Specific-heat evidence of strong electron correlations and thermoelectric properties of the ferromagnetic perovskite SrCoO$_{3-\delta}$

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A dense pellet of the polycrystalline SrCoO$_{3-\delta}$ ($0 \leq \delta < 0.2$) was obtained by a high-pressure method, and electronic transport properties of the stoichiometric perovskite were measured. A large electronic specific-heat coefficient was found [45.7(2) mJ mol^{-1} K^{-2}], indicating a moderate degree of electrons correlation: the mass enhancement factor was 6.1, which is higher than that for the $4d$ ferromagnetic perovskite SrRuO$_3$ (4.4). The thermoelectric properties of SrCoO$_3$ were found to be sensitive to band filling, in contrast to those of SrRuO$_3$.

The ferromagnetic perovskite SrCoO$_3$ attracts much attention due to the ferromagnetism at room temperature.[1,2] A strongly correlated nature could be essential to understand the magnetic manifestation as well as the half-metalliclike density of states at the Fermi level (E_F).[3,4] However, experimental studies of the perovskite SrCoO$_3$ seem very limited probably due to an inherent chemical problem: the compound holds robust oxygen deficiencies to influence the magnetism largely.[5]

A decade ago, an oxygen stoichiometric sample was obtained by a high-pressure method,[2] and an x-ray absorption study on it revealed that SrCoO$_3$ is in the negative-charge-transfer regime, indicating that covalence between O $2p$ holes and Co e_g states have a major impact on the magnetism.[6] Combination of the Co-$2p$ x-ray absorption study[7,8] and the band structure calculation[3,4] suggested that the magnetic ground state of SrCoO$_3$ is in the intermediate-spin state ($t_{2g}^{4} e_g^{1}$, the major configuration was $3d^6L$). While the magnetism of the oxygen stoichiometric SrCoO$_3$ has emerged to a certain degree, however, the electrical transport properties remained to be verified, as neither a high-quality single crystal nor a sufficiently dense polycrystalline pellet was attained yet. We thus focused our attention on preparing the dense pellet of high-quality polycrystalline SrCoO$_3$. As a result, we achieved it under improved synthesis condition. In this paper, we report the specific heat, the electronic resistivity, and the thermoelectric properties of the stoichiometric SrCoO$_3$.

Polycrystalline pellets of the perovskite SrCoO$_{3-\delta}$ were prepared from SrO$_2$,[9] Co$_3$O$_4$ (3N), and Co (3N). Mixtures of those at nominal compositions between SrCoO$_{2.6}$ and SrCoO$_{3.3}$ in O$_{0.1}$ step were each set in gold capsule, and those were each heated at 1450 °C for 2 h in a high-pressure apparatus, which is capable of maintaining 6 GPa during heating. The capsule was quenched in the press before releasing the pressure. The as-made sample was well sintered in a pellet shape ($\sim$5 mm in diameter and $\sim$4 mm in height) and the density was above 98% of the calculated value (5.75 g/cm^3).

All pellets were examined in an x-ray diffractometer (RIGAKU RINT2000, CuK$_\alpha$), and the x-ray diffraction profiles indicated that those were of high quality. Besides, we carefully tested a possibility of structure distortion related to CoO$_6$ tilting or defects under the high-pressure condition. However, any indications were not detected in the x-ray analysis. Perhaps, electron diffraction studies would be needed to test the possibility. Within our investigation, the cubic symmetry (Pm-$3m$) is best for the structure of SrCoO$_{3-\delta}$ under the synthesis condition.

Samples at nominal oxygen concentration of 3.4 per the formula unit or higher were prepared by adding KClO$_4$ on the same way. We would like to note that the additional samples were not employed for the electronic transport studies, as the oxygen dispenser must leave impurities in the inside of the pellet, which could possibly cause K/Cl contamination. Thermogravimetric analysis (TGA) for all the samples was conducted in a course of independent study,[10] and the 3.0 nominal oxygen sample was partially studied there; the results should not disturb the current discussion.

The magnetic susceptibility of the pellets was measured in a commercial apparatus (Quantum Design, MPMS) from 350 K to 1.8 K at 1 kOe, and the electrical resistivity (four-terminal method, ac-gage current was 1–5 mA at a fixed frequency of 30 Hz, 320 K to 5 K), the Seebeck coefficient (Constantan was used as a reference, 400 K to 10 K), and the specific heat (a time-relaxation method, 60 K to 1.8 K) were measured in another apparatus (QD, PPMS). Magnetization to 70 kOe was measured at 1.8 K in MPMS.

As the oxygen deficiency significantly impacts the magnetism of SrCoO$_{3-\delta}$,[5] we focused our efforts on the chemical issue at first. Synthesis conditions were carefully tested under the high-pressure condition, and we found a way to improve the pellet density and the oxygen-stoichiometry of SrCoO$_{3-\delta}$. The main panel of Fig. 1 shows oxygen concentration and temperature dependence of the electrical resistivity, $\rho(T)$. The set of $\rho(T)$ plots clearly indicates that the electronic state becomes metallic with increasing the oxygen concentration in good accord with results reported elsewhere.[1] The room temperature resistivity decreases with increasing the oxygen concentration, and it reaches the minimum at 3.0. Further increment of the oxygen concentration resulted in a small rigid lift of the $\rho(T)$ curve, probably due to additional scatterings.

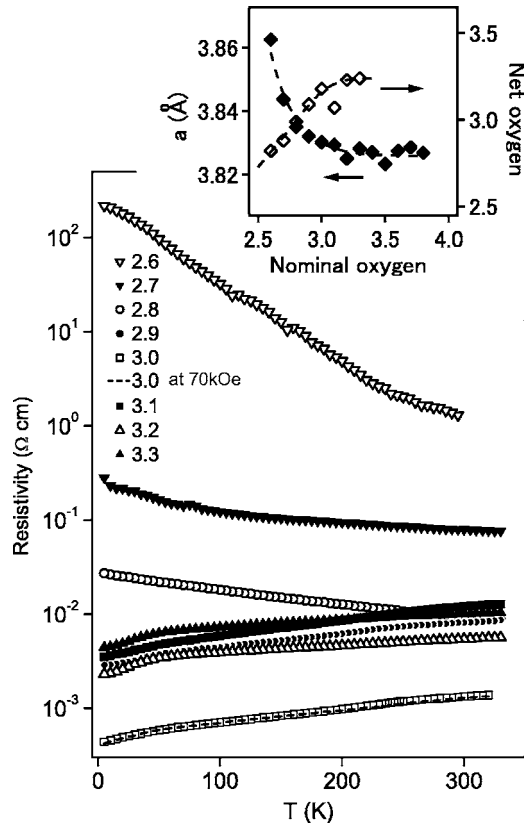While the sample prepared by an electrochemical method

FIG. 1. Temperature and oxygen concentration dependence of the resistivity of the perovskite cobalt oxide. The numbers inside indicate the nominal oxygen composition per the formula unit. Small panel shows the lattice constant of the cubic unit cell vs nominal oxygen composition, and the TGA results (Ref. 10).
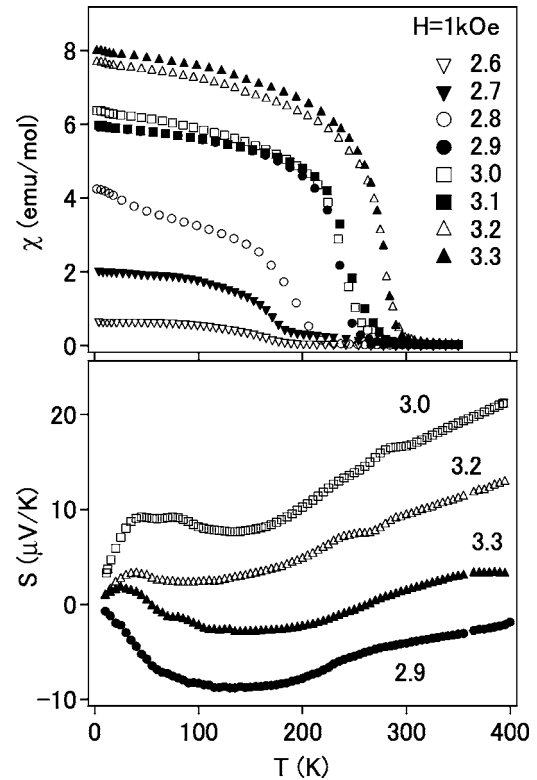

FIG. 2. (Top) magnetic susceptibility measured at 1 kOe on cooling and (bottom) the thermopower of the dense polycrystalline pellets. The numbers inside indicate the nominal oxygen composition per the formula unit.

was indeed metallic, however, the resistivity was ~ 0.03 Ω cm at room temperature, which is more than one magnitude higher than the present data.[1] The results thus indicate that the synthesis method is highly effective in reducing the degree of extra electron scatterings.

The inset of Fig. 1 shows varieties of the cubic lattice parameter and the TGA results (net oxygen, taken from Ref. 10), suggesting that the real oxygen content in the perovskite structure is saturated at ~ 3.2 nominal oxygen. Because the cubic perovskite structure has no space to accommodate such a large amount of excess oxygen, ~ 0.2 per the formula unit, true oxygen content could be 3.0 or possibly slight higher. As the electrical resistivity becomes minimum in the stoichiometric concentration 3.0, we thus speculate that the extra oxygen, ~ 0.2, is concentrated on the surface or grain boundaries in an undetected form.

On the other hand, an orthorhombic symmetry was found in a lower oxygen concentration elsewhere,[1] while the cubic symmetry was suggested for all the samples. The TGA data indicated that net oxygen content was 2.8 for the sample prepared at 2.6.[10] The composition mismatch could be a clue to solve the problem.

While $\rho(T)$ for the ferromagnetic perovskite SrRuO$_3$ shows a clear kink at the ferromagnetic transition temperature (T_c) whether it is single crystal[11] or polycrystalline pellet,[12] a corresponding anomaly was not obvious in the

data for SrCoO$_{3-\delta}$. The absence would suggest a qualitative difference of the critical behavior at T_c; otherwise, other scattering mechanisms are superior. Magnetoresistivity was found too small to be intensively studied over the temperature range, as shown in Fig. 1.

Temperature dependence of the magnetic susceptibility of the pellets was measured at 1 kOe on cooling and the data are plotted in the top panel of Fig. 2. A clear ferromagnetic transition near room temperature was observed: the maximum "kink point" was 292 K, slightly higher than the value reported elsewhere.[1,2] The effective Bohr magneton (μ_{eff}) was estimated to be $\sim 3.2 \mu_B$/Co (Table I) by a Curie-Weiss fit between 310 K and 390 K,[13] which suggests the $t_{2g}^4 e_g^1$ configuration for Co^{4+} in consistent with what was found elsewhere.[3,4,7,8] The Weiss temperature was indeed positive (Table I),[13] indicating that a certain ferromagnetic correlation governs the magnetism of SrCoO$_{3-\delta}$.

Magnetization curves measured at 1.8 K are shown in Fig. 3, indicating that the saturated magnetic moment of the stoichiometric pellets is $\sim 2.1 \mu_B$/Co (Table I). While an unexpected small drop at the last data point was observed (inset of Fig. 3), the reason for this is not yet known. The 2.6 and 2.7 pellets show additional hysteresis, which probably indicates additional pinning of magnetic domains. The pinning could be due to extra defects caused under the synthesis condition. Detailed study of the probable defects is left for future evaluation. The data clearly confirm that the present SrCoO$_3$ pellet is magnetically equivalent to or better than those reported elsewhere.[1,2]

TABLE I. Net oxygen quantity [TGA result (Ref. 10)] of the dense $SrCoO_{3-\delta}$ pellets, and the lattice parameters and the CW parameters of the perovskite.

Nominal	Net	a (Å)	T_c (K)	Θ (K)	$\mu_{eff}(\mu_B/Co)$
2.60	2.82	3.863(1)	182	99	2.57
2.70	2.88	3.844(1)	185	182	2.51
2.80	2.99	3.835(1)	216	222	3.95
2.90	3.09	3.832(1)	245	263	3.23
3.00	3.18	3.830(1)	258	257	2.90
3.10	3.07	3.829(1)	275	275	3.27
3.20	3.23	3.825(1)	292	260	3.09
3.30	3.24	3.828(1)	292	265	3.06

Several dense pellets of $SrCoO_{3-\delta}$ were selected; these are in the metallic composition range, for the measurement of the thermoelectric properties. We found that temperature dependence of thermopower, $S(T)$, shows rather complicated features (bottom of Fig. 2), indicating an influence of multiple contributions. To a first approximation, $S(T)$ is governed by the density of states at E_F because it is proportional to $(1/E_F)T$, if the Sommerfeld model is valid for the data.[14] However, it is not at all sufficient to understand the data. There must be other contributions, in which a naive balance of electronlike and holelike carriers in multibands structure is at least included, as evidenced by the sign switch.

The early sample shows only negative values over the temperature range (4.2 K < T < 300 K),[1] as does the 2.9 pellet, confirming the data quality. However, the 3.0 pellet, which is less influenced by extra scattering mechanisms, shows a different character at all: only positive values were obtained over the studied range. While $SrRuO_3$ shows the thermoelectric property that does not almost depend on defects and impurities,[15] the $SrCoO_{3-\delta}$ does depend on those.
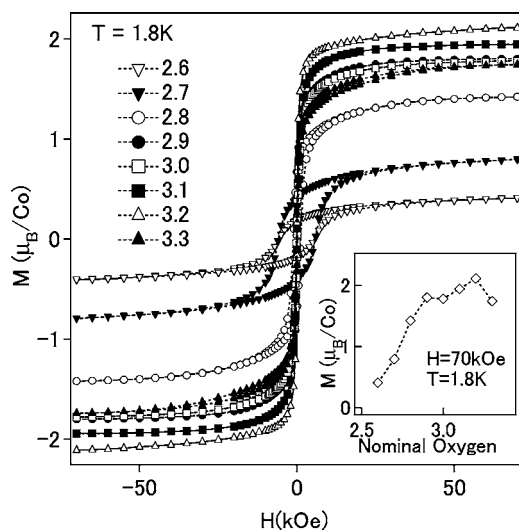

FIG. 3. Magnetization of the dense polycrystalline pellets at 1.8 K. The numbers inside indicate the nominal oxygen composition per the formula unit. Inset: variation of the magnetization at 70 kOe.
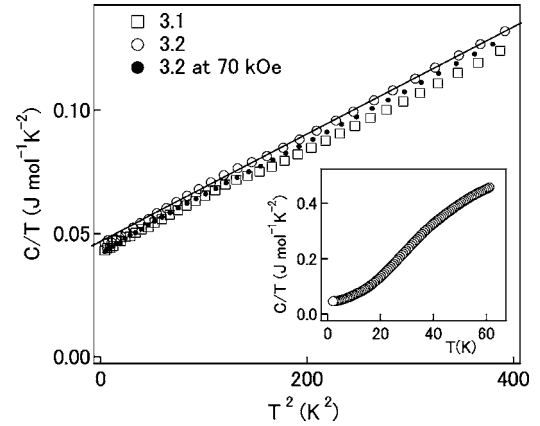

FIG. 4. Specific heat data of the $SrCoO_3$ samples, measured with (open symbols) and without (closed circle) applying a magnetic field of 70 kOe. The number indicates the nominal oxygen concentration. The solid line denotes the least-squares fit to the 3.2 data. Inset: another plot of the data.

The sensitivity of the $SrCoO_{3-\delta}$ was remarkable. The data therefore indicate that a true thermopower could be positive in a wide temperature range, suggesting that holelike carriers are dominant at the stoichiometric end of $SrCoO_{3-\delta}$.

At this moment, we are unable to reasonably explain whole parts of the thermopower of $SrCoO_{3-\delta}$ because it is technically difficult to separate each contribution definitely. A convergence of the thermoelectricity at the high-temperature limit, as found in $SrRuO_3$,[15] is not obvious for $SrCoO_{3-\delta}$, suggesting additional contributions are involved. In addition, the ferromagnetic range in $S(T)$ must be complicated somewhat by magnon drag as well as phonon drag and impurity scattering.[16] Thus, we decide to leave most of the analysis for future investigation.

Figure 4 shows the specific-heat data plotted in the C_p/T versus T^2 form. As the data points are linear, we applied the least-squares method to fit the 3.2 data with the well-established formula $C/T = \gamma + 2.4\pi^4 r N_0 k_B (1/\Theta_D^3)T^2$, where k_B, N_0, and r are the Boltzmann constant, Avogadro's constant, and the number of atoms per formula unit, respectively. The two parameters γ (electronic-specific-heat coefficient) and Θ_D (Debye temperature) are material dependent. The γ was estimated 45.7(2) mJ mol^{-1} K^{-2}, which is 6.1 times larger than the first-principals estimation [7.5 mJ mol^{-1} K^{-2} (Ref. 17)]. The Debye temperature was 353.0(6) K. The enhanced γ directly evidences a moderate degree of electrons correlation of $SrCoO_3$, which is higher than that of the significant ferromagnetic perovskite $SrRuO_3$ [the mass enhancement factor is 4.4 (Ref. 18)]. If spin fluctuations are dominant in the ferromagnetically ordered states,[19] the result may be reflected on the relatively higher $T_c \sim 290$ K than that of $SrRuO_3$. The inset of Fig. 4 shows another plot of the 3.2 data, indicating absence of anomalous feature below 60 K. The magnetic field dependence was found insignificant in the studied temperature and field range. We measured two samples (3.1 and 3.2) to secure the data quality.

In summary, the electron mass enhancement factor was

found to be 6.1, which provides a direct evidence of a moderate degree of strong electron correlation of $SrCoO_3$. The thermopower data for $SrCoO_{3-\delta}$ clearly indicate that $S(T)$ is highly sensitive to extra electron scattering mechanisms related to the oxygen defects, in contrast to that for $SrRuO_3$. The data also suggest that the true thermopower of the stoichiometric $SrCoO_3$ is positive in a wide temperature range, unlike a former report.[1] In order to accomplish an exact analysis of the ferromagnetically critical behaviors of $SrCoO_3$, further theoretical and experimental investigations are needed, including quantitative evaluation of influence of the intermediate spin state on the transport properties and a role of the nearly half-metallic characters. A large single crystal, if it becomes available, could be significant for future study.

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