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Abstract

We have measured the electrical resistance and the high-field magnetoresistance (MR) up to 30 T for nano-scale misfit layered compounds $Ca_{3-x}Y_xCo_4O_9$ ($x = 0, 0.1, 0.2$). The resistance shows the characteristic behaviour $\propto \exp(\sqrt{T_0/T})$ of the variable range tunnelling at low temperatures. The negative MR ratio increases remarkably with decreasing temperature and with increasing x at temperatures below 20 K. We propose that the MR in the cobaltite can be explained by the magnetic tunnelling effect.

Discovery of superconductivity in $Na_{0.35}CoO_2 \cdot 1.3H_2O$ [1] has stimulated extensive studies for cobalt oxides having a CoO_2 layered structure. In a CoO_2 layer, a two-dimensional triangular lattice of Co^{3+} and Co^{4+} ions forms a network of edge-sharing CoO_6 octahedra, which is key for unique transport and magnetic properties.

The cobaltite $Ca_3Co_4O_9$ has a nano-scale misfit layered structure composed of CoO_2 and Ca_2CoO_3 layers [2], and exhibits three magnetic transitions; a spin-state transition at around 380 K, an incommensurate spin-density-wave (IC-SDW) completed below 30 K and a transition to a ferrimagnetic state at 19 K [3, 4]. Different oxidation states +2, +3 and +4 for Co ions have been proposed to agree with the oxygen content analysis [2]. Electrical resistivity shows large anisotropy between in-plane and out-of-plane transport [2]. In-plane resistivity shows a metallic behaviour above 80 K but it turns to semiconducting below 80 K. A large negative magnetoresistance (MR) reaches 35% at 7 T at 4.2 K. Out-of-plane resistivity shows a semiconducting behaviour below 300 K and is 100–200 times larger than in-plane resistivity.

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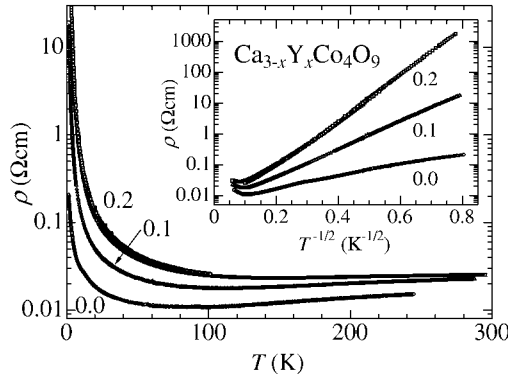
Figure 1. Temperature dependence of the electrical resistivity of $Ca_{3-x}Y_xCo_4O_9$ ($x = 0.0, 0.1,$ 0.2). The inset shows a log ρ versus $T^{-1/2}$ plot.

$Ca_3Co_4O_9$ has a large positive thermoelectric power, indicating the majority of charge carriers have hole-like character [2].

The mechanism for the transport properties of cobalt oxides is complicated because they have a rich variety of the spin-states due to the competition between crystalline field and Hund's rule coupling. The spin state and the electrical resistivity can be controlled by a perturbation such as the magnetic field and the carrier doping. In this paper, we report the electrical resistance and the high-field MR of the polycrystalline $Ca_3Co_4O_9$ by Y^{3+} substitution for the Ca^{2+} site. We discuss the tunnelling magnetoresistance (TMR) in nano-scale misfit layered cobaltite $Ca_3Co_4O_9$.

Polycrystalline samples of $Ca_{3-x}Y_xCo_4O_9$ ($x = 0, 0.1, 0.2$) were prepared by a solid-state reaction. Starting materials of $CaCO_3$, Co_3O_4 and Y_2O_3 were dehydrated at $200\,^\circ C$ for one night, mixed with a cationic composition of $(Ca, Y):Co = 3:4.1$ for 1 h, pressed into pellets and heated in air atmosphere at $910\,^\circ C$ for 24 h. Samples were checked to be a single phase from the powder x-ray diffraction. Lattice constants of $Ca_{3-x}Y_xCo_4O_9$ were not appreciably altered. This is in marked contrast to the $Ca_{3-x}Y_xCo_2O_6$ system reported by us [5]. Electrical resistance was measured by using a conventional four-probe method between 1.5 and 300 K, and MR was obtained by using a pulsed-magnet system up to 30 T at several temperatures below 25 K.

In figure 1, we show the electrical resistivity of $Ca_{3-x}Y_xCo_4O_9$ ($x = 0.0, 0.1, 0.2$) as a function of temperature. The resistivity shows a metallic behaviour at high temperatures above 100 K, but increases like a semiconductor at low temperatures. The semiconducting profile is enhanced with increasing x. As shown in the inset of figure 1, the $\exp(\sqrt{T_0/T})$ dependence of the resistivity appears at low temperatures. The parameters T_0 obtained from the least-squares fittings are 19.4, 106 and 299 K for $x = 0$, 0.1 and 0.2, respectively. The TMR in granular magnetic films also follows the $\exp(\sqrt{T_0/T})$ dependence and is explained as a variable range tunnelling (VRT) [6, 7], where $T_0 = 8\kappa s E_c/k_B$, κ is the wavevector of the tunnelling electron, s is the mean tunnelling barrier width and E_c is the average charging energy. If we apply the VRT theory to $Ca_{3-x}Y_xCo_4O_9$ extensively, the tunnelling barrier width s and/or the charging energy E_c increase with increasing x, where κ is supposed to be independent of x.

In figure 2, we show MR for $Ca_3Co_4O_9$ at 1.9, 4.2 and 10.7 K. We define the MR ratio by $1 - R(H)/R(0)$ as a measure of the MR effect. The MR ratio is 25% at 7 T (4.2 K), which is consistent with the previous report [2, 8], and becomes 50% at 30 T (4.2 K). The MR ratio at 1.9 K reaches 65% at 30 T. We consider that the spin-dependent tunnelling should be relevant
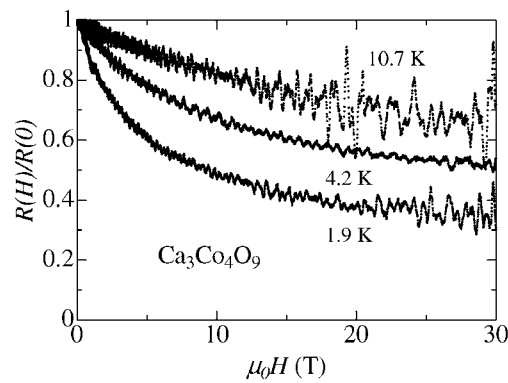
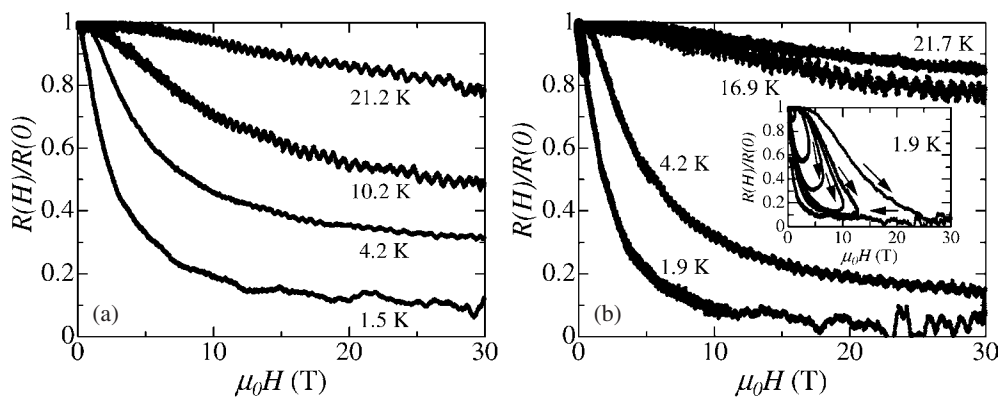**Figure 2.** Magnetoresistance of $Ca_3Co_4O_9$ at 1.9, 4.2 and 10.7 K.

Figure 3. Magnetoresistance of (a) $Ca_{2.9}Y_{0.1}Co_4O_9$ at 1.5, 4.2, 10.2 and 21.2 K and (b) $Ca_{2.8}Y_{0.2}Co_4O_9$ at 1.9, 4.2, 16.9 and 21.7 K. Large hysteresis is observed at 1.9 K as shown in the inset.

in the MR at 4.2 K in 30 T because the magnetic moments of Co ions could be aligned under a high field at low temperatures along the field direction.

In figure 3, we show that the MR ratio of $Ca_3Co_4O_9$ can be enhanced appreciably by Y substitution. The MR ratio of $Ca_{2.9}Y_{0.1}Co_4O_9$ in 30 T can be read in figure 3(a) as 70% at 4.2 K and 90% at 1.5 K. Figure 3(b) shows the MR of $Ca_{2.8}Y_{0.2}Co_4O_9$, and the MR ratio in 30 T is 87% at 4.2 K and 97% at 1.9 K. Note that the MR ratio of $Ca_3Co_4O_9$ is not significantly enhanced in the case of Sr substitution [8] in marked contrast with Y substitution. This suggests that the valence change is essential to determine the MR ratio of $Ca_3Co_4O_9$. As shown in the inset of figure 3(b), the MR of $Ca_{2.8}Y_{0.2}Co_4O_9$ shows a large hysteresis at 1.9 K. The hysteresis of $Ca_{2.8}Y_{0.2}Co_4O_9$ is dependent on the maximum pulse field in the MR measurements. The MR of $Ca_{2.8}Y_{0.2}Co_4O_9$ on decreasing field traces almost the same curve where the field changes slowly compared to the increasing field. Therefore, we consider that the hysteresis is extrinsic, and can be attributed to the capacitive action in high resistivity at zero field.

In $Ca_3Co_4O_9$, the Co^{3+} ions in a low-spin state are non-magnetic and related to an insulating phase. Substitution of Y^{3+} for Ca^{2+} causes a partial change in the valence state of the CoO_2 layer from Co^{4+} to Co^{3+} as well as the Ca_2CoO_3 layer. We expect that the effective magnetic moment and the electrical conductivity of the Y-substituted system decrease by Y substitution,

and the transition temperature for the IC-SDW state increases as was reported by Sugiyama *et al* [3, 4]. We consider that the collapsing of the IC-SDW states as well as the suppression of spin-fluctuation by strong field are not enough to explain a remarkable enhancement of the MR observed for the Y-substituted sample thoroughly. It reminds us of the MR of granular magnetic films. There, the higher-order tunnelling processes with strong Coulomb blockade are crucial at low temperatures ($T < T_0$) [9] and the MR ratio is expressed as $1 - (1 + m^2 P^2)^{-(n^*+1)}$, where $n^* \simeq (E_c/8\kappa s k_B T)^{1/2}$, m is the normalized magnetization and P is the spin polarization of the tunnelling electrons. The MR ratio increases as a function of increasing n^*. We argue that a similar physics to granular magnetic films occurs in $Ca_{3-x}Y_xCo_4O_9$ samples. There are no appreciable differences in the MR ratio between single and polycrystalline samples of the non-doped $Ca_3Co_4O_9$. This suggests that the origin for the tunnelling process lies not in the grain boundaries but in the intrinsic nature of the $Ca_3Co_4O_9$ crystal. We reasonably conclude that a charging energy E_c has to increase with x so as to be consistent with the fact that both T_0 and n^* increase with x. Since the doped electrons due to Y-substitution compensate the hole carriers, the fraction of the nano-scale conducting area in the CoO_2 layer would be reduced, and is responsible for the increase in the charging energy E_c in a conducting domain.

In conclusion, we reveal evidence for VRT in resistivity for $Ca_{3-x}Y_xCo_4O_9$ at lower temperatures. We explain that the magnetic tunnelling effect is involved in determining the remarkable MR ratio.

Acknowledgment

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