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Thermoelectric power of delafossite-derived compounds, $R\text{CuO}_{2+\delta}$ ($R=\text{Y}$, La, Pr, Nd, Sm, and Eu)

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The thermoelectric power of triangle planar cuprates, $R\text{CuO}_{2+\delta}$ ($\delta \geqslant 0.5$), of the delafossite-type with various rare-earth elements R: Y, La, Pr, Nd, Sm, and Eu has been studied. The thermoelectric power coefficient (S) was found to be positive for all the samples in the temperature range between 20 and 320 K. Contrary to the semiconducting behavior in the electrical conductivity, a small value of $S \leqslant 50\ \mu\text{V/K}$ was observed at room temperature. Except for the case of $R=\text{Pr}$, S of each sample decreased nonlinearly down to around 50 K and then increased rapidly as the temperature decreased, suggesting a phase transition or crossover to the insulating phase. For the case of $\text{PrCuO}_{2+\delta}$, on the other hand, S increased monotonically with decreasing temperature. Taking into account both the carrier-diffusion and the phonon-drag process, the nonlinear temperature dependence of S between 50 and 320 K was analyzed. In spite of rather small S in magnitude, which is comparable to that of metals and/or semimetals, the observed thermopower from hopping contributions may indicate that the sample is still in the nonmetallic state. [S0163-1829(98)03213-5]

I. INTRODUCTION

A great deal of interest has accumulated in the transition metal oxides that possess antiferromagnetic exchange interactions containing magnetic frustration due to the geometrical spin configuration.[1] One group of such compounds is the delafossites $R\text{CuO}_2$ ($R=\text{Y}$, La, Pr, Nd, Sm, and Eu) (Refs. 2–6) constituted with alternating triangular planes of R^{3+} octahedra and O-Cu$^+$-O sticks. Recently, Cava *et al.*[7,8] succeeded in oxidizing ordinary delafossite-type compounds to yield new oxides with excess oxygen, i.e., $\text{YCuO}_{2+\delta}$ and $\text{LaCuO}_{2+\delta}$, in which the excess oxygen ($\frac{1}{2} \leqslant \delta \leqslant \frac{2}{3}$) is presumably located at the center of Cu triangles in the triangular Cu plane such that all the copper ions are converted to Cu^{2+} with $S=\frac{1}{2}$, and, for $\delta > \frac{1}{2}$, mobile carriers are likely induced by the excess oxygen. Previously, we synthesized delafossite-derived oxides, $R\text{CuO}_{2+\delta}$, with various rare-earth elements, $R=\text{Y}$, La, Pr, Nd, Sm, and Eu, containing excess oxygen by thermal oxidation.[9] The structure of the oxides was revealed to be of a hexagonal $2H$-polytype for the case of $R=\text{La}$, Pr, Nd, Sm, and Eu, and orthorhombic for $R=\text{Y}$.[7–10] The site for the excess oxygen in the $R\text{CuO}_{2+\delta}$ structure has not been clearly identified yet. However, it is believed[11] that, for $\delta=\frac{2}{3}$, the hexagonal phase possesses a high degree of oxygen order to form a hexagonal $\sqrt{3}\times\sqrt{3}$ superlattice, while, in the orthorhombic phase of $\text{YCuO}_{2.5}$, the excess oxygen atoms are incorporated at the center of the Cu triangles in an ordered manner so that a pair of triangles may be coupled to form a 120° O-Cu-O exchange path in the triangular Cu plane. For such a unique O-Cu-O conjunction structure, some theoretical models have been proposed: (i) Brinkman-Rice localization,[12] (ii) lack of magnetic ordering in an $s=\frac{1}{2}$ diluted Kagomé lattice,[13] and (iii) kink-antikink broken symmetry in the Majumdar model that is usually called the sawtooth lattice model[14] or the Δ-chain model.[15,16] In particular, predictions by the sawtooth lattice or the Δ-chain model for the spin excitation energy gap of $\text{YCuO}_{2.5}$ are interesting.[14–17] Some unusual magnetic behaviors, which may be attributed to a spin gap as previously done for two-leg ladder compounds,[18–20] have been observed in $\text{YCuO}_{2+\delta}$ and Ca-doped $\text{YCuO}_{2+\delta}$ (with $\delta \sim \frac{1}{2}$).[9]

According to a band calculation[21] in the absence of strong electronic correlations, the $R\text{CuO}_{2+\delta}$ compounds could be metallic conductors for δ near $\frac{2}{3}$, if the available oxygen sites in the Cu plane are fully occupied. Contrary to this expectation, all the available data for electrical resistivity (ρ) of polycrystalline samples (no resistivity data for single crystals has been reported) show that $R\text{CuO}_{2+\delta}$ are semiconductors.[7–10] Since the grain-boundary effect on resistivity might not be negligible it has not clearly determined whether the $R\text{CuO}_{2+\delta}$ compounds are intrinsically semiconducting or metallic. On the other hand, thermoelectric power data is considered to provide us with more reliable data on the transport properties, because the temperature gradient is less affected by the grain boundary. However, to our knowledge, thermoelectric data for the $R\text{CuO}_{2+\delta}$ compounds have not been reported. Lastly, we discuss the carrier scattering mechanism in the $R\text{CuO}_{2+\delta}$ compounds in comparison with some theoretical models.

II. EXPERIMENTAL

Polycrystalline samples of $R\text{CuO}_2$ ($R=\text{La}$, Pr, Nd, Sm, and Eu) delafossites were prepared by a solid-state reaction technique from reagent grade R_2O_3 and Cu_2O powders. The powder mixtures were pressed into pellets and sintered at 900–1075 °C for 12–24 h in a vacuum furnace with molybdenum heaters. The synthesis of the $YCuO_2$ sample was not straightforward. First, an intermediate reactant $Y_2Cu_2O_5$ (Ref. 22) was synthesized from reagent-grade Y_2O_3 and CuO powders by firing at 1000 °C for 80 h in air. After grinding, the calcined $Y_2Cu_2O_5$ powder was pressed into pellets and sintered at 1175 °C for 16 h in N_2/60–100 ppm O_2 gas mixture. In order to produce bulk delafossite-derived oxides with excess oxygen, i.e., $R\mathrm{CuO}_{2+\delta}$, quite long for post-annealing periods (usually $\sim$96 h) were required at 380–450 °C in flowing O_2 gas. Powder x-ray diffraction was used to confirm the phase content and to determine the lattice constants. All the samples except the one with $\mathrm{R}=\mathrm{Y}$ were found to be nearly single phase of the aforementioned hexagonal structure. Single-phase $\mathrm{YCuO}_{2+\delta}$ samples could not be obtained by the preparation method stated above, but the Y-Cu-O bulk product always contained a secondary phase, i.e., a higher polytype of $3R$-$\mathrm{YCuO}_{2+\delta}$ that was identified for the first time in Refs. 3, 7, and 9. The oxygen content of the samples was analyzed by a thermogravimetric hydrogen reduction (H_2/TG) method. Note that, the accuracy of the oxygen content determined by this method is ± 0.03 oxygen atoms per formula unit.[23] The preparation, structural data, and physical properties of the samples are described in detail elsewhere.[9]

The thermoelectric power was measured by a dc method in the temperature range between 20 and 320 K. The temperature gradient (ΔT) over the sample was measured using two pairs of copper-constantan thermocouples. Electrical contacts with low resistance were made using commercial gold paste (ULVAC Au-001T). The magnitude of ΔT was kept at $\sim$0.4 K throughout the measurement. To eliminate the effects from the reference leads (Cu wires), the absolute thermoelectric power of Cu was subtracted from the measured thermoelectric voltage.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the temperature dependence of thermoelectric power (S) for the $R\mathrm{CuO}_{2+\delta}$ ($R=\mathrm{Y}$, La, Pr, Nd, Sm, and Eu) samples. The sign of S was positive for all the samples in the temperature range between 20 and 320 K. Therefore, the dominant charge carriers are most likely holes. The magnitude of S was quite small for all the $R\mathrm{CuO}_{2+\delta}$ samples ($\leqslant 50\ \mu$V/K at room temperature). Especially, S for $\mathrm{EuCuO}_{2.65}$ was as low as $\sim 10\ \mu$V/K. Such small values of S are inherent to metallic and/or semimetallic conductors. The S vs T curves for all the other samples but $\mathrm{PrCuO}_{2.62}$ are very similar. That is, as temperature decreases the magnitude of S decreases first nonlinearly, exhibits a minimum at a temperature between 60 and 40 K, and then suddenly starts to increase rapidly to indicate an insulating nature. For example, in the case of $R=\mathrm{La}$, S decreased from 43 to 3.5 μV/K, and then increased rapidly up to $\sim 100\ \mu$V/K at temperatures below 40 K, as shown in the inset of Fig. 1(a). Note that, such minima in S were observed at 50, 45, 47.5, 52.5, and 60 K for $\mathrm{LaCuO}_{2.64}$, $\mathrm{NdCuO}_{2.62}$, $\mathrm{SmCuO}_{2.63}$, $\mathrm{EuCuO}_{2.65}$, and $\mathrm{YCuO}_{2.58}$, respectively. However, in $\mathrm{PrCuO}_{2.62}$, S increased with decreasing temperature rather rapidly as compared with other samples [Fig. 1(b)]. As shown in the inset of Fig. 1(b), a linear dependence of S on T^{-1} is observed at temperatures above $\sim$200 K. The temperature dependence of S of each sample is discussed in more detail in the following.

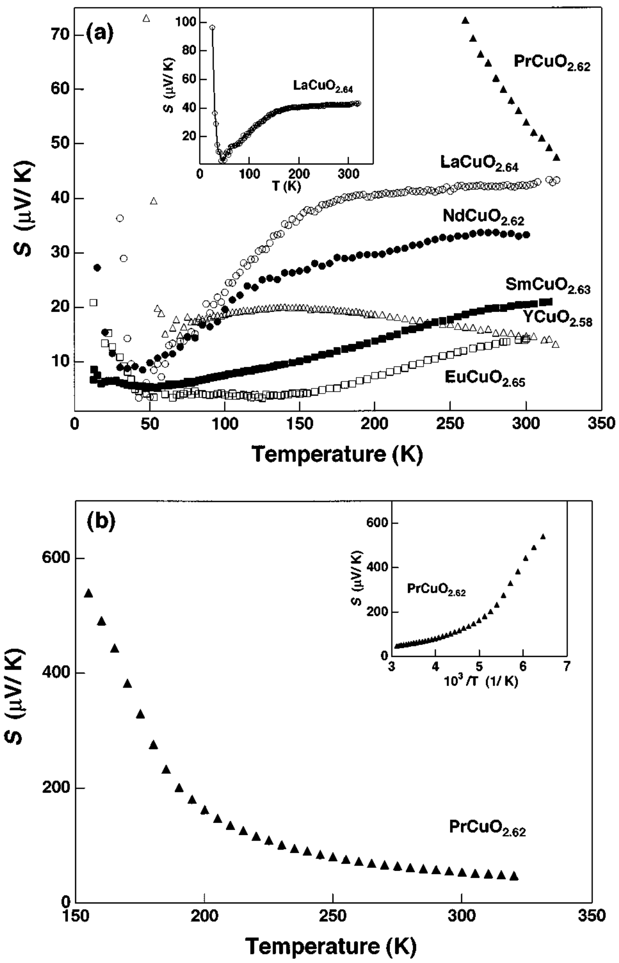

FIG. 1. (a) Temperature dependence of thermoelectric power (S) of delafossite-derived oxides $R\mathrm{CuO}_{2+\delta}$ ($R=\mathrm{Y}$, La, Pr, Nd, Sm, and Eu). Note that $\mathrm{YCuO}_{2.58}$ sample included a minor impurity phase of $3R$-polytype. Inset: S vs T curve for $\mathrm{LaCuO}_{2.64}$ in full scale. (b) Thermoelectric power of $\mathrm{PrCuO}_{2.62}$ as a function of temperature. The relationship between S and T^{-1} is shown in the inset.

In Figs. 2(a), 2(b), and 2(c), quantities, $(a/\sqrt{3})$, S, and ρ, respectively, are plotted for $R\mathrm{CuO}_{2+\delta}$ samples in terms of the rare-earth ionic radius, r_R.[24] Note that, quantity $(a/\sqrt{3})$ represents the in-plane Cu-Cu distance, in which a is the lattice constant of the hexagonal structure. The shrinkage in $(a/\sqrt{3})$ with decreasing r_R [as shown in Fig. 2(a)] is expected to result in an increase in the degree of hybridization between Cu $3d$ and Cu $3d$ orbital, or between Cu $3d$ and O $2p$ orbital, as in the case of Ti_2O_3 of the corundum structure.[25] According to photoabsorption data,[7] the itinerant holes in both $\mathrm{YCuO}_{2+\delta}$ and $\mathrm{LaCuO}_{2+\delta}$ possess more Cu $3d$ character, and the overlap between the O $2p$ and Cu $3d$ orbital is small. In our previous work on a series of polycrystalline $R\mathrm{CuO}_{2+\delta}$ ($R=\mathrm{Y}$, La, Pr, Nd, Sm, and Eu) samples,[9] electrical resistivity (ρ) was found to exhibit semiconducting behavior at temperatures below 325 K, in agreement with the data by Cava *et al.*[7,8] for $\mathrm{YCuO}_{2+\delta}$ and $\mathrm{LaCuO}_{2+\delta}$. Note

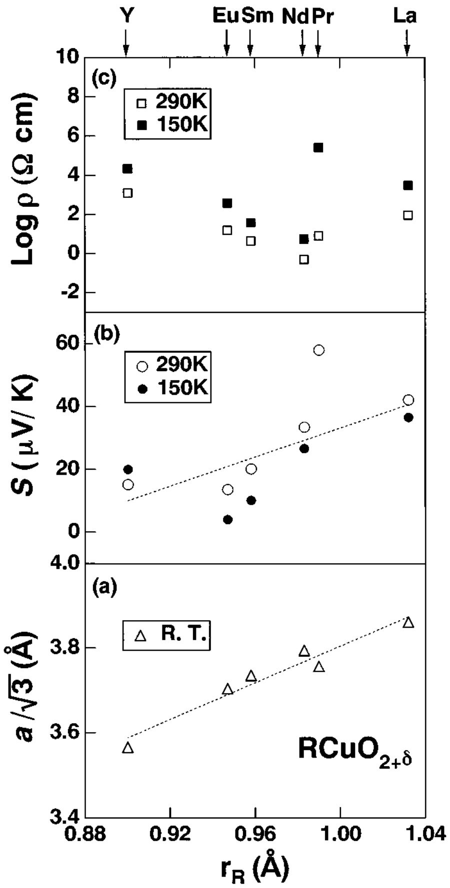

FIG. 2. Dependence upon the rare-earth ionic radius r_R of the rare-earth element R of (a) $a/\sqrt{3}$ (where a is the lattice constant of hexagonal unit cell), (b) S (the Seebeck coefficient), and (c) ρ [the resistivity (as given in Ref. 9)] of compounds $R\mathrm{CuO}_{2+\delta}$.

that, as seen in Fig. 2(c), the magnitude of ρ varies in the range of $\sim 10\ \Omega$ cm to $\sim 10^5\ \Omega$ cm, being nearly independent of R. This tendency indicates that the grain-boundary effect is significant and might dominate the resistivity. On the other hand, the magnitude of S at 290 K decreases pseudolinearly as r_R decreases from 1.032 Å for La^{3+} to 0.9 Å for Y^{3+} (Ref. 24) (except in the case of $R=\mathrm{Pr}$), which may be explained by an orbital hybridization as previously mentioned.

Now, we discuss the reason why the thermoelectric power (S) exhibits a complicated temperature dependence. Quantity S usually consists of three main contributions: (1) thermal diffusion of conduction electrons, S_d, (2) phonon drag, S_p, and (3) magnon drag, S_m. As a first approximation, the three contributions are thought to be independent of each other. It is known that the phonon drag is suppressed by a certain structural disorder but enhanced in a situation when the carrier density is low.[26] Furthermore a peak is observed for $|S_p|$ in the temperature range between $\theta_d/10$ and $\theta_d/5$ (Ref. 27) where θ_d is the Debye temperature. By means of specific-heat measurements,[28] θ_d was reported at 284 and 375 K for $\mathrm{LaCuO}_{2.64}$ and $\mathrm{YCuO}_{2.55}$, respectively. Therefore, a phonon-drag peak could be observed at a temperature around $\leqslant 80$ K. Note that, the measured S vs T curves are nonlinear in this temperature regime. The contribution, S_m, may be ignored, because no significant magnetic ordering has been seen in $R\mathrm{CuO}_{2+\delta}$.[7–9] Now we assume that S_d and S_p are predominant, so that the total S may be expressed as

$$S=S_d+S_p. \tag{1}$$

The diffusion thermoelectric power S_d is usually described by the Mott formula[29]

$$S_d=\frac{\pi^2}{3}\frac{k_B^2T}{e}\left[\frac{d\ \ln\sigma(E)}{dE}\right]_{E=E_F}, \tag{2}$$

where k_B is Boltzmann's constant, e the elementary charge, and $\sigma(E)$ the energy-dependent conductivity. For metals possessing a spherical Fermi surface, Eq. (2) reduces to

$$S_d\propto\frac{T}{E_F}, \tag{3}$$

where E_F is the Fermi energy. In conventional metals, the magnitude of S_d is considered to be in a range from $\sim 10\ \mu$V/K to $\sim 1\ \mu$V/K for E_F ranging from 1 to 10 eV.[30] However, the data given in Figs. 1(a) and 1(b) are mostly beyond this range and therefore additional contribution should be taken into account in S. We employed a criterion of 40 μV/K, described in Ref. 31, for differentiating the itinerant state from the localized state at low doping levels within the extrinsic conduction regime. Since the magnitude of S for each $R\mathrm{CuO}_{2+\delta}$ sample (except for $R=\mathrm{Pr}$) is smaller than this criterion value in the temperature range between ~ 50 and 320 K, we may apply Eq. (3) to describe the temperature dependence of S.

The phonon-drag contribution S_p from a single band of carriers with an isotropic scattering is expressed as[27]

$$S_p\propto\frac{\tau_{px}}{\tau_{px}+\tau_{pe}}, \tag{4}$$

in which τ_{px} is a mean phonon relaxation time involving all the processes, e.g., scattering by other phonons, impurities, and defects, and τ_{pe} that associated with scattering by carriers alone. At high temperatures where $T\geqslant\theta_d/4$, e.g., 70 K for $\mathrm{LaCuO}_{2.64}$, the phonon-phonon contribution τ_{pp} is predominant so that $\tau_{px}\sim\tau_{pp}$, and τ_{pp} is proportional to T^{-1}.[27,32] In this temperature range τ_{pe} is constant and much larger than τ_{px}. Thus,

$$S_p\propto\frac{1}{T}. \tag{5}$$

Combining the diffusion term [Eq. (3)] with the phonon-drag term [Eq. (5)], we obtain a simple relation valid for metals at high temperatures, e.g., $T\geqslant 70$ K:[32]

$$S=AT+C\,\frac{1}{T}. \tag{6}$$

Figure 3(a) shows the relationship between quantities ST and $(T/100)^2$ for each $R\mathrm{CuO}_{2+\delta}$ sample. The ST vs $(T/100)^2$ curves are nearly linear at temperatures above ~ 200 K, but deviate from linearity below that temperature. Thus, we need consider an additional effect to the expression given by Eq.

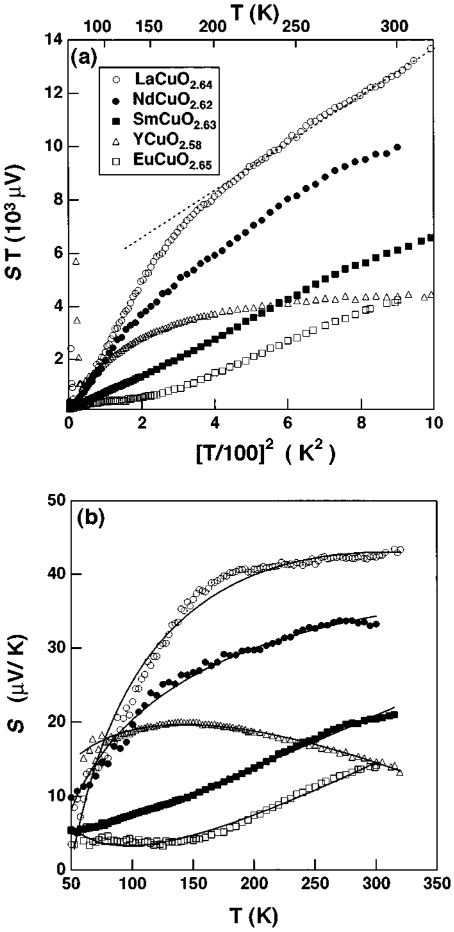

FIG. 3. (a) Relationship between ST and T^2 for $R\mathrm{CuO}_{2+\delta}$ (R=Y, La, Nd, Sm, and Eu), based upon Eq. (6) in the text. The ST vs T^2 curves deviate from linearity at low temperatures. The dashed line is drawn for eye guidance. (b) Temperature dependence of S of $R\mathrm{CuO}_{2+\delta}$ (R=Y, La, Nd, Sm, and Eu) in the temperature range between 50 and 320 K: solid lines represent fitted curves by employing Eq. (7). The fitting parameters A, B, and C are given in Table I.

(6). Based on Kaiser's model for moderately doped conductors,[33] we may modify Eq. (6) as

$$S=AT+B\sqrt{T}+C\,\frac{1}{T}, \tag{7}$$

where the first term is the linear Mott term, the second the hopping term given by Eq. (8), and the third the phonon-drag contribution with fitting constants A, B, and C, respectively. For the contribution from a variable-range-hopping mechanism, the contribution S_h was given by[29]

$$S_h=\frac{1}{2}\,\frac{k_B^2}{e}\,(T_0T)^{1/2}\left[\frac{d\ \ln N(E)}{dE}\right]_{E=E_F}\propto\sqrt{T}, \tag{8}$$

in which $N(E)$ is the density of states and T_0 is the Mott variable-range-hopping constant. Since $N(E)$ is considered to be independent of T, S_d due to hopping conduction is proportional to $\sqrt{T}$, as taken into account in the second term of Eq. (7). The fitted curves based on Eq. (7) are given in Fig. 3(b) (solid lines). It is seen that experimental data can be well represented by Eq. (7) at temperatures above 50 K. Note that, no reasonable fitting results were obtained when the third term of Eq. (7) was neglected. The fitting constants A, B, and C for Eq. (7) are summarized in Table I. The values of A and B obtained for $R\mathrm{CuO}_{2+\delta}$ are of the same order of magnitude as those of moderately doped conductors.[33] Furthermore, it is found that, for a compound, with S in the smaller range, i.e., for $\mathrm{SmCuO}_{2.63}$ or $\mathrm{EuCuO}_{2.65}$, the value of A is larger than the value of B. Therefore, the two compounds are expected to be more metallic than the other ones. For $\mathrm{LaCuO}_{2.64}$, $\mathrm{NdCuO}_{2.62}$, and $\mathrm{YCuO}_{2.58}$, the hopping term is likely predominant, though no clear reasons for this are known. The observation from hopping contributions may indicate that the sample is still in the nonmetallic state. In addition, the behavior of the S vs T curve, i.e., dS/dT, of $\mathrm{YCuO}_{2.58}$ is different from those of other compounds. Note that, the sign of constant C corresponds to that of the phonon-drag contribution.

TABLE I. Fitted constants A, B, and C for Eq. (7) for various $R\mathrm{CuO}_{2+\delta}$.

	A (μV/K^2)	B (μV/K$^{3/2}$)	C (10^3 μV)
$\mathrm{LaCuO}_{2.64}$	−0.189	6.076	−1.638
$\mathrm{NdCuO}_{2.62}$	−0.073	3.361	−0.598
$\mathrm{SmCuO}_{2.63}$	0.078	−0.170	0.133
$\mathrm{EuCuO}_{2.65}$	0.122	−1.365	0.482
$\mathrm{YCuO}_{2.58}$	−0.162	3.679	−0.164

The magnitude of S for $\mathrm{PrCuO}_{2.62}$ exceeds the criterion, i.e., 40 μV/K. Now, we try to treat this compound as a p-type semiconductor:[29]

$$S_d=\frac{k_B}{e}\left(\frac{E_C-E_F}{k_BT}+\frac{5}{2}+r\right)\propto\frac{1}{T}+\mathrm{const}, \tag{9}$$

where E_C is the bottom level of the conduction band, and r is approximated by a constant. If E_C-E_F is independent of T, S_d increases as T^{-1} increases. Actually, the S vs T^{-1} curve for $\mathrm{PrCuO}_{2.62}$ is quasilinear at temperatures above ~200 K [cf. the inset of Fig. 1(b)].

Finally, we discuss the observed rapid increase in S at temperatures below ~50 K. For each compound, the value of S tends to fluctuate due to a rather small conductivity at low temperatures. As we previously reported,[9] in $\mathrm{NdCuO}_{2.63}$, $\mathrm{SmCuO}_{2.62}$, and $\mathrm{EuCuO}_{2.65}$, an anomalous behavior was observed in the electrical resistivity at the same temperature as that where the minimum appeared in the S vs T curve. Since both the diffusion and hopping terms in Eq. (7) approach zero as $T\rightarrow 0$,[34] the rapid increase in S may not be explained unless it has a large contribution from the phonon-drag effect. Recently, Núñez-Regueiro and co-workers[13] proposed a quantum phase diagram for $R\mathrm{CuO}_{2.66}$, employing a random-phase approximation. Two different instabilities are predicted to occur in the paramagnetic phase when both intraatomic Coulomb repulsion U and interatomic Coulomb repulsion V increase. That is, for $U \geqslant W$ (W: the band width), a magnetic instability takes place and a spin-density wave (SDW) is excited. On the other hand, increasing V possibly drives a charge-density wave (CDW). Since the $R\mathrm{CuO}_{2+\delta}$ phase is considered to be close to a magnetic instability state,[12] the rapid increase in S below ~ 50 K may stem from a phase transition to a SDW or CDW state. Actually, the specific-heat data for $\mathrm{LaCuO}_{2.64}$ measured by Ramirez *et al.*[28] represented a mass enhancement, i.e., $m^*/m_0 \sim 5$. Furthermore, the possibility of a Brinkman-Rice transition driven by a moderate value of V, has been proposed for $R\mathrm{CuO}_{2.66}$ by means of a slave-boson technique.[12] However, the experimental value for the Wilson ratio[28] was nearly half of the theoretical value,[35] indicating an incompleteness of the story aforementioned.

IV. SUMMARY

We measured temperature dependence of S of various delafossite-derived oxides, $R\mathrm{CuO}_{2+\delta}$ with a rare-earth element $R=$ Y, La, Pr, Nd, Sm, and Eu. The dominant charge carriers were considered to be holes in all $R\mathrm{CuO}_{2+\delta}$ because S was positive in the temperature range between 20 and 320 K. In spite of the rather high electrical resistivity (as previously reported for polycrystalline $R\mathrm{CuO}_{2+\delta}$ samples), the magnitude of S was in a range of 10 to 50 μV/K at room temperature, showing a metallic or semimetallic behavior. The S vs T curve for each sample (except for the case of $R=\mathrm{Pr}$) at temperatures above ~ 50 K was successfully fitted by an expression which consisted of the diffusion thermopower, including a hopping contribution, for moderately doped conductors and a phonon-drag effect. The observation from hopping contributions may indicate that the sample is still in the nonmetallic state. On the other hand, $\mathrm{PrCuO}_{2.62}$ was concluded to be a p-type semiconductor. The rapid increase of S below ~ 50 K was also discussed. It was suspected to be caused by the following possible mechanisms: (i) an extremely large phonon-drag effect, (ii) a phase transition (e.g., SDW or CDW), and/or (iii) a Brinkman-Rice localization.

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