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Efros-Shklovskii-type Variable-Range-Hopping Conduction and Ferromagnetism in the Layered Cobalt Oxide $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$

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Efros-Shklovskii (ES)-type variable range hopping (VRH) conduction was found gradually transformed from the Mott-type on cooling in the title ferromagnetic compound by resistivity and thermopower studies. The crossover temperature and magnitude of the Coulomb gap are ~170 K and ~57 K, respectively, unusually large compared to those of non-magnetic disordered materials. The peculiar electronic state for the ferromagnetic Coulomb gap is probably due to interacting *d* electrons in disordered system.
Key words: Efros-Shklovskii, variable range hopping, ferromagnetic, Coulomb gap, cobalt oxides

1. INTRODUCTION

The layered cobalt oxides $Sr_2(Y,Ca)Co_2O_{7-\delta}$ are structurally analogue to the 2126-type superconducting (T_c ~ 60 K) copper oxide [1,2], and shows distinctive features of crucial interplay between structure, magnetism, and electrical conductivity. At the composition $Sr_2Y_{0.8}Ca_{0.2}Co_2O_6$, anomalous evolution of crystal structure distortion on cooling and development of anisotropic antiferromagnetic ordering are clearly coupled [3]. At the composition $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$, where the formal cobalt valence is +3.75 highest in the cobalt series thus far experimentally achieved, the compound is ferromagnetic and shows crossover phenomena between two types of VRH conductions, suggestive of association between ferromagnetism and Coulomb gap [4]. Further investigations into the compounds might help to reveal nature of interacting electrons in disordered electronic system. This article describes recent results of magnetic and electronic transport studies on $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$.

2. EXPERIMENTAL

Details of the synthesis and characterization of the polycrystalline single-phase precursor $Sr_2Y_{0.5}Ca_{0.5}Co_2O_{5.76}$ has been reported elsewhere [2,4]. The single-phase polycrystalline precursor was prepared by solid state reaction technique at 1200 °C in nitrogen for 24 hrs [2]. The precursor was mixed with $KClO_4$ and placed in a gold capsule. The capsule was compressed at 6 GPa and heated at 650 °C for 5 min, followed by a heating at 450 °C for 1 hr. The obtained pellet was hard enough to carve a bar for electronic transport measurements. The magnetic and electric properties of the sample were studied by a commercial apparatus between 5 and 400 K. The highest applied magnetic field was 50 kOe. A conventional four-probe ac technique with a gauge current of 50 μA at 1 kHz was employed for the electrical resistivity measurements. The Seebeck coefficient was measured in a commercial apparatus between 5 and 500 K.

A part of pellet was ground and then studied by powder X-ray diffraction. A tetragonal phase with lattice parameters a = 3.759(1) Å and c =20.00(1) Å was found to coexist with a small amount of KCl. Comparison of the lattice parameters with those of tetragonal phases previously reported at different oxygen contents indicates that the present phase has seven moles of oxygen per formula unit or possibly more (Fig.1) [2].

Studies on polycrystalline samples sometimes lead to the observation of a misleading temperature dependence of resistivity of materials due to external factors such as grain boundaries. In this study, the occurrence of two types of hopping conductivity was observed through

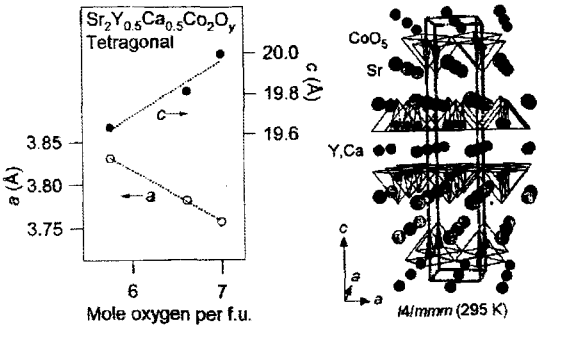

Fig.1 The lattice parameters vs. oxygen quantity in the tetragonal cobalt oxides and structural view at the composition $Sr_2Y_{0.8}Ca_{0.2}Co_2O_6$ [2].

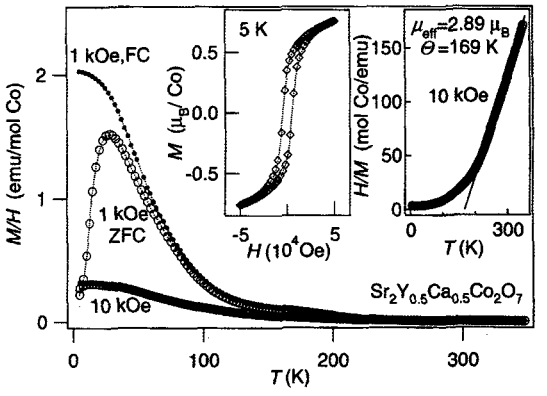

Fig.2 Temperature dependence of the magnetic susceptibility of $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$, measured at 1 and 10 kOe on heating (open circles) and cooling (closed circles). The inverse magnetic susceptibility and magnetic field dependence of magnetization at 5 K are shown in the insets. The Curie-Weiss law fit to the linear part is indicated by the solid line.

independent measurements in the same temperature regions. As the thermopower data are not expected to be as sensitive to the effects of grain boundaries as resistivity data are, the external factors in this sample therefore could be small.

3. MAGNETIC PROPERTES

The magnetic susceptibility data are shown in Fig.2 for the sample of $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$. The temperature dependence of the magnetic susceptibility was measured at magnetic fields of 1 and 10 kOe on zero field cooling and field cooling. The data for the magnetic field dependence of the magnetization at 5 K are shown in the inset in Fig.2. It is clearly seen in the data that ferromagnetic components are dominant in the compound as are observed the ferromagnetic characteristic Weiss temperature and the ferromagnetic hysteresis loop at 5 K. The thermomagnetic hysteresis between zero field cooling and field cooling data observed in low temperature suggest coexisting of antiferromagnetic characters, which might disturb long range ferromagnetic order [2].

At high temperature, above 230 K, the inverse magnetic susceptibility is linearly dependent on temperature (inset in Fig.2). A fit to the Curie-Weiss law yields an effective magnetic moment of 2.89 μ_B per Co. As $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$ is electrically insulating, the observed effective magnetic moment is expected to be the average of those of localized Co^{3+} and Co^{4+} present in the ratio 1: 3. None of the combinations except the one with high-spin Co^{3+} and low-spin Co^{4+} yields an average moment close to the observed value: the calculated effective magnetic moment is 2.87 μ_B per Co at g = 2. The next and third closest values calculated on other spin-state combinations are 3.35 μ_B and 2.06 μ_B per Co, respectively, which are therefore unlikely.

4. RESISTIVITY AND THERMOPOWER

The series of $Sr_2(Y,Ca)Co_2O_{7-z}$ never go into a conducting state [2,4]. For the title compound $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$, the resistivity at room temperature, approximately 2×10^{-1} ohm-cm, is still two orders of magnitude larger than what is expected for a material which is approaching metallic behavior. A plot of the resistivity data of $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$ shows a linear part below approximately 30 K (Fig.3a). The temperature dependence of the Seebeck coefficient for $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$ is approaching a constant with decreasing temperature below ~30 K (Fig.4a). The observed temperature dependence of the transport properties is in agreement with those expected for VRH conduction where Coulomb correlation between localized electrons are not insignificant, as proposed by Efros and Shklovskii [5]. Whichever the effective dimensionality of the electronic state of $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$, either two or three, a temperature independent Seebeck coefficient and a linear dependence of logarithmic resistivity to the -1/2th power of temperature are expected [6-8].

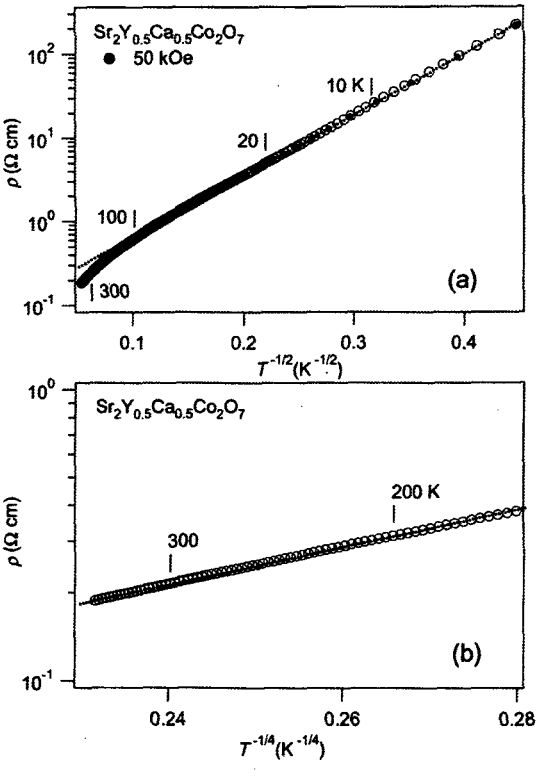

Fig.3 (a) Temperature dependence of the resistivity of $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$ measured with and without a magnetic field of 50 kOe. The data are shown as logarithmic ρ vs. $T^{-1/2}$ and (b) $T^{-1/4}$ plots. Dotted lines indicate linear parts.

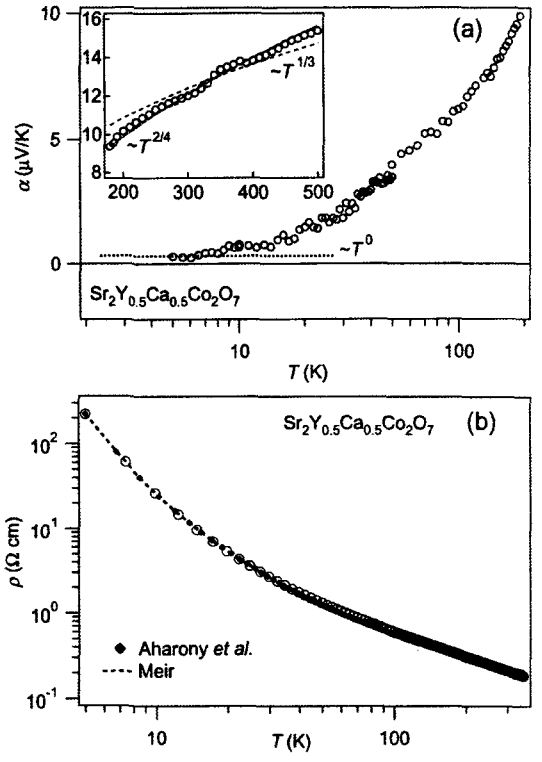

Fig.4 (a) Temperature dependence of the thermoelectric coefficient of $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$. Dotted and broken curves and dotted line indicate the ideal temperature dependence to the nth power [n = 0 (thick dotted line), 1/3 (broken curve), and 2/4 (thin dotted curve)]. (b) Broken and filled lozenge curves are calculated using theoretical models for crossover between Mott- and ES-VRH resistivity [12,15].

Above approximately 200 K, on the other hand, a Mott-type VRH conduction [9] was found in $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$ as observed in a verity of disordered materials, in which believed Coulomb correlation among electrons are not significant. The resistivity in this temperature regime varies as what was expected for the disordered materials as shown in Fig.3b. At the same time, the thermoelectric coefficient goes as the 2/4th power of temperature, as indicated by a fit to the thin dotted curve (inset in Fig.4a): For the fitting, $\alpha = C \times T^{2/4}$, where C = 0.6994 is the only adjustable parameter (the form $\alpha = C' \times T^{1/3}$ does not fit the data). For 2D (d = 2) and 3D (d = 3) Mott-VRH thermopower, a temperature dependence to the $(d-1)/(d+1)$th power is expected, where d is the dimensionality, if the material has a constant density of localized states near the Fermi level [6-10]. The agreement of the curve with the thermopower data indicates that the effective dimensionality of the Mott-VRH state of the layered compound $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$ is 3D. Although $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$ is structurally 2D, 3D VRH conduction probably appears in the high temperature region because the optimum hopping distance exceeds the inter-layer distance ~10 Å.

Temperature-dependent preexponential factor in the Mott-VRH resistivity model is expected if electronic transport was affected by association with such as phonon or polaron [11]. The thermopower (Fig.4a) and resistivity (Fig.3b) data, however, show clear $\sim T^{2/4}$ and $\sim \exp(T^{-1/4})$ dependence, respectively, as expected with temperature-independent preexponential, suggesting the association is insignificant.

To characterize the thermally induced transformation between ES- and Mott-VRH conduction in $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$, several theoretical models for the crossover in VRH resistivity was employed. The following, proposed by Aharony *et al.*, were applied to analyze the resistivity data [12]:

$$\ln(\rho / \rho_0) = A f(T/T_x), \quad (1)$$

where A and T_x are scale factors depending on

Materials	T_{Mott} (K)	T_{ES} (K)	T_{cross} (K)	Δ_{CG}/k_B (K)	Ref.
$Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$	8 600(500)	300(10)	170(30)	57(5)	This work
In_xO_y amorphous film	27 500	352	71.9	39.8	[13]
n-GaAs (at B = 0 T)	50.5	6.65	14.0	2.41	[14]
Si:B	1 220	18.8	4.64	2.33	[15,16]
Si:As (ion-implanted)	420	11.2	4.78	1.83	[17]
n-CdSe ($N = 2.18 \times 10^{17}$cm^{-3})	75.0	5.25	5.88	1.39	[12]
Ge:As ($N = 3.2 \times 10^{17}$cm^{-3})	1 400	10.5	1.26	0.909	[18]

Table I Characteristic temperatures for the VRH crossover between ES- and Mott- regimes. Arrangement of materials is in descending order of Δ_{CG}. T_{cross} and Δ_{CG} for all of the materials were calculated or re-calculated using the Eqs.3 and 4.

materials, and $f(x)$ is a universal function for VRH resistivity, which yields $f(x) \sim x^{-1/4}$ at $x >> 1$ and $f(x) \sim x^{-1/2}$ at $x << 1$,

$$f(x) = \{1+[(1+x)^{1/2}-1]/x\}/\{[(1+x)^{1/2}-1]^{1/2}\}. \quad (2)$$

Values of A of 11.3(1) and T_x of 0.53(1) were obtained from the least-squares fit indicated in Fig.4b, using Eqs.1 and 2. T_{Mott} (= A^4T_x) and T_{ES} (= $9A^2T_x/2$) were calculated from these values to be $8.6(5)\times10^3$ K and $0.30(1)\times10^3$ K, respectively [12]. T_{Mott} and T_{ES} were then used in $\rho(T) = \rho_0\exp(T_{Mott}/T)^{1/4}$ and $\rho(T) = \rho_0\exp(T_{ES}/T)^{1/2}$, respectively [13]. The crossover temperature (T_{cross}) and the Coulomb gap (Δ_{CG}) were calculated using [13]:

$$T_{cross} = 16T_{ES}^2/T_{Mott} \quad (3)$$

and

$$\Delta_{CG}/k_B = (T_{ES}^3/T_{Mott})^{0.5}. \quad (4)$$

The characteristic parameters obtained for the VRH crossover in $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$ are compared with those of previously reported materials in Table I. The present compound has unusually large values compared with those of non-magnetic semiconductors. A model for the crossover in VRH resistivity proposed by Meir was also tested (Fig.4b) [15]. The characteristic temperatures were not found to be significantly different from those of Aharony's model.

5. DISCUSSIONS AND CONCLUSIONS

In contrast to Mott insulators, in which Coulomb correlation drive the antiferromagnetic insulating properties, the present insulating cobalt oxide has significant ferromagnetic character, even though a substantial Coulomb gap is present. Although antiferromagnetic contributions likely remain in $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$, both the ferromagnetic character and the Coulomb gap could be characterized as the properties of the correlated *d* electrons in $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$. It is significant that the appearance of ferromagnetic character was found at approximately the VRH crossover temperature. To investigate the implied association between the gap and ferromagnetism, a magnetic field 50 kOe was applied in the whole temperature range studied, however, no significant difference was detected in the transport data with and without the field. In previous reports, positive and negative magnetoresistivity effects were reported on the non-magnetic VRH crossover materials with much smaller magnitude of the gap 2.41 K (at $H = 0$ Oe) or less [14,17,18]. Possibly because the gap in $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$ is large, more than one order of magnitude larger than those in the reported materials, the present experimental conditions are unfavorable for testing magnetoresistivity in $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$.

In disordered electronic system, roll of interacting electrons remains largely unexplored, while that of non-interacting those has been intensively investigated [19]. Further studies of the peculiar electronic state in $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$ with additional investigations include measurements of effective density of state and other VRH transport properties might help to reveal nature of the interacting electrons, and then answer the question how *d* electrons yield ferromagnetism coincides with the gap in $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$.

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REFERENCES

[1] R.J. Cava, B. Batlogg, R.B. van Dover, J.J. Krajewski, J.V. Waszczak, R.M. Fleming, W.F. Peck, Jr., L.W. Rupp, Jr., P. Marsh, A.C.W.P. James, and L.F. Schneemeyer, Nature 345, 602 (1990).

[2] K. Yamaura, Q. Huang, and R.J. Cava, J. Solid State Chem. 146, 277 (1999).

[3] K. Yamaura, Q. Huang, R.W. Erwin, J.W. Lynn, and R.J. Cava, Phys. Rev. B 60, 9623 (1999).

[4] K. Yamaura, D.P. Young, and R.J. Cava, Phys. Rev. B, in press.

[5] A.L. Efros, and B.I. Shklovskii, J. Phys. C 8, L49 (1975).

[6] N.V. Lien, and D.D. Toi, Phys. Lett. A 261, 108 (1999).

[7] N.V. Lien, Phys. Lett. A 207, 379 (1995).

[8] R. Rosenbaum, N.V. Lien, M.R. Graham, and M. Witcomb, J. Phys.: Condens. Matter 9, 6247 (1997).

[9] N.F. Mott, J. Non-Cryst. Solids 1, 1 (1968).

[10] M.J. Burns, and P.M. Chaikin, J. Phys. C 18, L743 (1985).

[11] B.I. Shklovskii, and A.L. Efros, Electronic Properties of Doped Semiconductors, edited by Manuel Cardona (Springer-Verlag, 1984), pp. 222-227.

[12] A. Aharony, Y. Zhang, and M.P. Sarachik, Phys. Rev. Lett. 68, 3900 (1992).

[13] R. Rosenbaum, Phys. Rev. B 44, 3599 (1991).

[14] B. Capoen, G. Biskupski, and A. Briggs, Solid State Commun. 113, 135 (2000).

[15] Y. Meir, Phys. Rev. Lett. 77, 5265 (1996).

[16] J.G. Massey, and M. Lee, Phys. Rev. Lett. 75, 4266 (1995).

[17] I. Shlimak, M. Kaveh, R. Ussyshkin, V. Ginodman, S. D. Baranovskii, P. Thomas, H. Vaupel, and R. W. van der Heijden, Phys. Rev. Lett. 75, 4764 (1995).

[18] I. Shlimak, M. Kaveh, M. Yosefin, M. Lea, and P. Fozooni, Phys. Rev. Lett. 68, 3076 (1992).

[19] E. Abrahams, P.W. Anderson, D.C. Licciardello, and T.V. Ramakrishnan, Phys. Rev. Lett. 42, 673 (1979).

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