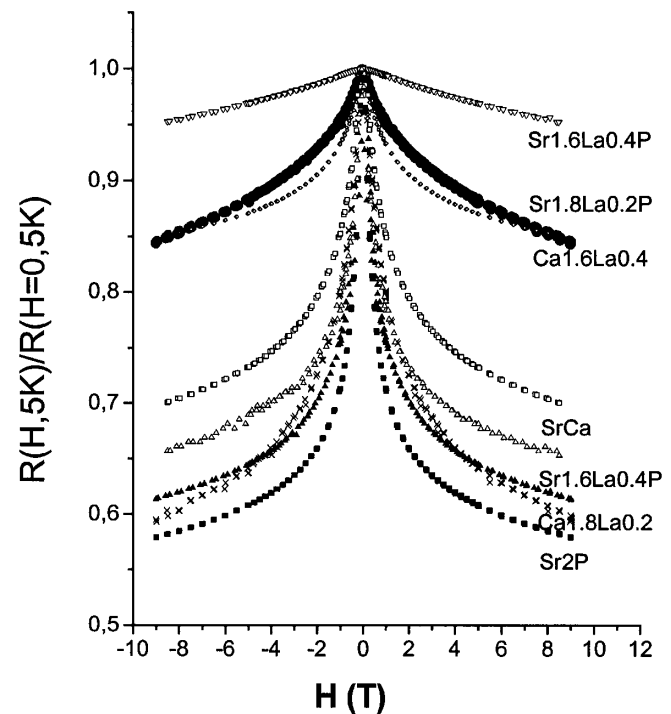


FIG. 2. Normalized resistance vs applied magnetic field for a set of representative samples. Samples synthesized under hot pressure holds a P at the end of the name. Chemical formulas are derived by dropping the final P , when used, and adding FeMoO_6 to the characters in the plot.

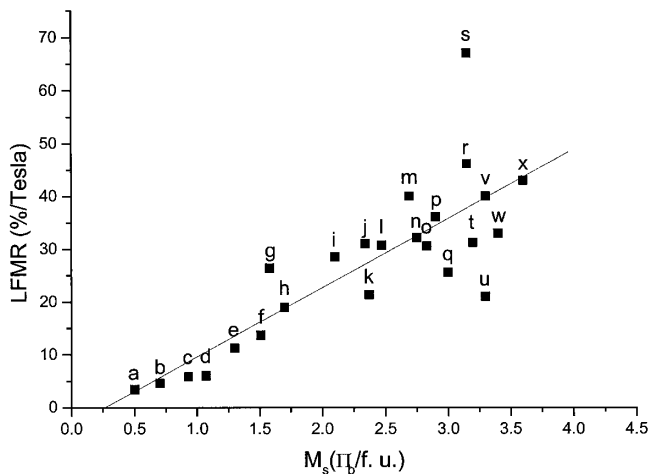


FIG. 3. LFMR per unit of applied field vs saturated magnetic moment. Sample chemical formulas are derived as in Fig. 2 and within parentheses, when explicitly available, coercive field in Oe, the measured x-ray percentage of antisite disorder: *a*: $\text{Sr}_{1.6}\text{La}_{0.4}$ (710, 93); *b*: $\text{Sr}_{1.8}\text{La}_{0.2}$ (550, 88); *c*: Sr_2 (350, 85); *d*: Sr_2 (275, 79); *e*: $\text{Ca}_{1.6}\text{La}_{0.4}$ (125, -); *f*: Sr_2 (-, 60); *g*: $\text{Sr}_{1.8}\text{La}_{0.2}\text{P}$ (300, 75); *h*: $\text{Ca}_{1.8}\text{La}_{0.2}$ (505, -); *i*: $\text{Sr}_{1.9}\text{La}_{0.1}$, Ref. [12], (135, -); *j*: Sr_2 , Ref. [12], (125, 18^{ex}); *k*: Sr_2 (120, 49); *l*: $\text{Sr}_{1.9}\text{Ba}_{0.1}$, Ref. [12], (105, -); *m*: $\text{Sr}_{1.9}\text{Ca}_{0.1}$, Ref. [12], (95, -); *n*: SrCa (390, 22); *o*: Sr_2 (275, 36); *p*: Sr_2 , Ref. [13], (-, 20); *q*: Ca_2 (240, 24); *r*: Sr_2P (160, 18); *s*: Sr_2 , Ref. [9], (-, 9); *t*: Sr_2 , Ref. [2], (-, 13); *u*: Ba_2 , Ref. [6], (-, 8^{ex}); *v*: Ba_2 , Ref. [6], (-, 8^{ex}); *w*: Ba_2P (50, 20); *x*: Sr_2 , Ref. [4], (-, 2.5^{ex}). Notice that, for A_2FeMoO_6 samples, “ex” means extrapolated value using the linear relation in Refs. [8,11].

change leading to different levels of antisite disorder; and finally, the samples correspond to a variety of morphologies that determine the different physical connectivities of the polycrystal (the higher the applied pressure in the synthesis of the powder, the higher the connectivity between

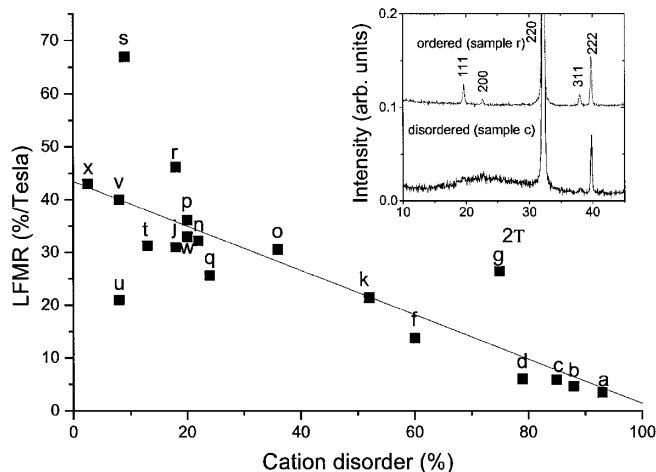


FIG. 4. LFMR per unit of applied field vs percentage of cation disorder. Letters describe samples as in Fig. 3. Inset shows Bragg reflections (111) and (311) related to the superstructure peaks in two diffractograms corresponding to representative disordered and ordered samples (*c* and *r*, respectively).

grains). The observed correlation between the antisite disorder and the LFMR can be considered a result of general validity for the FeMo perovskites since: LFMR is not linked to the choice of the alkaline earth cation or even to an aliovalent substitution; samples displaying dissimilar coercivities coexist in the same region of the graph and, conversely, samples with similar coercivities lay far apart; connectivity between grains is not a key question since samples synthesized at pressures of 20 kbar show the same ratio as those prepared without the hot pressing stage. However, as shown in Fig. 1, the basic ingredients seen in the dependence of the magnetoresistance defined as

$$MR(H, T) = [R(H = 0, T) - R(H, T)]/R(H, T) \quad (1)$$

on the applied field are coarsely present in the variation of $(M/M_s)^2$ with the field. This confirms an electron spin dependent crossing of barriers as the mechanism responsible for the LFMR [2]. The remarked dependence of the LFMR on M_s is in contrast with the high field magnetoresistance result which is found to be independent of the saturated moment and amounts to just a few percent for most samples, in coincidence with the low values of magnetoresistance reported for the single crystal [5].

We propose the following model to explain the observed behavior as a direct consequence of the antisite disorder stated above. Antisite disorder implies the existence of Fe-O-Fe (AF) and Mo-O-Mo (paramagnetic, PM) patches across a sample in between “stoichiometric” volumes, where the alternating ordering of Fe and Mo is fulfilled, as illustrated in Fig. 5, upper. The existence of the AF patches has been firmly established by Mossbauer spectroscopy and related to the high spin component Fe^{3+} while a fluctuating valence state $\text{Fe}^{2.5+}$ would correspond to the perfectly ordered volumes [14]. The AF Fe-O-Fe patches, and to a much lesser extent the PM Mo-O-Mo ones, act as barriers to the electronic transport between the ordered volumes. As the antisite disorder decreases, the average width of the AF islands decreases and the tunneling between stoichiometric patches becomes more probable, as soon as the orientation of the local magnetizations line up. This occurs at low magnetic fields because of the domain rotation process in the stoichiometric volumes (as seen in Fig. 5, upper). As a side product of the alignment of the latter, provided the Fe-O-Fe patches are not very large, the AF interaction within the Fe-O-Fe patches has to compete with the FM ones imposed by the surrounding material. In consequence, the AF order is partially broken, effectively thinning the barriers. Thus, the crossing of the spin polarized electron is easier and the LFMR is enhanced (see Fig. 5, lower). For wide AF patches, at low fields, the AF interactions within the patch dominate in the core, and these paths remain closed to the electronic transport. This, in turn, generates an important frustration around the AF patches [8], in agreement with what is observed in hysteresis cycles. Obviously, as antisite disorder increases and the saturated moment decreases, the

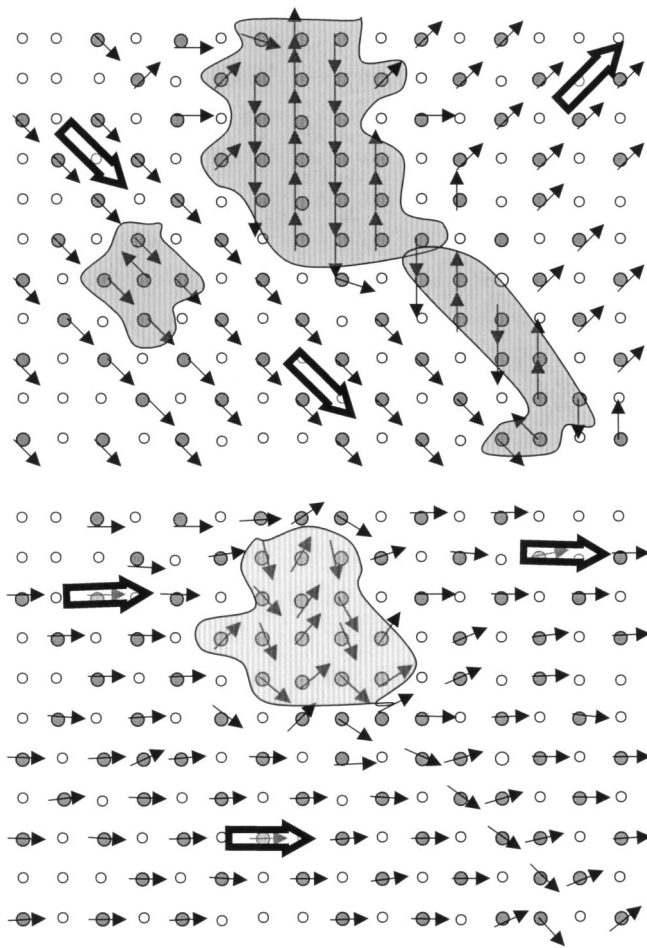


FIG. 5. Sketch of a microscopic portion of an idealized double FeMo perovskite presenting antisite disordered patches (Mo atoms are open circles and Fe atoms are solid circles). For clarity, only Fe spins are represented by arrows. The effect of the applied field can be inferred from the comparison between the upper ($H = 0$), and lower ($0 < H < 2$ T) plots.

effective width of the Fe-O-Fe patches increases and tunneling across the barrier becomes increasingly difficult up to the point in which the stoichiometric volumes lay so far apart that, even if they align with the field, no LFMR is observed. This is the case for the samples in the lower end of the range of M_s and constitutes a plausible explanation for the fitting line not crossing the origin.

It should be noted that, according to our picture, LFMR has also an extrinsic origin but does not require an intergrain mechanism. The latter can, however, be at the root of the explanation of the observed behavior of the dispersion of the data in Fig. 3 for the higher range of values of M_s . In fact, this dispersion can be qualitatively explained by invoking effects such as a different distribution of the disorder as well as particular details of the morphology, connectivity, and type of defects for each sample. To substantiate this, we note a general trend that is observed in the dispersion of LFMR values for samples with high M_s : higher LFMR ratios are present in samples for which the plots of LFMR and $(M/M_s)^2$ versus the applied field run

very close to each other, while samples with lower LFMR scores do not exhibit this concordance. The latter points to effects such as stronger degradation of grain surface that hardly affects the magnetization of the sample but strongly change its effective electrical connectivity, similar to the observed behavior in manganites [15]. The fact that the dispersion is larger for large M_s samples can hardly be casual. It is for these samples that the intragrain barriers are no longer the limiting factor to the electronic conduction and, hence, the intergranular effects comes into play.

In conclusion, moderate levels of antisite disorder seems to be at the very root of low field magnetoresistance in Fe-Mo double perovskites. This is evidenced by the described linear dependence of this magnitude with the saturation magnetic moment. Superimposed on this general trend, other effects such as disorder distribution, connectivity, defects, or morphology add their contribution.

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- [1] G. A. Prinz, *Science* **282**, 1660 (1998).
- [2] K. I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, *Nature* (London) **395**, 677 (1998).
- [3] Y. Tomioka, T. Okuda, Y. Okimoto, R. Kumai, K. I. Kobayashi, and Y. Tokura, *Phys. Rev. B* **61**, 422 (2000).
- [4] T. H. Kim, M. Uehara, S. W. Cheong, and S. Lee, *Appl. Phys. Lett.* **74**, 1737 (1999).
- [5] H. Q. Yin, J. S. Zhou, R. Dass, J. P. Zhou, J. T. McDevitt, and J. B. Goodenough, *Appl. Phys. Lett.* **75**, 2812 (1999); *J. Appl. Phys.* **87**, 6761 (2000).
- [6] A. Maignan, C. Martin, M. Hervieu, and B. Raveau, *J. Magn. Magn. Mater.* **211**, 173 (2000); A. Maignan, B. Raveau, C. Martin, and M. Hervieu, *J. Solid State Chem.* **144**, 224 (1999).
- [7] C. L. Yuan, S. G. Wang, W. H. Song, T. Yu, J. M. Dai, S. L. Ye, and Y. P. Sun, *Appl. Phys. Lett.* **75**, 3853 (1999).
- [8] A. Ogale, S. Ogale, R. Ramesh, and T. Venkatesan, *Appl. Phys. Lett.* **75**, 537 (1999).
- [9] D. D. Sarma, E. V. Sampathkumaran, S. Ray, R. Nagarajan, S. Majumdar, A. Kumar, G. Galini, and T. N. Guru Row, *Solid State Commun.* **114**, 465 (2000).
- [10] J. A. Alonso, M. T. Casais, M. J. Martínez-Lope, J. L. Martínez, P. Velasco, A. Muñoz, and M. T. Fernández-Díaz, *Chem. Mater.* **12**, 161 (2000).
- [11] Ll. Balcells, J. Navarro, M. Bibes, A. Roig, B. Martínez, and J. Fontcuberta, *Appl. Phys. Lett.* **78**, 781 (2001).
- [12] J. P. Zhou, R. Dass, H. Q. Yin, J. S. Zhou, L. Rabenberg, and J. B. Goodenough, *J. Appl. Phys.* **87**, 5037 (2000).
- [13] A. Arulraj, R. Ramesha, J. Gopalakrishnan, and C. N. R. Rao, *J. Solid State Chem.* **155**, 233 (2000).
- [14] J. Linden, T. Yamamoto, M. Karppinen, and H. Yamauchi, *Appl. Phys. Lett.* **76**, 2925 (2000).
- [15] A. de Andrés, M. García-Hernández, and J. L. Martínez, *Phys. Rev. B* **60**, 7328 (1999).