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## LETTER TO THE EDITOR

**Magnetic properties of the double perovskites  $A_2FeMoO_6$ ;  
 $A = Ca, Sr, Ba$** 

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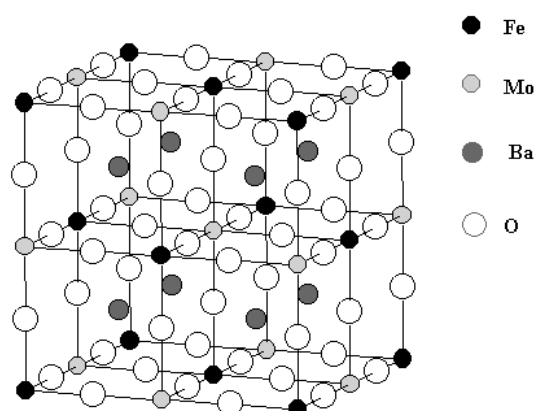
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**Abstract.** The double-perovskite oxides  $Ca_2FeMoO_6$ ,  $Sr_2FeMoO_6$  and  $Ba_2FeMoO_6$  show evidence of ferromagnetic metallic behaviour, with Curie temperatures of 345–426 K and saturation magnetization of 3.5–3.9  $\mu_B$ /formula unit. Ceramics show little anisotropic magnetoresistance, but the low-field isotropic negative magnetoresistance of  $Sr_2FeMoO_6$  is 7% in 1 T at room temperature and reaches 15% at 77 K. An effect of about 1% is found in 20 mT at room temperature in both ceramics and pressed powders of this compound.

Double perovskites  $A_2BB'O_6$  with two ordered B-site cations are known to be ferromagnetic for  $B = Cr, Fe$  and  $B' = Mo, W, Re$  [1–5] where A is an alkaline earth cation. Recent interest in the family [6–12] derives from a report by Kobayashi *et al* [6] that  $Sr_2FeMoO_6$  is a half-metallic ferrimagnet, with an electronic structure where only minority spins are present at the Fermi level. The calculated electronic structure is analogous to that for the B-sites of  $Fe_3O_4$  except that the minority spin electron has  $4d(Mo)t_{2g}$  character, rather than  $3d(Fe)t_{2g}$  character. A neutron diffraction study of  $Sr_2FeMoO_6$  by Garcia-Landa *et al* indicated that there was an iron moment of 4.1  $\mu_B$  but no localized moment on Mo. A study of  $Ca_2FeMoO_6$  by the present authors using neutron diffraction and Mössbauer spectroscopy has shown that there is a formal  $Fe^{3+}/Mo^{5+}$  charge configuration, and an iron moment of 4.0(1)  $\mu_B$  with  $-0.2(3)$   $\mu_B$  on the Mo [10]. The molybdenum electrons are delocalized, and they contribute to the ferromagnetic  $Fe^{3+}$ – $Fe^{3+}$  coupling by overlap with the empty  $3d(Fe)t_{2g}$   $\downarrow$  orbitals.

Much of the interest in double perovskites arises from the prospects of finding half-metallic oxides with high Curie temperatures. It is now plain that Curie temperatures of mixed-valence manganites of the type  $(R_{1-x}A_x)MnO_3$  cannot be increased above 400 K by any manipulation of the composition or stoichiometry [13]. The Curie temperature for  $CrO_2$  is similar. Substantially higher Curie points are required if devices which rely on spin-polarized transport in half-metallic oxides are to operate in a practically-useful temperature range around room temperature. These devices will rely on low-field switching of the magnetization of adjacent decoupled ferromagnetic regions which are separated by some sort of barrier, across which electrons may pass without completely losing their spin polarization. Examples are planar tunnel junctions with an insulating barrier [14], polycrystalline material with grain boundaries [15] and pressed powder with interparticulate contacts [16].

Here we report on the magnetic properties and magnetoresistance of three  $A_2FeMoO_6$  ceramics. Compounds were prepared from a mixture of oxides or carbonates, calcined at



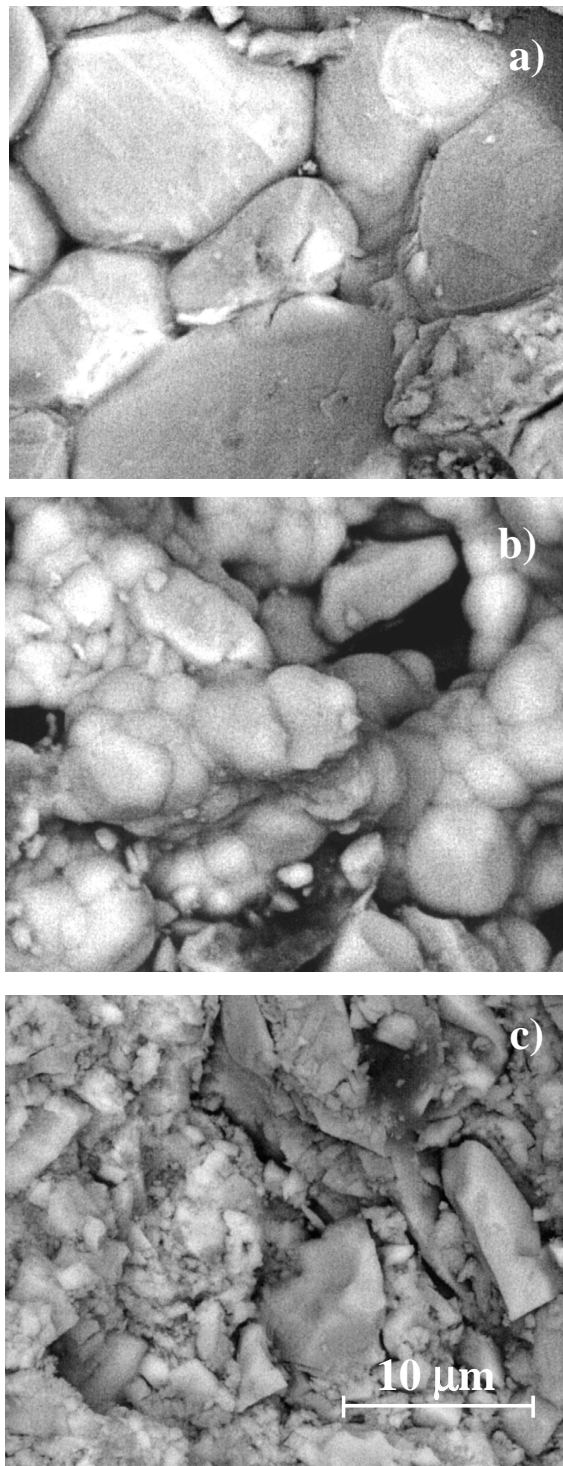
**Figure 1.** Crystal structure of  $\text{Ba}_2\text{FeMoO}_6$ .

**Table 1.** Properties of  $\text{A}_2\text{FeMoO}_6$ ; A = Ca, Sr, Ba.

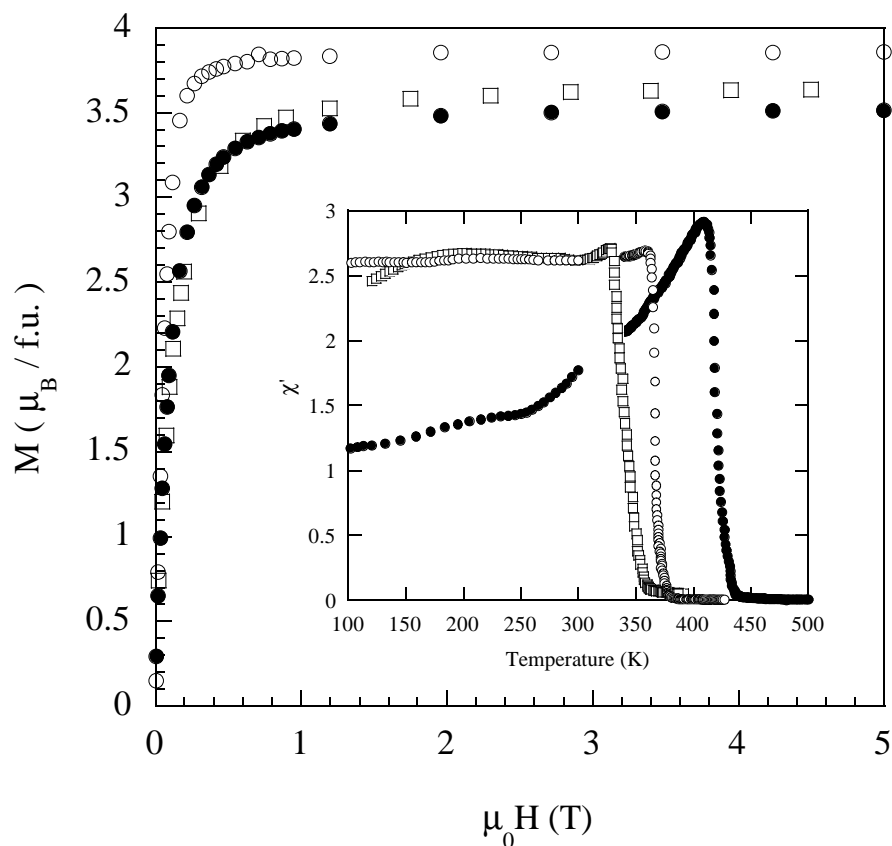
		$\text{Ca}_2\text{FeMoO}_6$	$\text{Sr}_2\text{FeMoO}_6$	$\text{Ba}_2\text{FeMoO}_6$
Crystal structure		Monoclinic $P2_1/n$	Tetragonal $P_4/mmm$	Cubic $Fm\bar{3}m$
Lattice parameters	$a$ (pm)	541.6	557.3	806.2
	$b$ (pm)	552.7		
	$c$ (pm)	769.8	790.5	
	$\beta$ ( $^\circ$ )	90.04		
X-ray density	$\rho_X$ ( $\text{kg m}^{-3}$ )	4727	5714	6623
Curie temperature	$T_c$ (K)	345	426	367
Saturation magnetization	$m_0$ ( $\mu_B \text{ fu}^{-1}$ )	3.63	3.51	3.85
Spontaneous magnetization at 290 K	$m_s$ ( $\mu_B \text{ fu}^{-1}$ )	1.58	2.04	1.56
Resistivity at 290 K	$\rho$ ( $\mu\Omega \text{ m}$ )	10	$4.5 \times 10^6$	$5.5 \times 10^4$
Magnetoresistance in 1.0 T at 77 K (ceramic)	$(\Delta R/R)\%$	—	15.0	13.3
Magnetoresistance in 50 mT at 290 K (ceramic)	$(\Delta R/R)\%$	—	2.6	1.6
Magnetoresistance in 1 T at 77 K (pressed powder)	$(\Delta R/R)\%$	3.5	6	
Magnetoresistance in 50 mT at 290 K (pressed powder)	$(\Delta R/R)\%$	—	1	

980  $^\circ\text{C}$  and then reground and refired, with a final firing for 5–10 hours at 1100  $^\circ\text{C}$  in an atmosphere of 1% H in Ar. All compounds were single phase and exhibited a series of superstructure reflections due to cation order of Fe and Mo on alternate B-sites of the perovskite structure. The ordered NaCl-type superstructure of  $\text{Ba}_2\text{FeMoO}_6$  is illustrated in figure 1. Lattice parameters and x-ray densities are listed in table 1. The ceramics all have a density of about 90% of the x-ray density. Microstructures of the sintered polycrystalline ceramics are illustrated in figure 2.

Curie temperatures were determined by ac susceptibility measurements on ceramic bars. The excitation field was 80  $\text{A m}^{-1}$  at 1 kHz. Magnetization was measured using a SQUID



**Figure 2.** Microstructure of polycrystalline  $\text{Ca}_2\text{FeMoO}_6$  (a), polycrystalline  $\text{Sr}_2\text{FeMoO}_6$  (b) and a pressed  $\text{Ca}_2\text{FeMoO}_6$  powder (c).



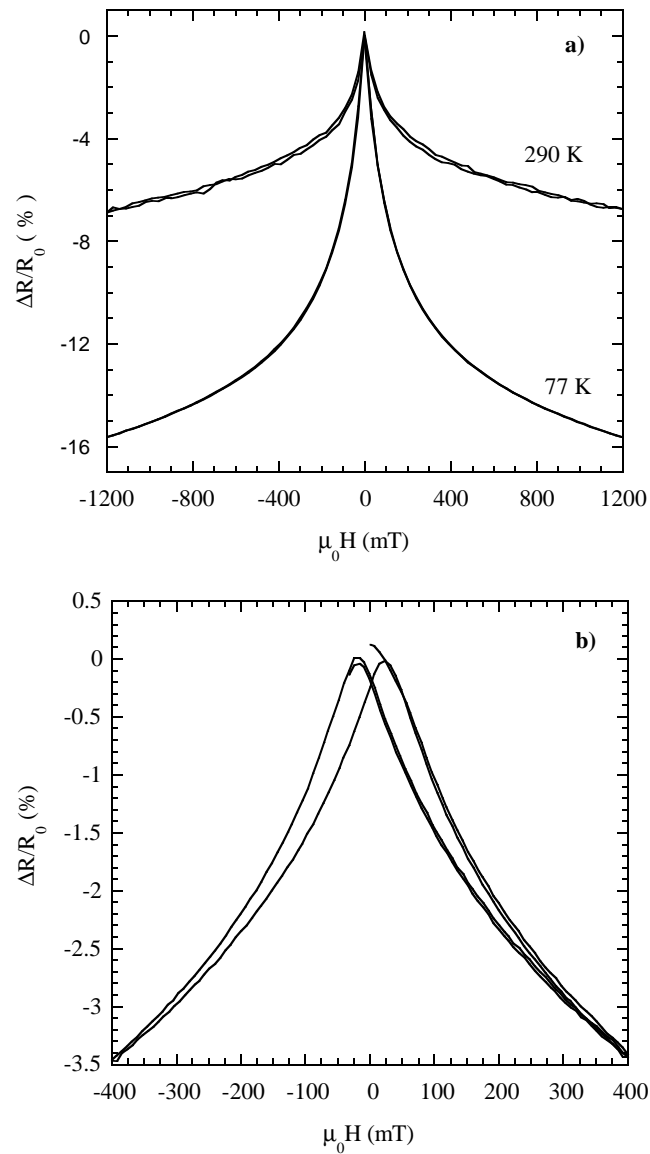
**Figure 3.** Magnetization curve of  $A_2FeMoO_6$  at 5 K ( $A = Ca$ , squares;  $A = Sr$ , full circles;  $A = Ba$ , empty circles). The insert shows the real part of the susceptibility measured in  $100 \mu T$  at 1 kHz.

magnetometer in fields up to 5 T. Resistivity was measured using the standard four-probe technique, and magnetoresistance was determined in fields of up to 1.2 T using a MULTIMAG MM 1200-27.5 permanent magnet flux source [17], where the magnetic field is variable, both in magnitude and direction in the plane of the sample.

Some typical magnetization and susceptibility data are shown in figure 3. The susceptibility is characteristic of a ferromagnet. The saturation magnetization reaches a value of  $3.5\text{--}3.9 \mu_B/\text{formula}$ , as shown in the table.

Resistivity of the ceramic samples is quite variable, but all have the positive temperature coefficient of resistivity characteristic of a metal. The  $Ca_2FeMoO_6$  samples are the most conducting, with  $\rho \sim 10 \mu\Omega \text{ m}$ , comparable to the values for the more conducting ferromagnetic manganites. The resistivity of  $Sr_2FeMoO_6$  depends on the thermal treatment, with values in the range  $1\text{--}10\,000 \text{ m}\Omega \text{ m}$ . Much of the resistivity arises at grain boundaries. The microstructures of the sintered Ca and Sr compounds appear quite different (figure 2(b)). Anisotropic magnetoresistance is small, less than 0.3%, but the Sr and Ba samples exhibit a substantial isotropic magnetoresistance in quite low fields. Results shown in figure 4 are typical. Values of

$$\frac{R_{(H)} - R_{(H=0)}}{R_{(H=0)}} = \frac{\Delta R}{R_0}$$



**Figure 4.** Magnetoresistance of (a) polycrystalline  $\text{Sr}_2\text{FeMoO}_6$  measured at 290 K and at 77 K and (b) pressed powder of  $\text{Sr}_2\text{FeMoO}_6$  measured at 77 K.

in 1 T at 290 K and at 77 K are 7% and 15%, respectively, for  $A = \text{Sr}$ . There is no significant hysteresis but a substantial low-field response is seen. For example, a 1% magnetoresistance effect at room temperature requires a field of just 20 mT.

No magnetoresistance was measured on a ceramic sample of the Ca compound, perhaps because the low resistivity is almost entirely of intrinsic origin, with little grain-boundary contribution. However on a pressed powder sample (figure 2(c)) with 80% of the x-ray density, values in 1 T at 290 K and at 77 K were less than 0.5% and 4%, respectively. A pressed powder of the Sr compound shows 2% magnetoresistance at 290 K and 6% at 77 K in a field of 1 T (figure 4(b)).

The magnetic ordering temperature we find for  $A = \text{Sr}$  is comparable to values reported in the literature [4,6], although for  $A = \text{Ba}$ ,  $T_C$  is slightly higher than that reported by Maignan *et al* [8]. Energy-dispersive x-ray analysis shows that our samples have close to the expected cation ratio, but the oxygen stoichiometry and the extent of NaCl-type cation order were not accurately determined. The saturation magnetization is also lower than the  $(5 - 1) = 4 \mu_B/\text{formula}$  expected from the ionic ferrimagnetic configuration  $\text{Fe}^{3+}/\text{Mo}^{5+}$ . An  $\text{Fe}^{3+}$  charge state for the iron has been clearly confirmed by the isomer shift and hyperfine field determined by  $^{57}\text{Fe}$  Mössbauer spectroscopy [10]. The magnetization of the Sr compound comes closest to the expected value. Possible explanations for the discrepancy include covalent mixing with the unpolarized 2p(O) orbitals, spin canting or imperfect cation order on alternate sites, together with antiferromagnetic coupling of iron ions in adjacent B-sites. A stoichiometric, ordered half-metallic ferromagnet must have a saturation magnetization that is an integral number of Bohr magnetons because the number of electrons per formula is an integer, and the number of spin up (or spin down) electrons is also integral because of the gap in one or other density of states.

The most interesting result is that the magnetoresistance, which is comparable in all three double perovskites investigated, is higher in both ceramics and pressed powders than it is in manganites with a similar Curie temperature. The extended character of the  $4d(\text{Mo})t_{2g}$  orbitals containing the minority spin electrons, compared to the more localized  $3d(\text{Fe})e_g$  band electrons in the manganites may be the reason. The manganites are thought to have a few layers of canted spins at the surface which spoil the polarization of the emitted electrons [18]. In the double perovskites, there is less tendency for the Mo electrons to be localized and collinear ferromagnetic order may be sustained right up to a sharp magnetic interface at the surface. The results encourage further work to tune the Curie temperature to higher values by altering the oxide composition or stoichiometry, and also to fabricate planar tunnel junctions using these materials.

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## References

- [1] Longo J M and Ward R 1961 *J. Am. Chem. Soc.* **83** 1088
- [2] Sleight A W, Longo J M and Ward R 1962 *Inorg. Chem.* **1** 245
- [3] Patterson F, Moeller C and Ward R 1963 *Inorg. Chem.* **2** 196
- [4] Galasso F S 1969 *Structure, Properties and Preparation of Perovskite Type Compounds* (Elmsford, New York: Pergamon)
- [5] Sleight A W and Weiher J F 1972 *J. Phys. Chem. Solids* **33** 679
- [6] Kobayashi K I, Kimura T, Sawada H, Terakura K and Tokura Y 1998 *Nature* **395** 677
- [7] Garcia-Landa B, Ritter C, Ibarra M R, Blasco J, Algrabel P A, Mahendiran R and Garcia J 1999 *Solid State Commun.* **110** 435
- [8] Maignan A, Raveau B, Martin C and Hervieu M 1999 *J. Solid State Chem.* **144** 224
- [9] Kobayashi K I, Timura T, Tomioka Y, Sawada H, Terakura K and Tokura Y 1999 *Phys. Rev. B* **59** 11 159
- [10] Pinsard-Gaudart L, Suryanarayanan R, Revcolevschi A, Rodriguez-Carvajal J, Greneche J M, Smith P A I, Thomas R M, Borges R P and Coey J M D, submitted for publication
- [11] Asano H *et al* 1999 *Appl. Phys. Lett.* **74** 3696
- [12] Prellier W, Smolyaninova V, Biswas A, Galley C, Greene R L, Ramesha K and Gopalakrishnan J *Preprint*
- [13] Coey J M D, von Molnár S and Viret M 1999 *Adv. Phys.* **48** 167
- [14] De Teresa J M, Barthélémy A, Fert A, Contour J P, Lyonnet R, Montaigne F, Seneor P and Vaurès A 1999 *Phys. Rev. Lett.* **82** 4288
- [15] Hwang H Y, Cheong S W, Ong N P and Batlogg B 1996 *Phys. Rev. Lett.* **77** 2041
- [16] Coey J M D 1999 *J. Appl. Phys.* **85** 5576
- [17] Manufactured by Magnetic Solutions Ltd, IDA Centre, Unit 13, Pearse Street, Dublin 2, Ireland
- [18] Balcells L, Fontcuberta J, Martinez B and Obradors X 1998 *J. Phys.: Condens. Matter* **10** 1883