

Metallic and nonmetallic double perovskites: A case study of $A_2\text{FeReO}_6$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$)

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We have investigated the structure and electronic properties of ferrimagnetic double perovskites, $A_2\text{FeReO}_6$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$). The $A = \text{Ba}$ phase is cubic ($Fm\bar{3}m$) and metallic, while the $A = \text{Ca}$ phase is monoclinic ($P2_1/n$) and nonmetallic. ^{57}Fe Mössbauer spectroscopy shows that iron is present mainly in the high spin ($S = \frac{5}{2}$) Fe^{3+} state in the Ca compound, while it occurs in an intermediate state between high spin Fe^{2+} and Fe^{3+} in the Ba compound. It is argued that a direct $\text{Re } t_{2g} - \text{Re } t_{2g}$ interaction is the main cause for the metallic character of the Ba compound; the smaller size of Ca and the monoclinic distortion (which lifts the degeneracy of t_{2g} states) seem to disrupt the Re-Re interaction in the case of the Ca compound, making it nonmetallic for the same electron count.

I. INTRODUCTION

The compounds $A_2\text{FeMoO}_6$ and $A_2\text{FeReO}_6$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$) have attracted recent attention because they may be half metals with high magnetic transition temperatures and have spin-dependent transport properties which may be useful in magnetic devices.¹⁻³ These compounds were discovered in the 1960s,⁴⁻⁶ and are members of the broad class of $A_2BB'O_6$ “double perovskites.”⁷ Their conductivity properties are remarkable: $\text{Ba}_2\text{FeReO}_6$ compound has been known since the pioneering studies of Sleight and Weiher to have a ferrimagnetic metallic ground state,⁸ but our recent investigation³ has shown that the $\text{Ca}_2\text{FeReO}_6$ compound, which has a smaller magnetization and should have the same conduction-band filling, is an insulator. Although Kobayashi and co-workers,^{1,2} who investigated the strontium members $\text{Sr}_2\text{FeMoO}_6$ and $\text{Sr}_2\text{FeReO}_6$, seem to regard that half metallic ground state is a generic feature of the double perovskites, evidence contradicting this viewpoint exists. More generally, a survey of double perovskite $A_2BB'O_6$ compounds shows that only a very few of them exhibit both metallicity and magnetism, although several of them are ferrimagnetic. For example, among the series Ba_2MReO_6 ($M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) only the $M = \text{Fe}$ compound is both metallic and ferrimagnetic, while the $M = \text{Mn}$ and Ni compounds are ferrimagnetic semiconductors ($M = \text{Co}$ oxide is an antiferromagnetic semiconductor).⁸ Similarly $A_2\text{CrMoO}_6$ ($A = \text{Ca}, \text{Sr}$),⁴ $A_2\text{CrReO}_6$ ($A = \text{Ca}, \text{Sr}$),⁹ and $A\text{LaMnReO}_6$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$) (Ref. 10) are all ferrimagnetic but not me-

tallic. Available experimental data, however, are inadequate to make a correlation between the occurrence of metallicity and structural distortion.⁷

Changing the A -site cation from Ba to Sr to Ca drives a $T = 0$ metal-insulator transition in the $A_2\text{FeReO}_6$ system, even though the conduction-band filling is not changed. This and the widespread occurrence of insulating behavior in double perovskite systems suggest that the technologically interesting $\text{Sr}_2\text{FeReO}_6$ and $\text{Sr}_2\text{FeMoO}_6$ systems are, in some sense, “near” a nontrivial metal-insulator transition, which must be understood before these materials can be used with confidence in applications. To shed light on this subject, we have used ^{57}Fe Mössbauer spectroscopy along with the resistivity and structure determinations of the series $A_2\text{FeReO}_6$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$). We find that the changes in the transport and structure are correlated with the changes in the Fe valence, and present an interpretation of the data.

II. EXPERIMENT

Polycrystalline samples of $A_2\text{FeReO}_6$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$) were synthesized as reported earlier³ by a two-step process. First a precursor oxide of the composition $A_2\text{ReO}_{5.5}$ was prepared by reacting stoichiometric mixtures of ACO_3 and Re_2O_7 which were then reacted with required quantities of Fe and Fe_2O_3 in sealed evacuated silica tubes at 910°C for several days until single phase products were obtained. In the final stages, pellets were sintered in sealed silica tubes at 950°C . Powder x-ray diffraction (XRD) data were collected

TABLE I. XRD data collection and refinement conditions for $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$.

	$\text{Ba}_2\text{FeReO}_6$	$\text{Ca}_2\text{FeReO}_6$
Diffractometer	Siemens-D5005	Siemens-D5005
Geometry	Bragg-Brentano	Bragg-Brentano
Radiation	Cu K_α	Cu K_α
Counting time (h)	12	12
2θ range (degrees)	10–110	10–100
Step size (degrees)	0.02	0.02
Space group	$Fm\bar{3}m$	$P2_1/n$
Z	6	2
Profile function	Pseudo-Voigt	Pseudo-Voigt
R_{exp}	4.31	3.85
R_p	5.08	3.36
R_{wp}	6.52	4.40
χ^2	2.29	1.306
R_{Bragg}	3.67	6.20
R_F	6.28	7.91

using a Siemens D5005 diffractometer. ^{57}Fe Mössbauer spectra were recorded at room temperature and at 77 K using transmission Mössbauer setup with $^{57}\text{Co}(\text{Rh})$ source, and the resistivity was measured by the standard four-probe method.

Powder x-ray diffraction (XRD) shows that all the three $A_2\text{FeReO}_6$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$) oxides crystallize in ordered double perovskite structures, as reported previously,⁸ the $A = \text{Ba}$ and Sr phases adopting cubic ($Fm\bar{3}m$) symmetry and the $A = \text{Ca}$ phase, monoclinic ($P2_1/n$) symmetry. We have refined the structures of $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$ from powder XRD data using the Rietveld program FULLPROF.¹¹ Data collection and refinement details are given in Table I. We have used the position parameters of Ba_2YRuO_6 (Ref. 12) and Ca_2YRuO_6 (Ref. 13) as starting models for the refinement of the structures of $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$, respectively. The structural/atomic position parameters derived from the refinement are given in Table II. Observed, calculated, and difference profiles are shown in Fig. 1, and

TABLE II. Atomic positions, isotropic temperature factors, and occupancy for $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$.

Atom	x	y	z	B (\AA^2)	Occupancy
Ba	0.25	0.25	0.25	0.42(1)	2.024(4)
Fe1	0	0	0	0.20(3)	0.983(6)
Fe2	0.5	0.5	0.5	0.15(2)	0.017(6)
Re1	0.5	0.5	0.5	0.15(2)	0.983(6)
Re2	0	0	0	0.20(3)	0.017(6)
O	0.2521(1)	0	0	0.60(2)	6.000
Ca	0.5177(3)	0.5421(1)	0.2512(8)	1.28(1)	1.994(3)
Fe1	0	0.5	0	0.18(3)	0.947(3)
Fe2	0.5	0	0	0.47(4)	0.053(1)
Re1	0.5	0	0	0.47(4)	0.947(3)
Re2	0	0.5	0	0.18(3)	0.053(1)
O1	0.2261(4)	0.2244(4)	-0.0519(7)	1.12(4)	2.000
O2	0.2916(4)	0.7253(4)	-0.0416(7)	1.12(4)	2.000
O3	0.4327(2)	0.0023(5)	0.2540(2)	1.12(4)	2.000

TABLE III. Structural parameters for $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$ [for $\text{Sr}_2\text{FeReO}_6$, $a = 7.887(1)$ (\AA)].

	$\text{Ba}_2\text{FeReO}_6$	$\text{Ca}_2\text{FeReO}_6$
Space group	$Fm\bar{3}m$	$P2_1/n$
a (\AA)	8.0518(2)	5.4019(2)
b (\AA)		5.5246(2)
c (\AA)		7.6847(2)
β ($^\circ$)		90.02(1)
$d_{\text{Fe-O}}$ (\AA)	$2.030(3) \times 6$	$d_{\text{Fe-O1}}$ 1.992(3) $\times 2$ $d_{\text{Fe-O2}}$ 2.033(3) $\times 2$ $d_{\text{Fe-O3}}$ 1.925(3) $\times 2$
$d_{\text{Re-O}}$ (\AA)	$1.996(2) \times 6$	$d_{\text{Re-O1}}$ 1.971(3) $\times 2$ $d_{\text{Re-O2}}$ 1.916(2) $\times 2$ $d_{\text{Re-O3}}$ 1.986(2) $\times 2$
$\angle \text{Fe-O-Re}$	180	$\angle \text{Fe-O1-Re}$ 154.2(1) $\angle \text{Fe-O2-Re}$ 156.1(2) $\angle \text{Fe-O3-Re}$ 158.6(2)

the structures of $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$ are drawn in Fig. 2.

III. RESULTS AND DISCUSSION

The lattice parameters and the relevant bond lengths and bond angles are listed in Table III. Refinements of occupancy at B and B' sites indicate that the ordering of Fe and Re atoms is 98 and 95%, respectively, for the Ba and Ca oxides, showing that the B -site disorder is not important for the present discussion. Larger amounts of B -site disorder have been shown to influence the properties.¹⁴ The monoclinic distortion of the Ca compound is a clear manifestation of the smaller size and smaller tolerance factor t (0.963) for $\text{Ca}_2\text{FeReO}_6$ than for $\text{Ba}_2\text{FeReO}_6$ ($t = 1.06$). The monoclinic structure is the preferred structure for rocksalt-type ordering of double perovskites with smaller t values, while the cubic ($Fm\bar{3}m$) structure is preferred by double perovskites containing Ba ($t \sim 1.0$).⁷ A major consequence of the distortion is that the Fe-O-Re angle which is linear (180°) in the Ba compound is considerably bent to $\sim 156^\circ$ in the Ca compound. Also, the octahedral Fe-O and Re-O bond lengths which are equal in the Ba compound become unequal in the Ca compound (Table III). The volume per $A_2\text{FeReO}_6$ formula unit decreases from 65.25 to 57.34 \AA^3 as we go from Ba to Ca. Electrical resistivity measurements reveal that the Ba and the Sr oxides are metallic and the Ca oxide is nonmetallic.³

The powder XRD pattern of $\text{Sr}_2\text{FeReO}_6$ shows a single-phase double perovskite with $a = 7.887 \text{\AA}$. Since both the size of Sr^{2+} (1.44 \AA) and the lattice parameter of the Sr compound are intermediate between those of Ca^{2+} and Ba^{2+} , it is not surprising that the properties of the Sr compound are also intermediate showing metallic or semiconducting behavior depending on the sample history.²

In order to understand the difference in the behavior more clearly we have performed ^{57}Fe Mössbauer spectroscopy. At 77 K, both $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$ show the characteristic six-finger pattern (Fig. 3) of a ferro(ferri)magnet, but with different isomer shift δ (with respect to $\alpha\text{-Fe}$) and hy-

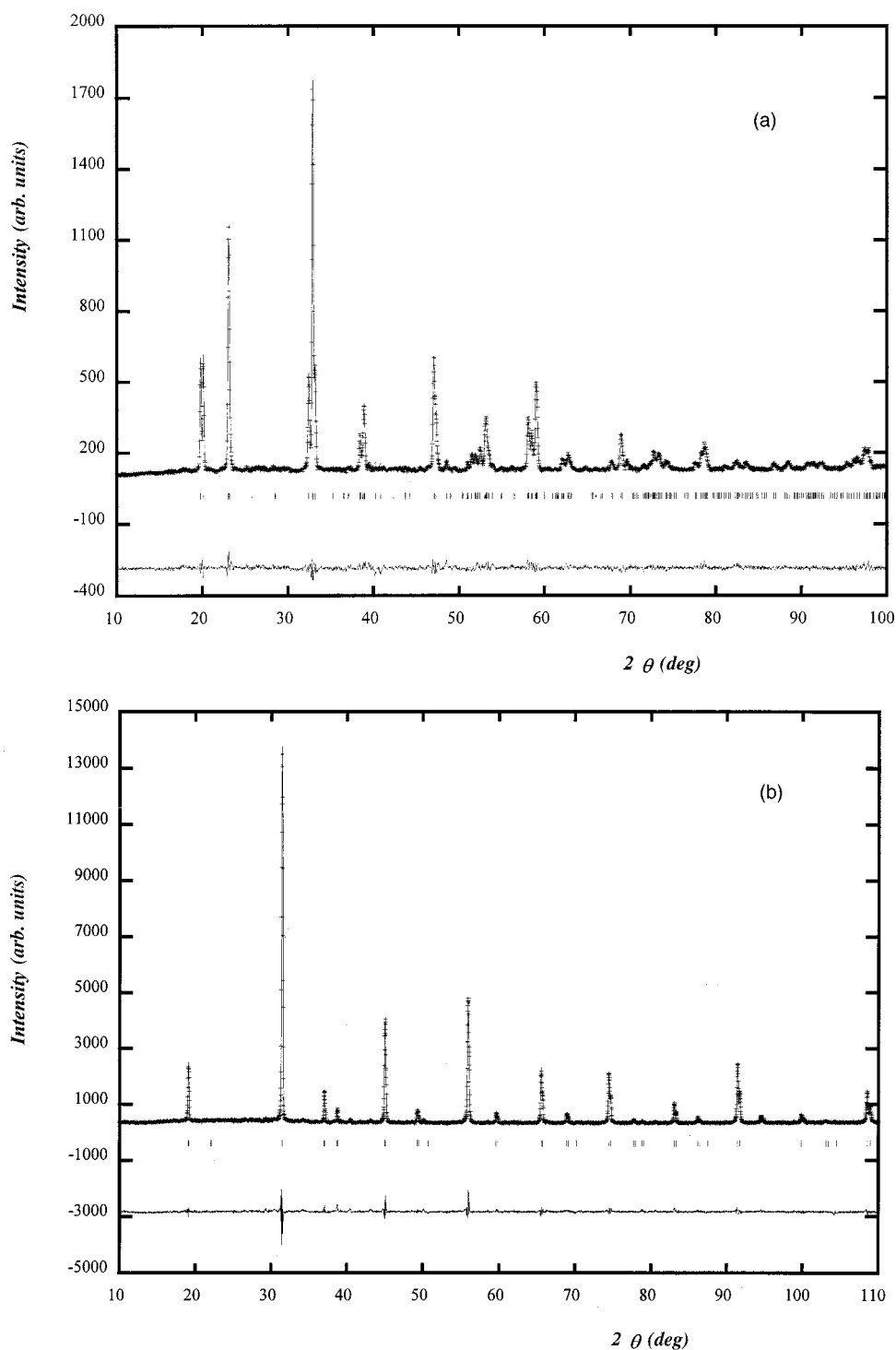
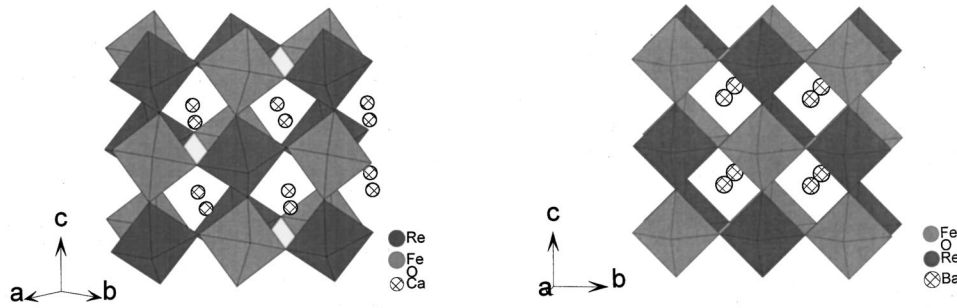


FIG. 1. Rietveld refinement of powder XRD data for (a) $\text{Ca}_2\text{FeReO}_6$ and (b) $\text{Ba}_2\text{FeReO}_6$. Calculated (full line), experimental (+), and difference (bottom) profiles are shown.

perfine field H_i : For the Ba compound, δ and H_i are 0.862 ± 0.009 mm/s and 43.79 ± 0.07 T, respectively, and the corresponding values for the Ca compound are 0.631 ± 0.004 mm/s and 49.87 ± 0.03 T. The values for the Sr compound are 0.71 ± 0.03 mm/s and 47.2 ± 0.03 T, which are intermediate between those for the Ba and the Ca compounds. The data for $\text{Ba}_2\text{FeReO}_6$ are comparable to those previously reported.⁸ Mössbauer data for $\text{Ca}_2\text{FeReO}_6$ and $\text{Sr}_2\text{FeReO}_6$ have not been reported earlier. The Mössbauer data for

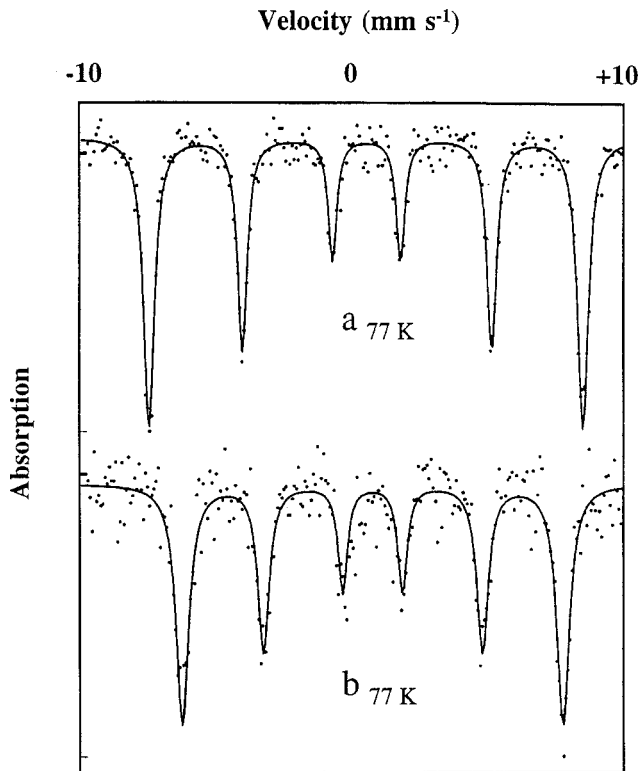
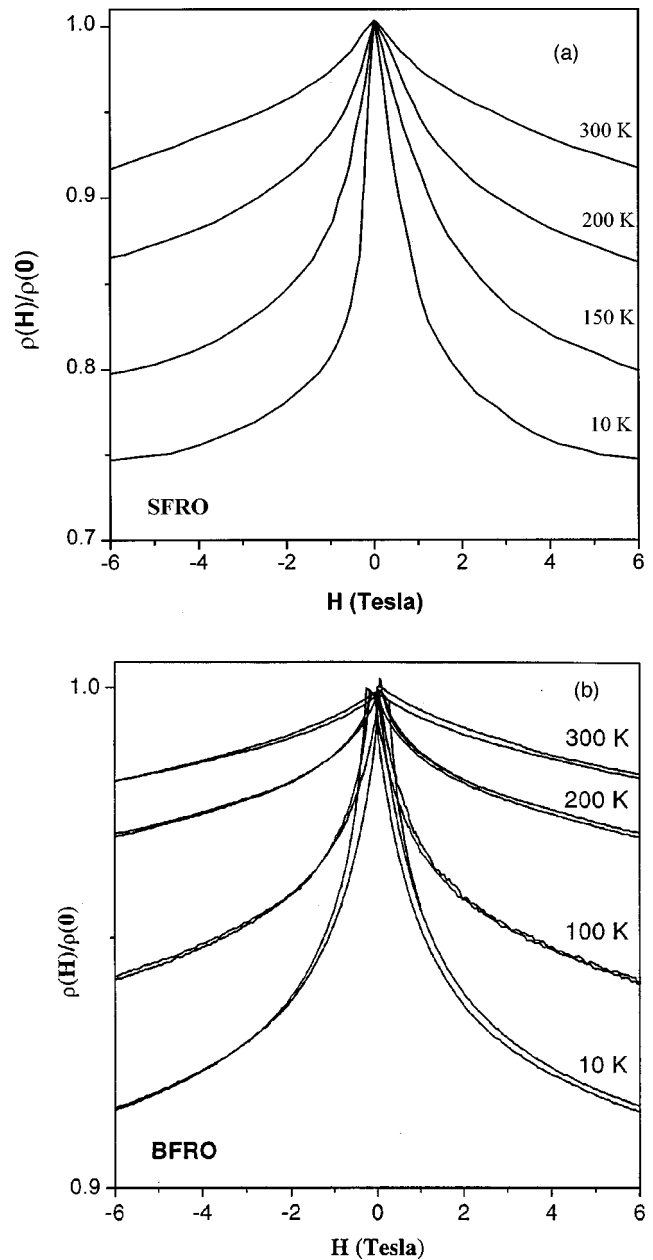
$\text{Ba}_2\text{FeReO}_6$ have been interpreted as indicating an intermediate valence state between high spin Fe^{3+} and Fe^{2+} , consistent with the metallic nature of this material.⁸ The distinctly smaller isomer shift of $\text{Ca}_2\text{FeReO}_6$ clearly indicates a more positive oxidation state for iron¹⁵ than in $\text{Ba}_2\text{FeReO}_6$. Further, the hyperfine field of the Ca compound is $\sim 15\%$ more than the value for the Ba compound, which suggests that the electron spin of Fe is larger in the Ca compound than the Ba case. Taken at face value, the measurement implies that spins

FIG. 2. Structures of $\text{Ca}_2\text{FeReO}_6$ (left) and $\text{Ba}_2\text{FeReO}_6$ (right).

of the two compounds are approximately in the 5:4.4 ratio, which means that iron is almost exclusively in the high spin ($S = \frac{5}{2}$) Fe^{3+} state in $\text{Ca}_2\text{FeReO}_6$, while in $\text{Ba}_2\text{FeReO}_6$, it is in a mixed valent state that is more close to high spin Fe^{2+} ($S = 2$). Mössbauer parameters of the Sr compound are intermediate between the two, although closer to the former in terms of the valence state.

We now turn to the interpretation of the data. Band theory calculations^{1,2} suggest that the ground state of the Sr compound is ferrimagnetic metal. The majority spin band structure is insulating (gap at the chemical potential), the Fe 3d states are fully occupied, and the Re 5d states are empty, leading to a $S = \frac{5}{2}$ ferromagnetic moment on each Fe site. The minority spin band is metallic (no gap at the chemical potential) and the occupied part of the band is composed mainly of Re d states of t_{2g} symmetry. In simple terms, one has a set of $S = \frac{5}{2}$ Fe states which polarize the Re band via what one may think of as a superexchange interaction. The published band structure calculations yield a reasonable bandwidth (~ 0.5 eV) for the minority spin Re band,² but the

available papers do not say whether the bandwidth arises from a Re-Fe-Re hopping or from a direct Re-Re overlap. Our attempts to fit the published band structure to simple tight-binding models suggest that the Re-Re hopping is the

FIG. 3. Mössbauer spectra of $\text{Ca}_2\text{FeReO}_6$ (top) and $\text{Ba}_2\text{FeReO}_6$ (bottom) at 77 K.FIG. 4. Comparison of the magnetoresistance behavior of (a) $\text{Sr}_2\text{FeReO}_6$ (SFRO) and (b) $\text{Ba}_2\text{FeReO}_6$ (BFRO).

dominant effect.¹⁶ Such a hopping is not unreasonable, given that we are dealing with t_{2g} orbitals which point from one Re to another (along the face diagonal of the cubic perovskite structure) and the $5d$ orbitals which are spatially extended.¹⁷

With this in mind, we turn to the chemical effects of different A -site cations. Ca^{2+} is distinguished from Ba^{2+} by its smaller size (1.34 vs 1.61 Å for 12-fold coordination). The smaller size of Ca^{2+} distorts the structure of $\text{Ca}_2\text{FeReO}_6$ to monoclinic. In the distorted structure, Fe-O-Re angle is bent from 180 to $\sim 156^\circ$. This bending decreases the overlap of e_g Fe and Re levels with $O_{2p\sigma}$, but might not affect the mobile t_{2g} electrons so much. In the materials of interest, the Re e_g levels are empty, so it is difficult to see how this influences the physics. However, it would reduce the Re-Re overlap, by misaligning the t_{2g} orbitals. It is not clear that this would reduce the Fe-Fe superexchange, since the change in symmetry might offset the loss of electrons.

A further important issue is the monoclinic distortion induced by Ca. This will lift the degeneracy of the t_{2g} levels on the Re site, making an insulating state easier to form in the Re sublattice. Indeed, because there are two t_{2g} electrons per Re, a large enough splitting would lead to an insulating state.

The magnetoresistance of these systems shows an interesting behavior. The Ca compound did not show any significant magnetoresistance (MR) even at high fields. Hence, in Fig. 4, we compare only the MR at different temperature for the Sr and Ba compounds. It is clear that the Sr compound shows a significantly higher MR than the Ba compound under comparable conditions. Kobayashi *et al.*² attribute the MR of $\text{Sr}_2\text{FeMoO}_6$ to intergrain tunneling process based on an indirect inference derived from the effects of annealing on the MR behavior. If grain boundary is indeed the origin on large MR, it would be interesting to explore why the transport across the grain boundary is less tunable in the Ba com-

pound as compared to the Sr compound. Another possibility is that the higher MR or a higher magnetic tunability of the kinetic energy of electrons in the Sr compound could be primarily due to its being on the metal-insulator boundary between the metallic Ba compound and the insulating Ca compound. Further work is needed to sort out these issues.

IV. CONCLUSION

In conclusion, the insulating and metallic behavior of $\text{Ca}_2\text{FeReO}_6$ and $\text{Ba}_2\text{FeReO}_6$, respectively, appears consistent with the Mössbauer data which show almost exclusively a high spin Fe^{3+} state for the Ca compound and a mixed high spin $\text{Fe}^{2+}/\text{Fe}^{3+}$ state for the Ba compound. However, it is paradoxical because the Ca compound has a higher T_c —one associates a higher T_c with a stronger exchange interaction which comes from a greater virtual hopping and thus more covalency. We have argued that the crucial issues are actually the Re-Re overlap and the lattice distortion which lifts the degeneracy of the Re t_{2g} levels, and this seems to give the insulating character to $\text{Ca}_2\text{FeReO}_6$ at two $5d$ electrons per Re. It must be mentioned that the occurrence of metallic and insulating states for isoelectronic series of $A_2BB'O_6$ double perovskite as a function of A site cation has not been reported to our knowledge, although it is known among isoelectronic series of ABO_3 oxides, for example, $R\text{NiO}_3$ (R = rare earth).¹⁸

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