Characterization and electronic structure calculations of the antiferromagnetic insulator Ca$_3$FeRhO$_6$

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(Received 4 October 2006; revised manuscript received 6 December 2006; published 6 March 2007)

We investigate the antiferromagnetic insulating nature of Ca$_3$FeRhO$_6$ both experimentally and theoretically. Susceptibility measurements reveal a Néel temperature of $T_N=20$ K and an effective magnetic moment of 5.3 $\mu_B$/fu. Mössbauer spectroscopy strongly suggests that the Fe ions, located at trigonal prismatic sites, are in a 3+ high-spin state. Transport measurements display a simple Arrhenius law, with an activation energy of $\sim 0.2$ eV. The experimental results are interpreted with local spin-density approximation band-structure calculations, which confirm the Fe$^{3+}$ state, the high-spin versus low-spin scenario, the antiferromagnetic ordering, and the value for the activation energy.

DOI: 10.1103/PhysRevB.75.115105 PACS number(s): 71.20.–b, 75.25.+z, 75.10.Pq, 75.50.Ee

I. INTRODUCTION

Interest in transition-metal oxides has never been restricted to the most spectacular phenomenon of the high-$T_c$ superconductivity but also concerns, inter alia, metal-insulator transitions, colossal magnetoresistance, and magnetic and orbital orderings. Among the numerous magnetic transitions that have been studied, most of them are associated with structural transitions. In contrast, no anomalous temperature dependence of the structural parameters has been reported in the $n_i=0$ and $n_i=1$ members of the oxide family $A_{3n_i}B^{3+}O_{3n_i+6}$, which are currently attracting much attention. These $A_{3}A'B'O_{6}$ compounds crystallize in the $K_2CdCl_6$ structure, which consists of infinite chains along the $c$ axis made of a 1:1 alternation of face-shared trigonal prisms ($A'O_6$)$_{TP}$ and octahedra ($BO_6$)$_{oc}$ (see, e.g., Refs. 4–7 for a detailed discussion of the crystal structure). According to their rhombohedral symmetry, the $A$ cations separate the chains, the latter forming a hexagonal array. For such compounds, when the $A'$ trigonal prism (TP) site is occupied by a magnetic cation, this provides interesting physical properties created by the coexistence of one-dimensionality character and geometrical frustration. This is illustrated by Ca$_3$Co$_2$O$_6$, for which the ordered antiferromagnetic state below $T_N\sim 26$ K bears some similarity to the partially disordered antiferromagnetic (PDA) state, as originally proposed for $ABX_3$ frustratedly one-dimensional (1D) compounds. However, in marked contrast with the $ABX_3$ members, the intrachain coupling in Ca$_3$Co$_2$O$_6$ is ferromagnetic and the magnetic-field-induced magnetization is very spectacular. Indeed, as a function of the applied magnetic field, several magnetization jumps with a constant field spacing are observed. Besides, the saturation magnetization is larger than expected from the assumption of different spin states for Co$^{3+}$ high spin (HS) and low spin (LS) at the trigonal prismatic and octahedral sites, respectively. Nonetheless, the ferromagnetic coupling along the chains is probably related to this “spin state ordering,” the latter resulting from the different crystalline electrical fields in each Co$^{3+}$ polyhedron. Such a coupling is likely to involve both LS Co$^{3+}$ and O ions. In that respect, the different magnetic behaviors of the two isostructural compounds Ca$_3$FeRhO$_6$ and Ca$_3$CoRhO$_6$ are worth mentioning. In the latter, the ferromagnetic intrachain coupling is expected as Rh$^{3+}$ is isoelectronic to Co$^{3+}$ ($3d^9$), whereas the global magnetic behavior of Ca$_3$FeRhO$_6$ appears to be antiferromagnetic although Fe$^{3+}$ ($3d^5$) or Fe$^{2+}$ ($3d^6$) are both HS cations with large $S$ values (5/2 or 2). Such different background states for the Ca$_3$MRhO$_6$ one–dimensional (1D) compounds (with $M$=Fe and $M$=Co) suggest subtle changes of the electronic structure.

In Ca$_3$FeRhO$_6$, contradicting results have been reported for the oxidation states of iron and rhodium cations, which add more complexity to the interpretation. In order to shed light on the magnetic and electronic behaviors of Ca$_3$FeRhO$_6$, we compare, in continuation of previous work, results of band-structure calculations to the electrical and magnetic properties, together with Mössbauer spectroscopy measurements.

II. EXPERIMENTS

The polycrystalline sample of Ca$_3$FeRhO$_6$ was prepared by mixing the precursors CaO, Fe$_2$O$_3$, and Rh$_2$O$_3$ in the molar ratios of 3:0.5:0.5. The thoroughly mixed powder, pressed in bars ($\sim 2 \times 2 \times 10$ mm$^3$), was first heated at 900 °C for 24 h and then at 1250 °C for a 3 $\times$ 24 h period with intermediate x-ray controls. The crystallinity and purity of the obtained black and dense (>90%) product were checked by x-ray powder diffraction. The diffraction peaks have been indexed in the space group $R\bar{3}c$ with $a=9.1970(1)$ Å and $c$
=10.7888(1) Å in agreement with Refs. 15 and 16, allowing us to refine the 3:1:1 ratio for the cation Ca:Fe:Rh with an uncertainty of approximately 3% which is acceptable in all respects. Besides, small intensity peaks were also found, which could be attributed to Ca$_3$Fe$_2$O$_5$ (less than 1%). Magnetic measurements were performed with a superconducting quantum interference device magnetometer. Electrical resistivity was measured by the four-probe technique. The four electrical contacts were ultrasonically deposited on a bar. The measurements were made by using a physical properties measurement system (Quantum Design). Such resistivity measurements on dense ceramics yield good results as compared to those of crystals, as previously shown in the case of Ca$_3$Co$_2$O$_6$ polycrystalline and single crystals. 11,24 The $^{57}$Fe Mössbauer resonance spectrum at room temperature consists of a paramagnetic doublet and is consistent with the measurements reported in Ref. 17. However, the best fit was obtained with two Mössbauer components, the hyperfine parameters of which are given in Table I. The observed isomer shift value (IS=0.45±0.1 mm/s) of the main component (%=96±2) is typical of Fe$^{3+}$ ions. Its high absolute quadrupole splitting value (QS=1.20 mm/s) shows that this is not in the octahedral symmetry, and therefore the Fe ions are located in trigonal sites. For the minor Mössbauer component (%=4±2), the IS value of 0.73±0.1 mm/s rather corresponds to Fe$^{2+}$ ions. Therefore, the vast majority of iron ions in Ca$_3$FeRhO$_6$ are in the trivalent state.

### B. Transport

The second set of measurements concerns the expected localized nature of the electrical transport. Indeed, as shown in Table II, Ca$_3$FeRhO$_6$ appears far more insulating than the related Co compounds since, for instance, at 300 K, the resistivity $\rho$ for Ca$_3$FeRhO$_6$ is 160 times larger than that of Ca$_3$Co$_2$O$_6$. 24 The $T$ dependence of the resistivity confirms that Ca$_3$FeRhO$_6$ is insulating, as shown in Fig. 2. As $T$ decreases, $\rho$ increases very rapidly in Ca$_3$FeRhO$_6$, reaching the setup limit (corresponding to $\sim 10^6$ Ω) at $\sim 230$ K. For the available temperature range, the linear $\ln \rho(T^{-1})$ curve shows that a simple Arrhenius law is followed from which an activation energy of 0.2 eV can be extracted. According to both, high $\rho$ value and thermally activated behavior, it turns out that in Ca$_3$FeRhO$_6$ the charge carriers are localized. These large resistivity values cannot be explained by the presence of a secondary phase at the grain boundaries due to its small

**III. RESULTS**

**A. Magnetism**

When compared to the $T$-dependent reciprocal magnetic susceptibility curve $[x^{-1}(T)]$ of Ca$_3$Co$_2$O$_6$ as given in Ref. 25, the $x^{-1}(T)$ curve of Ca$_3$FeRhO$_6$ (Fig. 1) exhibits a much more linear behavior extending over a larger temperature range. This result reflects a lack of ferromagnetic interactions for the latter compound, as also attested by the different extrapolated temperatures for $x^{-1}(T=\theta_{CW})=0$, the Curie-Weiss temperature $\theta_{CW}$ values being $-20\pm1$ and $+40\pm1$ K for Ca$_3$FeRhO$_6$ and Ca$_3$Co$_2$O$_6$, respectively. Furthermore, in Ca$_3$Co$_2$O$_6$ a $x^{-1}$ drop below $T_C$~26 K is observed, which indicates that a net ferromagnetic state is reached: on each triangle made by three neighboring CoO$_6$ chains, two chains are antiferromagnetically coupled (zero net magnetic moment), whereas the third one exhibits a net ferromagnetic magnetization along the direction of the external applied magnetic field. In contrast, the $x^{-1}(T)$ curve of Ca$_3$FeRhO$_6$ exhibits a $x^{-1}$ increase below $\sim 20$ K indicative of a three-dimensional (3D) antiferromagnetic phase. Analysis of the slope along the linear region yields an effective paramagnetic moment $\mu_{eff}$(expt.=$(5.3\pm0.1)\mu_B$/Fe+Rh). We will refer to this experimental value in Sec. III C.

**TABLE I. Refined $^{57}$Fe Mössbauer hyperfine parameters of Ca$_3$FeRhO$_6$ at room temperature including the linewidth $\Sigma$ and %: relative intensity of the Mössbauer site.**

<table>
<thead>
<tr>
<th></th>
<th>IS (mm/s)</th>
<th>$\Sigma$ (mm/s)</th>
<th>QS (mm/s)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45 (1)</td>
<td>0.28 (1)</td>
<td>1.20 (1)</td>
<td>96 (2)</td>
<td></td>
</tr>
<tr>
<td>0.73 (1)</td>
<td>0.36 (1)</td>
<td>1.49 (1)</td>
<td>4 (2)</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE II. Comparison of the resistivities at room temperature.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ca$_3$Co$_2$O$_6$</th>
<th>Ca$_3$CoRhO$_6$</th>
<th>Ca$_3$FeRhO$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$ (300 K) (Ω cm)</td>
<td>50$^a$</td>
<td>39$^a$</td>
<td>8300</td>
</tr>
</tbody>
</table>

$^a$Reference 24.
amount, but is rather consistent with the antiferromagnetic intrachain coupling. These data for Ca$_3$FeRhO$_6$ confirm that despite the existing similarities to isostructural Ca$_3$CoRhO$_6$, i.e., the $A_{TP}$ and $B_{oct}$ crystallographic sites are also occupied by trivalent cations with high spin ($S=5/2$ for Fe$^{3+}$) and low spin ($S=0$ for Rh$^{3+}$), respectively, the nature of the magnetic interactions differs strongly.

C. Band-structure calculations

For the local spin-density approximation (LSDA) band-structure calculations, we used the augmented spherical wave (ASW) method in its scalar-relativistic implementation. In the ASW method, the wave function is expanded in atom-centered augmented spherical waves, which are Hankel functions and numerical solutions of Schrödinger’s equation, respectively, outside and inside the so-called augmentation spheres. In order to optimize the basis set, additional augmented spherical waves were placed at carefully selected interstitial sites. The choice of these sites as well as the augmentation radii were automatically determined using the sphere-geometry optimization algorithm. The Brillouin-zone integrations were performed using the linear tetrahedron method with up to 85 $k$ points within the irreducible wedge. In contrast to our previous work, we here use a new version of the ASW code, which takes the nonspherical contributions to the charge density inside the atomic spheres into account.

All calculations are based on the powder data of Niitaka et al.$^{15}$ In a first step, we performed a set of calculations, where spin degeneracy was enforced. The resulting partial densities of states (DOSs) are shown in Fig. 3. While O 2$p$ dominated bands are located in the interval from $-6.8$ to $-2.4$ eV, three groups of bands of mainly metal 3$d$ character are found at higher energies. However, the strong 3$d$-p hybridization causes large p and d contributions, respectively, above and below $-2$ eV, reaching up to 50% especially for the Rh 4$d$ states.

According to the partial Fe 3$d$ densities of states shown in Fig. 4 the trigonal crystal field at the iron sites results in a splitting into nondegenerate $3d_{3z^2-r^2}$ as well as doubly degenerate $3d_{xy,x^2-y^2}$ and $3d_{xz,yz}$ states. The Rh 4$d$ states as given in Fig. 5 experience a nearly perfect separation of the 4$d$ states...
observed high-spin versus low-spin scenario. The polarization of the latter bands is highly favorable, with the calculations. These values reflect the experimental result of obtained in close agreement with those of previous calculations.30 In a second step, spin-polarized calculations were performed leading to the observed antiferromagnetic ordering, which is by 1 mRyd/Fe atom more stable than the ferromagnetic configuration. Well-localized magnetic moments of 0.00μB (Rh), 3.77μB (Fe), 0.13μB (O), and 0.01μB (Ca) are obtained in close agreement with those of previous calculations.30 These values reflect the experimental result of low- and high-spin states at the octahedral and trigonal prismatic sites, respectively. The total moment per sublattice amounts to ±4.58μB, which might be slightly altered by the inclusion of spin-orbit coupling, which is beyond the present work. The obtained total magnetic moment per sublattice, which corresponds to the saturation magnetization, is somewhat larger than that (=4.4μB, assuming a g factor of 2) calculated from the effective moment deduced from Fig. 1.

Worth mentioning are the rather high magnetic moments at the oxygen sites arising from the strong d-p hybridization, which sum up to about 0.8μB per trigonal prism. Adding to the 3d moment, they lead to the formation of extended localized moments already observed in Ca3Co2O6.13 Our calculated 4.58μB is, consequently, in favor of the Fe3+ S=5/2 configuration from which one expects a magnetic moment of 5μB in the ordered magnetic state. The high-spin behavior at the iron sites is clearly observed in the partial DOS shown in Fig. 6, where the Fe 3d minority states display sharp peaks above EF and the spin majority states are spread over a large energy interval as a result of the strong p-d hybridization.

The antiferromagnetic order growing out of the spin-polarized calculations goes along with the opening of an insulating gap of about 0.4 eV, as revealed by Fig. 6. This value corresponds to an activation energy of 0.2 eV, which is in remarkably good agreement with the experimental value deduced from Fig. 2.

IV. SUMMARY

In summary, we have performed susceptibility, Mössbauer spectroscopy, and transport measurements on the antiferromagnetic insulating compound Ca3FeRhO6. The experimental data have been compared with LSDA band-structure calculations, and the agreement is found to be very good. In particular, the calculations confirm several experimental key results as, e.g., the charge and spin states at the Fe and Rh sites including the characteristic high-spin versus low-spin scenario, the antiferromagnetic ordering, and the activation energy.

ACKNOWLEDGMENT

This work was supported by the Deutsche Forschungsgemeinschaft through SFB 484.