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## Properties of the ferrimagnetic double perovskites $A_2FeReO_6$ ( $A = Ba$ and $Ca$ )

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**Abstract.** Ceramics of  $A_2FeReO_6$  double perovskites have been prepared and studied for  $A = Ba$  and  $Ca$ .  $Ba_2FeReO_6$  has a cubic structure ( $Fm\bar{3}m$ ) with  $a \approx 8.0854(1)$  Å whereas  $Ca_2FeReO_6$  has a monoclinic symmetry with  $a \approx 5.396(1)$  Å,  $b \approx 5.522(1)$  Å,  $c \approx 7.688(2)$  Å and  $\beta = 90.4^\circ$  ( $P2_1/n$ ). The barium compound is metallic from 5 K to 385 K, i.e. no metal–insulator transition has been seen up to 385 K, and the calcium compound is semiconducting from 5 K to 385 K. At 5 K, we observed a negative magnetoresistance of 10% in a magnetic field of 50 kOe for  $Ba_2FeReO_6$ . Magnetization measurements show a ferrimagnetic behaviour for both materials, with  $T_c \approx 315$  K for  $Ba_2FeReO_6$  and above 385 K for  $Ca_2FeReO_6$ . A specific heat measurement on the barium compound gave an electron density of states at the Fermi level,  $N(E_F)$ , equal to  $5.9 \times 10^{24}$  eV<sup>-1</sup> mol<sup>-1</sup>. Electrical, magnetic and thermal properties are discussed and compared to those of the analogous compounds  $Sr_2Fe(Mo, Re)O_6$ .

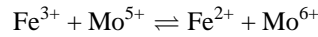
### 1. Introduction

Perovskite manganites exhibiting a variety of exotic electronic properties [1] that include a spectacular decrease of electrical resistance in a magnetic field [2], the so-called colossal magnetoresistance (CMR) [3], have attracted wide attention in recent years. A significant feature of the electronic structure of the ferromagnetic CMR manganites, revealed by recent experiments [4–6] and theory [7], is that the charge carriers are almost completely spin polarized at the Fermi level  $E_F$ . These materials are half-metallic ferromagnets, where the majority-spin states near  $E_F$  are delocalized and the minority-spin channel is effectively localized. Since half-metallic ferromagnetism and magnetoresistance (MR), especially at low fields, seem to be intimately related to each other [8]—the latter arising from the former—there is an intensive search for half-metallic magnets which could be candidate materials for the realization of MR applications. While several double-perovskite oxides of the kind  $A_2BB'O_6$  ( $A$  being an alkaline-earth or rare-earth ion and  $B, B'$  being d-transition-metal ions) have been theoretically predicted to be half-metallic antiferromagnets [9], one such material,  $Sr_2FeMoO_6$  [10], has recently [11, 12] been shown to be a half-metallic ferrimagnet exhibiting a significant tunnelling-type magnetoresistance at room temperature. More recently, Asano

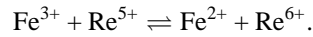
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et al [13] have shown that it is possible to have either positive or negative MR in thin films of  $\text{Sr}_2\text{FeMoO}_6$  grown by pulsed laser deposition.

$\text{Ba}_2\text{FeReO}_6$  [14] and  $\text{Ca}_2\text{FeReO}_6$  are double perovskites whose structure and properties are quite similar to those of  $\text{Sr}_2\text{FeMoO}_6$ . In both materials a valence degeneracy of the B-site cations occurs, giving rise to the observed metallic and magnetic properties; in the  $\text{Sr}_2\text{FeMoO}_6$  case, the valence degeneracy of the states is the following:



while in the  $\text{Ba}_2\text{FeReO}_6$  case, the degenerate oxidation states are as follows:

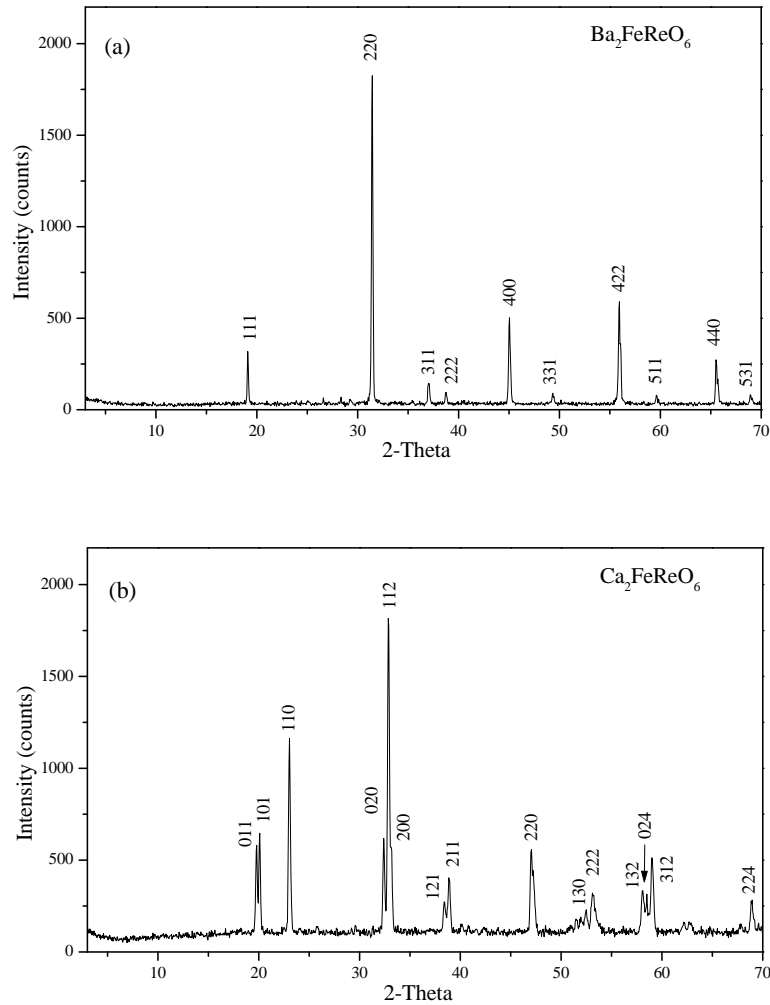


A major difference between the Mo and Re oxides, however, is that  $\text{Mo}^{5+}$  is a  $4d^1$  state, whereas  $\text{Re}^{5+}$  is a  $5d^2$  state. This would mean that the conducting charge-carrier density of the Re compound would be twice as much as in the Mo compound, while the localized spins centred on Fe remain the same in both oxides. We believe that this difference could have an influence on the magnetotransport behaviour, especially in view of the recent report [15] that the bulk low-field MR in ferromagnetic metals is mainly determined by the charge-carrier density. In view of the foregoing, we consider it important to investigate the magnetic and transport properties of  $\text{A}_2\text{FeReO}_6$  ( $\text{A} = \text{Ba}$  and  $\text{Ca}$ ) and our results are reported in this communication.

## 2. Results and discussion

Polycrystalline samples of  $\text{A}_2\text{FeReO}_6$  (with  $\text{A} = \text{Ba}$  or  $\text{Ca}$ ) were synthesized by standard solid-state methods. First, a precursor oxide of the composition  $\text{A}_2\text{ReO}_{5.5}$  ( $\text{A} = \text{Ba}$  or  $\text{Ca}$ ) was prepared by reacting stoichiometric amounts of  $\text{ACO}_3$  and  $\text{Re}_2\text{O}_7$  at  $1000^\circ\text{C}$  in air for 2 h. Second, this resultant oxide was mixed with required quantities of  $\text{Fe}_2\text{O}_3$  and Fe powder to obtain the desired composition  $\text{A}_2\text{FeReO}_6$ . Finally, pellets of this mixture were heated in an evacuated sealed silica tube at  $910^\circ\text{C}$  for four days and this was followed by another treatment at  $960^\circ\text{C}$  for the same time, with intermediate grinding. X-ray powder diffraction (XRD) patterns were recorded using a Siemens D5005 diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The XRD patterns of the final compounds are shown in figure 1(a) and figure 1(b). The DIAMOND program was used to calculate lattice parameters, bond lengths and bond angles.  $\text{Ba}_2\text{FeReO}_6$  is indexed on the basis of a cubic cell ( $Fm\bar{3}m$ ) with  $a \approx 8.054(1) \text{ \AA}$ , like  $\text{Ba}_2\text{YRuO}_6$  [16].  $\text{Ca}_2\text{FeReO}_6$  is distorted to a monoclinic symmetry ( $P21/n$ ) with  $a \approx 5.396(2) \text{ \AA}$ ,  $b \approx 5.522(2) \text{ \AA}$ ,  $c \approx 7.688(1) \text{ \AA}$  and  $\beta = 90.4^\circ$ , parameters similar to those of  $\text{La}_2\text{CuIrO}_6$  and  $\text{Nd}_2\text{MgTiO}_6$  [17]. These results indicate the formation of ordered double-perovskite structure (figure 2) for both compounds, as reported earlier [14] and consistent with recent results [11, 12]. One also notes that no impurity phase is detectable in the XRD, indicating a clean single phase in each case.

The resistivity ( $\rho$ ) was measured between 5 K and 300 K on bars with the approximate dimensions of  $1 \times 3 \times 8 \text{ mm}^3$ , using the standard four-probe method. The dependence on temperature ( $T$ ) of  $\rho$  is shown in figure 3 at various magnetic fields of 0, 2 and 50 kOe for  $\text{Ba}_2\text{FeReO}_6$ . The resistivity gradually decreases when the temperature decreases suggesting a metallic behaviour below 300 K. The zero-field resistivity was also measured up to 385 K (see the inset of figure 3) but no change in the metallic behaviour was observed in this region. In contrast,  $\text{Ca}_2\text{FeReO}_6$  shows a semiconducting behaviour from 5 K to 300 K (figure 4). While  $\text{Ba}_2\text{FeReO}_6$  exhibits a magnetoresistance at 5 K, the resistivity of  $\text{Ca}_2\text{FeReO}_6$  remains unchanged, even under an applied magnetic field of 80 kOe. We find that the latter resistivity does not fit with an activation energy ( $E_a$ ) law ( $\rho(T) \propto \exp(E_a/k_B T)$ ). As often found in



**Figure 1.** X-ray powder diffraction of double-perovskite (a)  $\text{Ba}_2\text{FeReO}_6$  and (b)  $\text{Ca}_2\text{FeReO}_6$ .

the manganites [18], the resistivity at room temperature is large ( $50 \text{ m}\Omega \text{ cm}$  for  $\text{Ba}_2\text{FeReO}_6$  and  $20 \text{ m}\Omega \text{ cm}$  for  $\text{Ca}_2\text{FeReO}_6$ ), well above the Mott limit, but perhaps reflecting intergrain resistance in these polycrystalline samples. The resistivity of  $\text{Ca}_2\text{FeReO}_6$  is however  $\sim 3 \times 10^3$  times higher than the resistivity of  $\text{Ba}_2\text{FeReO}_6$  at low temperatures. A difference of this magnitude can hardly be explained by scattering at the grain boundaries. A more detailed understanding of the transport of these materials will require studies performed on single crystals or oriented films.

To investigate the MR of the  $\text{Ba}_2\text{FeReO}_6$ , we present the MR data at different temperatures in figure 5. As shown in figure 3,  $\text{Ba}_2\text{FeReO}_6$  exhibits negative MR, with the MR defined as

$$\text{MR}(T, H) = [R(H) - R(0)]/R(H).$$

The MR is equal to 3% at 10 K in a 2 kOe magnetic field. The MR under low field at 10 K is smaller than that found in  $\text{Sr}_2\text{FeMoO}_6$  (10%) [11]. However, the zero-field  $\rho(T)$  behaviour of  $\text{Sr}_2\text{FeMoO}_6$  is rather different at low temperature to that of  $\text{Ba}_2\text{FeReO}_6$ —in  $\text{Sr}_2\text{FeMoO}_6$  it tends to increase slightly at 10 K [11]. The MR of  $\text{Ba}_2\text{FeReO}_6$  strongly increases at low

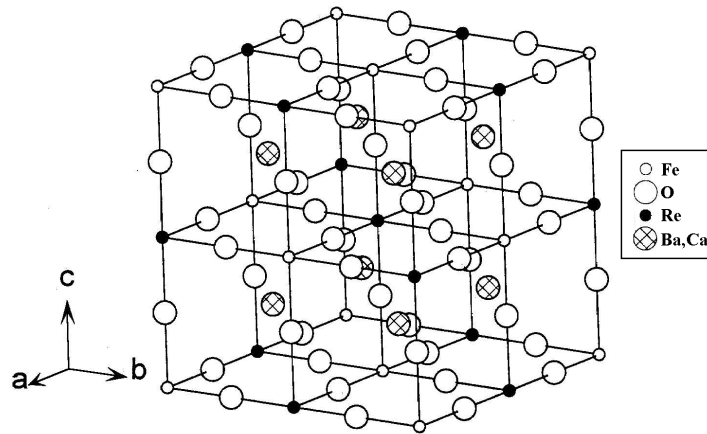


Figure 2. The idealized structure of the ordered double perovskite.

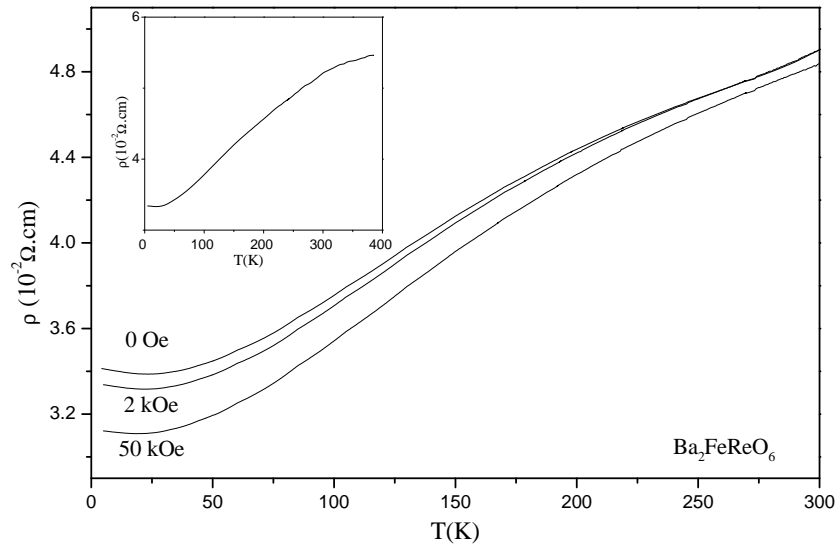


Figure 3. Resistivity versus temperature under different magnetic fields for  $\text{Ba}_2\text{FeReO}_6$ . The inset shows the zero-field dependence of the resistivity from 5 to 385 K.

fields with a slower increase at higher field. This effect occurs mainly at low temperature, and at room temperature the MR is very small. The features are characteristic of intergrain magnetoresistance [12]. At low temperature (figure 5), a small hysteretic behaviour also appears but this is not of relevance to the issues discussed in this paper. The contrasting electrical transport of  $\text{Ba}_2\text{FeReO}_6$  and  $\text{Ca}_2\text{FeReO}_6$  is indeed striking, and has not been reported before.

Magnetization ( $M$ ) measurements were made with a SQUID (MPMS Quantum Design) magnetometer. These DC measurements were carried out with increasing temperature after the sample was zero-field cooled (ZFC). Figure 6(a) shows the field dependence of  $M$  for both compounds at 5 K. Both samples have a significant high-field susceptibility (especially the  $\text{Ca}_2\text{FeReO}_6$ ), which makes it difficult to determine the exact value of the

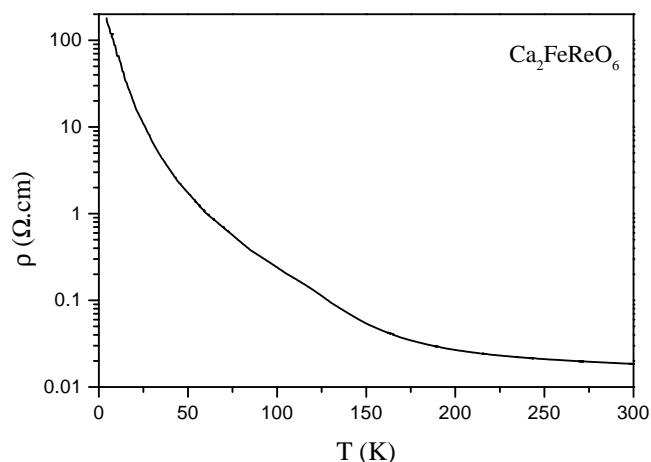


Figure 4. Resistivity versus temperature under zero field for  $Ca_2FeReO_6$ .

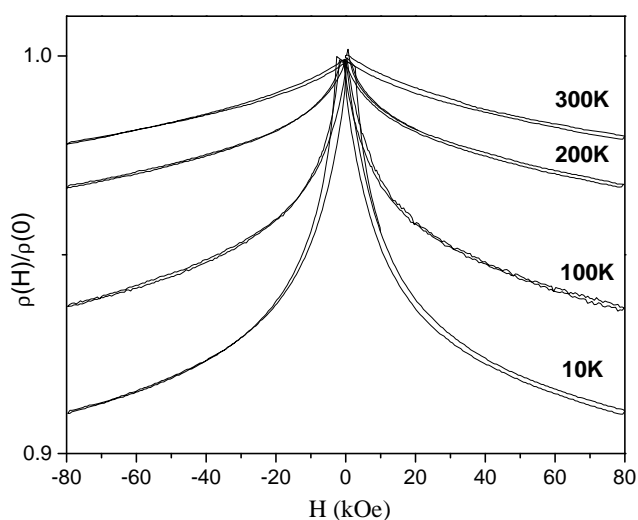
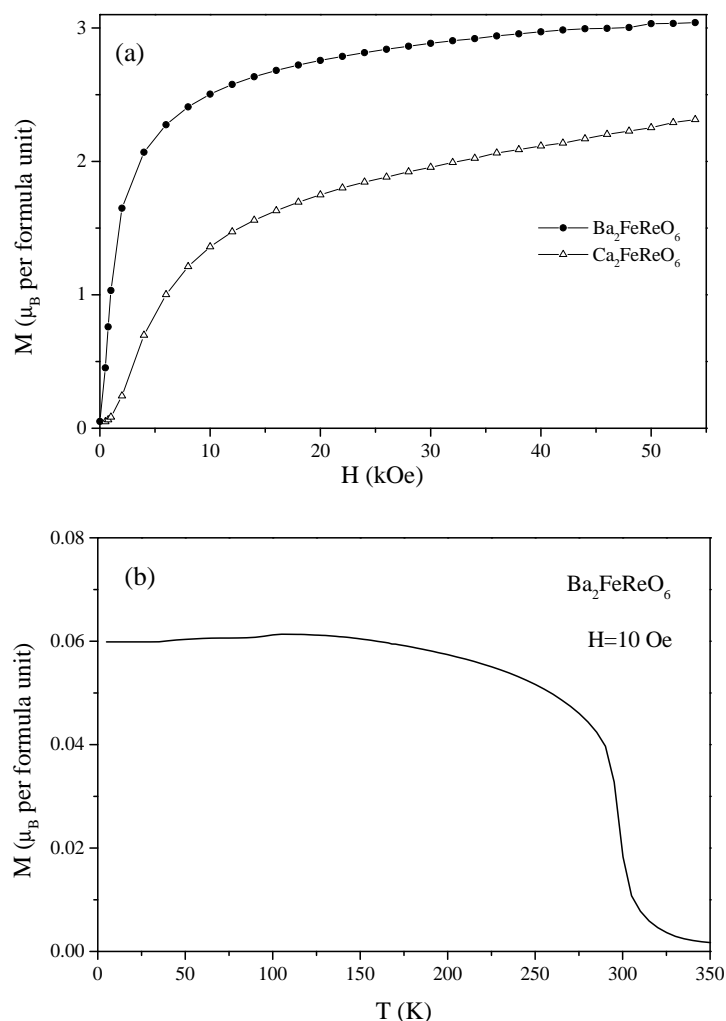


Figure 5. The field dependence of the normalized MR at different temperatures for  $Ba_2FeReO_6$ .

saturation magnetization at low temperature. Nevertheless, for  $Ba_2FeReO_6$ , the value of the magnetization at 54 kOe is  $3.04 \mu_B$ , which is close to the expected value based on  $Fe^{3+}$  and  $Re^{5+}$  moments ( $3 \mu_B$ ) for a ferrimagnetic state. In the same way, the high-field magnetization value for  $Ca_2FeReO_6$  is measured to be  $2.24 \mu_B$  which is smaller than the expected value for a ferrimagnetic state but in agreement with a previous report [19]. Thus, these values are consistent with the ferrimagnetic type of ordering like several other double-perovskite compounds [20–22].  $Sr_2FeReO_6$  also shows ferrimagnetic coupling of Fe and Re spins [23].

The temperature dependence of  $M$  under a magnetic field of 10 Oe is shown in figure 6(b) for  $Ba_2FeReO_6$ . Around 315 K, there is a sharp change in the magnetization indicating that a transition from a paramagnetic to a ferrimagnetic state occurs. Thus, the ferrimagnetic transition temperature ( $T_c$ ) of  $Ba_2FeReO_6$  was estimated to be  $315 \pm 5$  K.  $Ca_2FeReO_6$  exhibits a higher  $T_c$ , above 385 K (not determined since it is beyond our measurement range). The



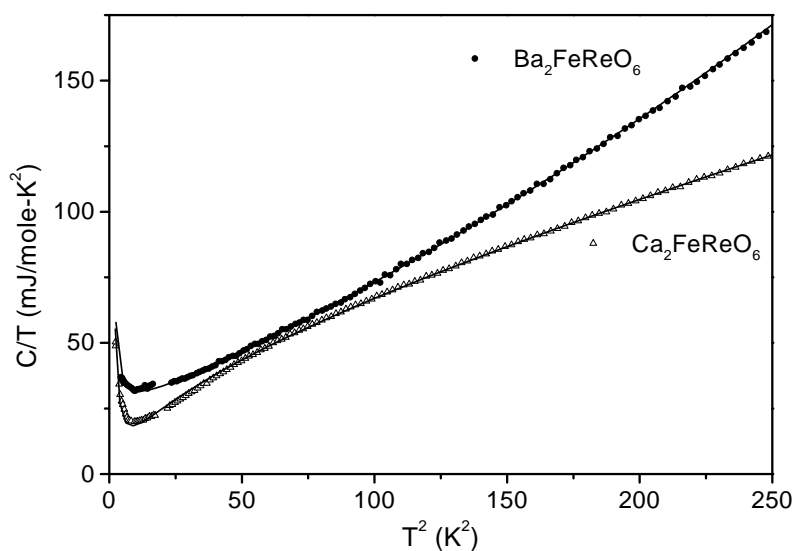
**Figure 6.** (a) Magnetization versus field at 5 K for  $A_2\text{FeReO}_6$  ( $A = \text{Ba}, \text{Ca}$ ). (b) Magnetization versus temperature under a magnetic field of 10 Oe for  $\text{Ba}_2\text{FeReO}_6$ .

ferrimagnetic transition temperature of  $\text{Ba}_2\text{FeReO}_6$  is lower than the reported value of  $T_c \approx 410$  K for  $\text{Sr}_2\text{FeReO}_6$  [20,22] but close to the value of  $\text{Ba}_2\text{FeMoO}_6$  ( $T_c = 340$  K) [21], whereas the  $T_c$  of  $\text{Ca}_2\text{FeReO}_6$  seems to be higher ( $>385$  K).

In the series  $\text{Ba}_2\text{FeReO}_6$ ,  $\text{Sr}_2\text{FeReO}_6$  and  $\text{Ca}_2\text{FeReO}_6$ , the Ba and Sr compounds are both cubic ( $Fm\bar{3}m$ ) while the Ca compound is monoclinic ( $P2_1/n$ ). It is known [17] that with ordered double perovskite,  $A_2\text{BB}'\text{O}_6$  having the rock-salt type of  $\text{BB}'$  cation sublattice, the symmetry is cubic for large A cations like  $\text{Ba}^{2+}/\text{Sr}^{2+}$  and monoclinic for small A cations like  $\text{Ca}^{2+}$  [24]. The electrical and magnetic properties of  $\text{Ba}_2\text{FeReO}_6$  and  $\text{Ca}_2\text{FeReO}_6$  could be rationalized in terms of the difference in structure. For cubic  $\text{Ba}_2\text{FeReO}_6$ , the mean Fe–O–Re bond distance and bond angle would be  $\approx 4.04$  Å and 180 degrees respectively, while for the monoclinic  $\text{Ca}_2\text{FeReO}_6$ , the mean Fe–O and Re–O bond distances are calculated to be  $\approx 2.04$  Å and  $\approx 1.94$  Å respectively (the Fe–O–Re distance is  $\approx 3.98$  Å), while the Fe–O–Re bond angle is  $\approx 151$  degrees.  $\text{Sr}_2\text{FeReO}_6$  remains cubic with  $a \approx 7.89$  Å. Accordingly, there

is a compression of the Fe–O–Re bond length as we move from the Ba to Sr to Ca compound in the series  $\text{A}_2\text{FeReO}_6$  ( $\text{A} = \text{Ba}, \text{Sr}, \text{Ca}$ ), which presumably results in an increase of the ferrimagnetic temperature transition  $T_c$ , while the bending of the Fe–O–Re bond angle away from 180 degrees in the Ca compound narrows down the conduction bandwidth and insulating behaviour. The narrowing of the conduction bandwidth and consequent insulating behaviour arising from the bending of the B–O–B angle in several  $\text{ABO}_3$  perovskites, for example in  $\text{RENiO}_3$  ( $\text{RE} = \text{rare earth}$ ), is well known in the literature [25]. A similar conclusion is reached when comparing  $\text{Ba}_2\text{FeMoO}_6$  and  $\text{Sr}_2\text{FeMoO}_6$  [11, 21];  $\text{Ba}_2\text{FeMoO}_6$  is metallic (and cubic) whereas  $\text{Sr}_2\text{FeMoO}_6$ , whose structure is tetragonal, has a resistivity which increases when  $T$  decreases [11].

The specific heat was measured by relaxation calorimetry in the temperature range 2–16 K. The specific heat data for  $\text{Ba}_2\text{FeReO}_6$  and  $\text{Ca}_2\text{FeReO}_6$  are shown in figure 7. In our analysis of the low-temperature specific heat we include lattice ( $C_{latt}$ ), metallic ( $C_{el}$ ) and hyperfine ( $C_{hyp}$ ) contributions. When the temperature decreases below 3 K, the specific heat increases due to the hyperfine contribution  $C_{hyp} = A/T^2$ . Since the nuclear spin of  $^{56}\text{Fe}$  is zero, the hyperfine contribution in our samples arises from the  $^{186}\text{Re}$  nuclear spin  $I = 1$ . The experimental values of  $A$  are found to be  $135 \pm 4 \text{ mJ K mol}^{-1}$  and  $180 \pm 5 \text{ mJ K mol}^{-1}$  for  $\text{Ba}_2\text{FeReO}_6$  and  $\text{Ca}_2\text{FeReO}_6$  respectively. In addition,  $\text{Ba}_2\text{FeReO}_6$  has the expected metallic contribution,  $\gamma T$ , with  $\gamma = 23.1 \pm 0.2 \text{ mJ mol}^{-1} \text{ K}^{-2}$ . Using  $\gamma = \pi^2 k_B^2 N(E_F)/3$ , we find the density of states at the Fermi energy  $N(E_F)$  to be  $5.9 \times 10^{24} \text{ eV}^{-1} \text{ mol}^{-1}$ . This value is larger than the  $N(E_F)$  obtained from the band-structure calculation for  $\text{Sr}_2\text{FeMoO}_6$  ( $1.2 \times 10^{24} \text{ eV}^{-1} \text{ mol}^{-1}$ ) [11], probably because  $\text{Re}^{5+}$  has two electrons on the d orbital ( $5d^2$ ), while  $\text{Mo}^{5+}$  has only one ( $4d^1$ ).



**Figure 7.** The specific heat of  $\text{Ba}_2\text{FeReO}_6$  and  $\text{Ca}_2\text{FeReO}_6$  plotted as  $C/T$  versus  $T^2$ . The lines are the best fits to the form  $C = A/T^2 + \gamma T + \beta_3 T^3 + \beta_5 T^5$  for  $\text{Ba}_2\text{FeReO}_6$  and to the form  $C = A/T^2 + \gamma T + \beta_3 T^3 + C'$  for  $\text{Ca}_2\text{FeReO}_6$  (see the text for the values of the parameters and the definition of  $C'$ ).

To achieve a good fit for our  $\text{Ba}_2\text{FeReO}_6$  specific heat data, two lattice terms are required:  $C_{latt} = \beta_3 T^3 + \beta_5 T^5$ , where  $\beta_3 = 0.438 \pm 0.003 \text{ mJ mol}^{-1} \text{ K}^{-4}$  and  $\beta_5 = 6.1 \times 10^{-4} \text{ mJ mol}^{-1} \text{ K}^{-6}$ . Since  $\Theta_D = (12\pi^4 p R / 5\beta_3)^{1/3}$ , where  $p = 10$  is the number of atoms per formula unit, we find the Debye temperature  $\Theta_D$  to be 354 K, which is similar to



$\Theta_D$  for other perovskites [26]. The best fit for  $\text{Ca}_2\text{FeReO}_6$  does not include  $\gamma T$  and  $\beta_5 T^5$  terms, but requires an additional term  $C' \approx \alpha T^a$ , where  $a$  is close to 2. The absence of the charge-carrier term  $\gamma T$  is consistent with the insulating resistivity of  $\text{Ca}_2\text{FeReO}_6$ . The  $C' \approx \alpha T^a$  term, or more precisely  $C' = C'(\Delta, B, T)$ , which is the specific heat of excitations with a dispersion relation  $\epsilon = \Delta + Bk^2$  of non-magnetic origin, was also found in the charge-ordered perovskite manganites [27]. In the case of insulating  $\text{Ca}_2\text{FeReO}_6$ , a charge of 3+ on the Fe site and a charge of 5+ on the Re site create a situation similar to the  $\text{Mn}^{3+}\text{--Mn}^{4+}$  charge ordering in manganites. The fit to our  $\text{Ca}_2\text{FeReO}_6$  specific heat data gives  $\Delta = 0.6$  meV and  $B = 22$  meV  $\text{\AA}^2$ —similar in magnitude to the parameters found for the manganites. We believe that the reasons for the presence of the  $C'(\Delta, B, T)$  term for  $\text{Ca}_2\text{FeReO}_6$  are similar to those for  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  [27]. The lattice contribution  $\beta_3 T^3$  ( $\beta_3 = 0.25 \pm 0.006$  mJ mol $^{-1}$  K $^{-4}$ ) in  $\text{Ca}_2\text{FeReO}_6$  is smaller than that in  $\text{Ba}_2\text{FeReO}_6$ . This is surprising, but perhaps can be understood from the effect of a difference in crystal structure (cubic for  $\text{Ba}_2\text{FeReO}_6$  and monoclinic for  $\text{Ca}_2\text{FeReO}_6$ ) and smaller Ca mass on the lattice vibrations.

A ferrimagnet has a magnetic contribution to the specific heat,  $C_{mag} = \delta T^{3/2}$ , which is similar to that of a ferromagnet. However, this contribution cannot be resolved from the specific heat data alone, since our data can be fitted well without the magnetic term. The value of the ferrimagnetic spin-wave contribution can be estimated as  $\delta = 0.113 V k_B (k_B/D)^{3/2}$ , where  $V$  is a molar volume and  $D$  is a spin-wave stiffness [28]. According to Keffer [28]

$$D = 2z J a^2 S_{\text{M}_0} S_{\text{F}_e} / 3(S_{\text{F}_e} - S_{\text{M}_0})$$

where  $z$  is the number of nearest neighbours,  $a$  is the lattice parameter,  $S_{\text{F}_e}$  and  $S_{\text{M}_0}$  are the spin values for  $\text{Fe}^{3+}$  and  $\text{Mo}^{5+}$  ions respectively and  $J$  is the exchange interaction between nearest neighbours. This exchange interaction can be estimated within the effective-field theory as [28]

$$J = 3k_B T_c / [2z(S_{\text{F}_e}(S_{\text{F}_e} + 1)S_{\text{M}_0}(S_{\text{M}_0} + 1))^{1/2}]$$

which gives  $J/k_B = 19$  K for  $\text{Ba}_2\text{FeReO}_6$  and  $J/k_B = 25$  K for  $\text{Ca}_2\text{FeReO}_6$  (assuming  $T_c \approx 420$  K). Thus, the estimated values of  $\delta$  are 0.67 mJ mol $^{-1}$  K $^{-5/2}$  and 0.43 mJ mol $^{-1}$  K $^{-5/2}$  for  $\text{Ba}_2\text{FeReO}_6$  and  $\text{Ca}_2\text{FeReO}_6$  respectively. The magnetic contribution of this magnitude is  $\sim 3\text{--}4\%$  of the total specific heat at 3 K and smaller at other temperatures. The ferrimagnetic contribution to the low-temperature specific heat can be successfully determined if the sample has only the lattice and magnetic contributions [28]. If the material has other contributions such as  $\gamma T$  in  $\text{Ba}_2\text{FeReO}_6$  and  $C'$  in  $\text{Ca}_2\text{FeReO}_6$ , the magnetic contribution of small magnitude cannot be resolved from the specific heat, as has been shown for perovskite manganites [26].

### 3. Conclusions

In summary, we have investigated the transport, magnetic and thermal properties of two polycrystalline double perovskites  $\text{Ba}_2\text{FeReO}_6$  and  $\text{Ca}_2\text{FeReO}_6$ .  $\text{Ba}_2\text{FeReO}_6$  displays a metallic behaviour from 5 K to 385 K, whereas  $\text{Ca}_2\text{FeReO}_6$  is insulating in this temperature range.  $\text{Ba}_2\text{FeReO}_6$  exhibits a negative MR at 10 K, smaller than that of the analogous compound  $\text{Sr}_2\text{FeMoO}_6$ . Magnetic measurements are consistent with a ferrimagnetic ordering, with  $T_c = 315 \pm 5$  K for  $\text{Ba}_2\text{FeReO}_6$  and above 385 K for  $\text{Ca}_2\text{FeReO}_6$ . The specific heat of  $\text{Ba}_2\text{FeReO}_6$  gives a low-temperature metallic contribution with an electron density of states at the Fermi level close to the band-structure value. Insulating  $\text{Ca}_2\text{FeReO}_6$  has no metallic term in the specific heat but rather an extra contribution most probably caused by valence freezing of  $\text{Fe}^{3+}$  and  $\text{Re}^{5+}$ . These data have been explained and compared with those for the analogous compounds  $\text{Sr}_2\text{Fe}(\text{Re}, \text{Mo})\text{O}_6$ .

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