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Microelectronics Journal 36 (2005) 900–906

Microelectronics Journal

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Electronic transport in one-dimensional $Ca_3Co_2O_6$ single crystal

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Available online 1 July 2005

Abstract

The electronic conductivity study of the quasi-one-dimensional $Ca_3Co_2O_6$ single crystal evidences a Variable Range Hopping - conductivity with temperature-induced crossover between 1D and 3D transport and the opening of a Coulomb gap in the d bands along with the ferromagnetic intra-chain ordering. A large negative magneto-resistance is observed at low temperatures. Both spin-dependent hopping and field-induced suppression of the Coulomb gap are discussed. The electronic hopping parameters we infer agree remarkably with the accessible Co sites. Finally, we present the first electronic noise study in a one-dimensional frustrated magnetic single crystal and we discuss the interplay between the low temperature 3D magnetic ordering and the spin-dependent hopping conductivity on the Co sites.

Keywords: Magnetization; Magnetotransport; High magnetic field; One dimensional system

1. Introduction

The $Ca_3Co_2O_6$ compound belongs to the A'_3ABO_6 formula oxides (A' = Ca, Sr…; A = Ni, Cu, Zn…; B = Co, Ir, Pt…). It consists of parallel one-dimensional $Co_2O_6^{6-}$ chains separated by Ca^{2+} ions [1–3]. The chains are built by successive alternating face-sharing CoO_6 trigonal prisms and CoO_6 octahedra along the hexagonal c-axis. The resulting short metal–metal intra-chain distance (0.28 nm) compared to the inter-chain separation (0.524 nm) strongly reinforces the one-dimensional character of the structure along the c-axis [3]. Each Co chain is surrounded by six chains constituting an hexagonal cell in the basal plane. Recent magnetic studies reveal an intra-chain ferromagnetic ordering ($T_{c1} \approx 24$ K) and a weaker anti-ferromagnetic (AF) inter-chain coupling ($T_{c2} \approx 12$ K) [4–8]. Experimental evidence of a field-induced transition from a ferrimagnetic (Fi, where only two out of three chains are oriented with the field), to a ferromagnetic state (Fo, where all chains follow the field), suggests that $Ca_3Co_2O_6$ behaves as a planar Ising-like Heisenberg AF triangular lattice where each chain acts as a single localized spin [6–8]. The triangular spin lattice with AF coupling is thought to induce a partially disordered anti-ferromagnetic (PDA) state between T_{c1} and T_{c2} and a spin frozen-like behavior at lower temperatures [6]. The Co spin state on the octahedra and trigonal prisms is still unclear, as discrepancy persists between low temperature neutron diffraction analysis and the high field magnetization values but, from the expected crystal fields, each site should have different moments [4].

In that respect, at least two different configurations have been sketched for the Co sites [4,7]: (i) Co^{III}_{oct}–d_6, low spin with $\mu \approx 0\ \mu_B$ and Co^{III}_{trig}–d_6, high spin with $\mu \approx 4\ \mu_B$ and (ii) Co^{IV}_{oct}–d_5, low spin with $\mu \approx 1\ \mu_B$ and Co^{II}_{trig}–d_7, high spin with $\mu \approx 3\ \mu_B$.

We report here unusual electronic transport properties of the $Ca_3Co_2O_6$ single crystal and their apparent association with the inter- and intra-chain magnetic ordering, the one-dimensional spin structure and Coulomb interactions among the valence electrons. The temperature dependence of the conductivity reveals a weak insulator behavior with four temperature regimes from 2 to 450 K. Conduction undergoes a dimensionality crossover from the intra-chain (1D) to a (3D) variable range hopping (VRH) transport associated with a Coulomb gap opening with energies of the order of 30 K. From the resistance fluctuations measurements, we explore the dynamics of local instabilities below the Ferromagnetic ordering.

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doi:10.1016/j.mejo.2005.05.007

2. Experimental

Needle like $Ca_3Co_2O_6$ single crystals were grown by heating a mixture of $Ca_3Co_4O_8$ and K_2CO_3, in a weight ratio 1/7, up to 880 °C for 48 h in an alumina boat in air and then cooling down to room temperature at 100 °C h^{-1}. X-ray diffraction and EDS cationic analysis confirm the rhombohedral structure and the phase stoichiometry. Magnetization and magneto-transport measurements have been performed in a 40 T pulsed magnetic field using the LNCMP (Toulouse) facilities. Special care has been taken for the electronic conductivity measurements working both in DC and AC low currents ($I<40$ nA, $J<0.2$ A m^{-2}), within the ohmic regime. Electronic noise study have been performed using the standard 4-probes DC technics, from 300 to 4 K in a 4 T super conducting coil.

3. Results and discussion

In the temperature range of anti-ferromagnetic inter-chain interactions, our magnetization measurements exhibit a step-by-step magnetization reversal with a plateau at one-third of the total magnetization (1.33 μ_B mol^{-1} of $Ca_3Co_2O_6$) (Fig. 1). This plateau reveals a magnetic transition from a partially disordered AF coupling between chains toward a field-induced ferrimagnetic state. Higher fields are required to induce a second magnetization jump corresponding to a full ferromagnetic alignment along the field. The sharpness of the magnetic transitions confirms the mono-crystalline nature of our samples with the *c*-axis parallel to the applied field. Comparable results are obtained on oriented polycrystalline $Ca_3Co_2O_6$ compounds [7] and $Ca_3Co_2O_6$ single crystals [8]. The magnetization measurements in a transversal field (not shown here) support the strong magnetic anisotropy with saturation fields larger than 30 T. The field transitions and the magnetic hysteresis in the longitudinal configuration depend on the temperature and the magnetic field sweeping rate (5–500 T s^{-1}) applied during the pulsed field in agreement with dynamic measurements [7]. On account of the large sweeping rates, we were not able to reproduce the finer detail of the magnetization at low temperatures observed by Maignan et al. [8] on single crystals. The dependence on the sweep rate indicates the predominant role of cooperative effects with slow dynamic processes ($\tau \sim 1$ ms) that govern the low temperature magnetization switch within the chains.

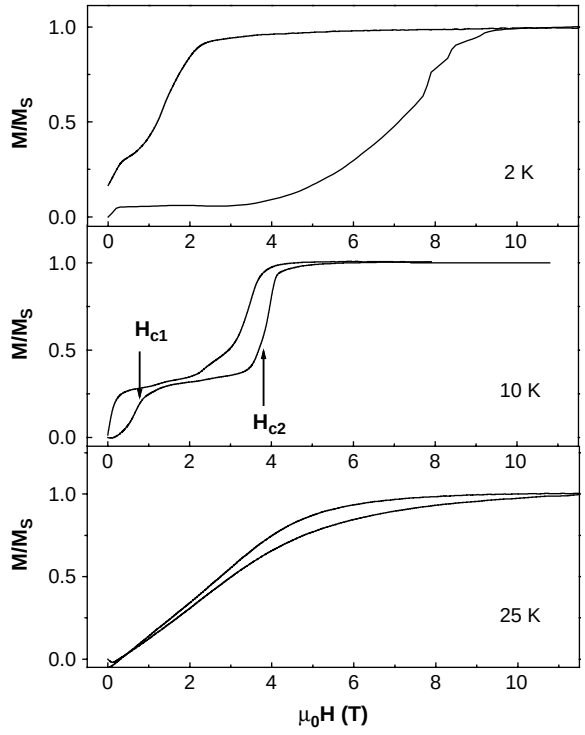

Fig. 1. Magnetization measurements in pulsed field on the $Ca_3Co_2O_6$ single crystal with *H* parallel to the *c*-axis, at 2, 10, and 25 K.

The resistivity, from 2 to 450 K, was measured along the *c*-axis (inset, Fig. 2). Our result extends preliminary measurements performed by one of us in higher temperatures [8]. A thermally activated behavior is observed over the whole temperature range with a room temperature resistivity around 4 Ω cm, far above the metallic limit. The room temperature resistivity we report is around one order of magnitude smaller than the value previously measured [8]. We attribute this difference to a substantial improvement of the sample's growth towards a grainless structure. The resistivity perpendicular to the chains at 300 K is about 10^4 times larger than the longitudinal one. A small hump on the resistivity curve occurs at 22 K corresponding to the intra-chain Fo temperature, whereas no significant change appears between the PDA phase and the frozen spin state. We shall remark that the ferromagnetic ordering within the chains does not induce a conductivity change toward more metallicity as it is usually observed in transition metal

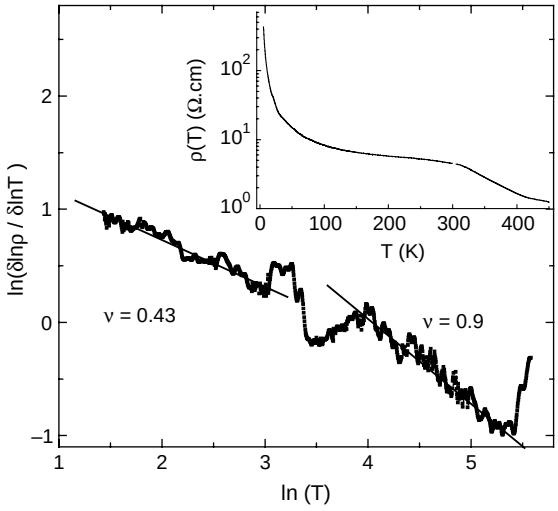

Fig. 2. The log derivative of the resistivity of the $Ca_3Co_2O_6$ single crystal measured along the chains. The slope of the fit lines equals $-\nu$ (see text). In inset, the resistivity versus temperature of the $Ca_3Co_2O_6$ single crystal.