

# Impurity-induced transition and impurity-enhanced thermopower in the thermoelectric oxide $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$

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Various physical quantities were measured and analyzed for the Cu-substituted thermoelectric oxide  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ . As was previously known, the substituted Cu enhances the thermoelectric power, while it does not increase the resistivity significantly. The susceptibility and the electron specific heat are substantially decreased with increasing  $x$ , which implies that the substituted Cu decreases the effective-mass enhancement. Through a quantitative comparison with the heavy-fermion compounds and the valence-fluctuation systems, we have found that the Cu substitution effectively increases the coupling between the conduction-electron and the magnetic fluctuations. The Cu substitution induces a phase transition at 22 K that is very similar to a spin-density-wave transition.

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## I. INTRODUCTION

Recently layered cobalt oxides have been extensively investigated as promising candidates for thermoelectric material. The thermoelectric material is a material that shows large thermopower ( $S$ ), low resistivity ( $\rho$ ), and low thermal conductivity ( $\kappa$ ),<sup>1</sup> and a quantity of  $Z \equiv S^2/\rho\kappa$  called the figure of merit characterizes the thermoelectric conversion efficiency. A thermoelectric device can generate electric power from heat through the Seebeck effect, and can pump heat through the Peltier effect. Thus far oxides have been regarded as unsuitable for thermoelectric application because of their poor mobility, but some years ago Terasaki *et al.* found that a single crystal of the layered oxide  $\text{NaCo}_2\text{O}_4$  exhibits good thermoelectric performance.<sup>2</sup> Fujita *et al.* showed that the dimensionless figure of merit  $ZT$  of a  $\text{NaCo}_2\text{O}_4$  single crystal exceeds unity at  $T=1000$  K,<sup>3</sup> and Ohtaki *et al.*<sup>4</sup> measured  $ZT \sim 0.8$  at 1000 K even in the polycrystalline samples of  $\text{NaCo}_2\text{O}_4$ . Thus this compound is quite promising for thermoelectric power generation at high temperature.

Following  $\text{NaCo}_2\text{O}_4$ , other layered cobalt oxides, Ca-Co-O,<sup>5-8</sup> Bi-Sr-Co-O,<sup>9-11</sup> and Tl-Sr-Co-O,<sup>12</sup> have been found to show good thermoelectric performance. In particular, Funahashi *et al.*<sup>8</sup> showed  $ZT > 1$  at 1000 K for Ca-Co-O. The most important feature is that the  $\text{CdI}_2$ -type triangular  $\text{CoO}_2$  block is common to the layered cobalt oxides. We have proposed that the high thermoelectric performance of the layered cobalt oxides cannot be explained by a conventional band picture based on the one-electron approximation, but is understood in terms of the strong electron-electron correlation effects, similar to the case of heavy-fermion compounds. In fact the material dependence of the thermopower

quite resembles that of  $\text{CeM}_2\text{X}_2$ .<sup>13</sup>

A prime example for the difficulties of the one-electron picture is observed in the Cu-substitution effects in  $\text{NaCo}_2\text{O}_4$ .<sup>14</sup> The thermopower of  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$  is significantly enhanced, while the resistivity is nearly independent of  $x$ . This is quite surprising in comparison with normal impurity effects in a metal. The doped impurity acts as a scattering center in usual cases, and does not make a significant change in thermopower, because it is a quantity of the zeroth order of scattering time. Indeed this is what was observed in high-temperature superconductors.<sup>15</sup> Importantly, correlation effects can explain the large impurity effect on the thermopower, similar to the case of dilute magnetic alloys.<sup>16</sup> In this paper, we report on measurement of specific heat, susceptibility, Hall coefficient, and transverse magnetoresistance for  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$  polycrystalline samples, and discuss the Cu-substitution effects quantitatively.

## II. EXPERIMENT

Polycrystalline samples of  $\text{Na}_{1.2}\text{Co}_{2-x}\text{Cu}_x\text{O}_4$  ( $x=0, 0.1, 0.2$  and  $0.3$ ) were prepared through a solid-state reaction. A stoichiometric amount of  $\text{Na}_2\text{CO}_3$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{CuO}$  was mixed and calcined at  $860^\circ\text{C}$  for 12 h in air. The product was finely ground, pressed into a pellet, and sintered at  $920^\circ\text{C}$  for 12 h in air. Since Na tends to evaporate during calcination, we added 20% excess Na. Namely, we expected samples of the nominal composition of  $\text{Na}_{1.2}\text{Co}_{2-x}\text{Cu}_x\text{O}_4$  to be  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ .

The x-ray diffraction was measured using a standard diffractometer with  $\text{Fe } K_\alpha$  radiation as an x-ray source in the  $\theta-2\theta$  scan mode. The resistivity was measured through a four-terminal method, and the thermopower was measured using a steady-state technique with a typical temperature gra-

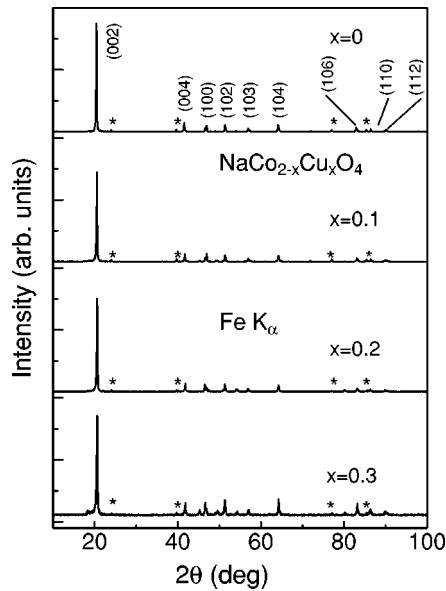


FIG. 1. The x-ray-diffraction patterns of the polycrystalline samples of  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ . The  $\text{Fe } K_\alpha$  is used as an x-ray source.

dient of 0.5 K/cm. The Hall coefficient ( $R_H$ ) and the transverse magnetoresistance were measured from 15 to 100 K in a closed cycle refrigerator inserted into a room-temperature bore of a liquid-He free superconducting magnet. To eliminate the unwanted voltage arising from the misalignment of the voltage pads, the magnetic field was swept from  $-7$  to  $7$  T with a typical period of 20 min at constant temperatures with a stability of 10 mK. The specific heat was measured using a standard relaxation method with a mechanical heat switch. The mass of the samples used for the measurement is typically 1000 mg and the heat capacity of the samples is always more than two orders-of-magnitude larger than the heat capacity of glue. The susceptibility was measured with a superconducting quantum interference device susceptometer in a magnetic field of 1 T.

### III. RESULTS

Figure 1(a) shows the x-ray-diffraction patterns of the prepared samples of  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ . Almost all the peaks are indexed as the  $\gamma$  phase,<sup>17,18</sup> though a small amount (approximately less than 5%) of unreacted  $\text{Co}_3\text{O}_4$  is observed. With increasing Cu content  $x$ , no additional peak appears, with the patterns unchanged, which shows that Cu is substituted for Co. However, the sample of  $x=0.3$  shows a higher background noise, indicating that the crystal quality becomes worse, possibly owing to the limit of solid solution with Cu.

Figure 2(a) shows the temperature dependence of the resistivity for  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ . All the samples are metallic down to 4.2 K without any indication of localization. It should be noted that the increased resistivity due to the substituted Cu is of the order of  $10 \mu\Omega \text{ cm}$  for 1 at. % Cu, which is anomalously small in the layered transition-metal oxides.<sup>19</sup> Another important feature is that the resistivity for the Cu-substituted samples shows a kink near 22 K as indicated by the dotted line. Since the temperature dependence is

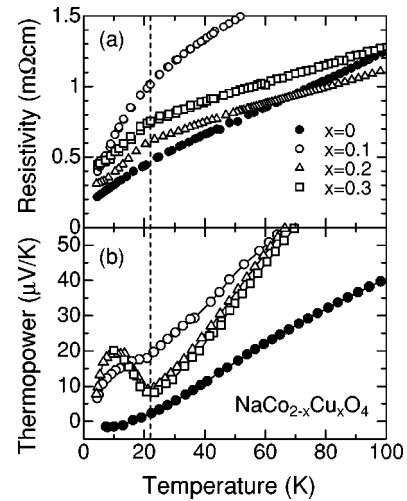


FIG. 2. (a) The resistivity and (b) the thermopower of polycrystalline samples of  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ .

steeper below 22 K, the density of states (or the carrier concentration) decreases below 22 K.

Figure 2(b) shows the temperature dependence of the thermopower for  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ . Thermopower increases with increasing  $x$  with a dip near 22 K and a peak near 10–15 K. As we previously showed in the analysis for Bi-Sr-Co-O,<sup>10</sup> the low-temperature thermopower ( $S$ ) of the layered Co oxides is determined by the diffusive term that is proportional to temperature ( $T$ ). Accordingly  $S/T$  is an essential parameter similarly to the electron specific-heat coefficient. Thus, the dip, rather than the peak, is a meaningful temperature, which corresponds to the onset of the enhancement in  $S/T$  at low temperatures. It should be emphasized that the dip temperature is nearly the same as the kink temperature for the resistivity, which strongly suggests that this temperature is related to a kind of phase transition.

Figure 3(a) shows the specific heat  $C$  for  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ . In order to emphasize the  $T$ -linear electron specific heat, we plot  $C/T$  as a function of temperature. As shown in Fig. 3(a), the  $C/T$  value at 2 K decreases with increasing the Cu content from 0 to 0.2, which means a decrease in the electron specific-heat coefficient  $\gamma$  with  $x$ . (For the sample of  $x=0.3$ , the  $C/T$  value increases again, which might be due to an extrinsic origin such as the solid-solution limit of Cu.) Since  $\gamma$  is proportional to the density of states and the mass-enhancement factor, the present results indicate that either or both decrease with the Cu substitution. As for high temperatures, all the data show a peak near 30 K which is the antiferromagnetic transition of the unreacted  $\text{Co}_3\text{O}_4$ , as shown by the solid curve.<sup>20</sup> As mentioned above, the x-ray-diffraction patterns reveal less than 5 at. % of unreacted  $\text{Co}_3\text{O}_4$ , which is consistent with the peak height of the specific heat at 30 K. We should emphasize here that the existence of  $\text{Co}_3\text{O}_4$  does not seriously affect the estimation of  $\gamma$ , because the  $C/T$  value for  $\text{Co}_3\text{O}_4$  is negligibly small at low temperatures. For  $x=0.2$  and 0.3, another peak appears in the specific heat near 22 K, which is close to the kink temperature in  $\rho$ , and the dip temperature in  $S$ . We thus conclude

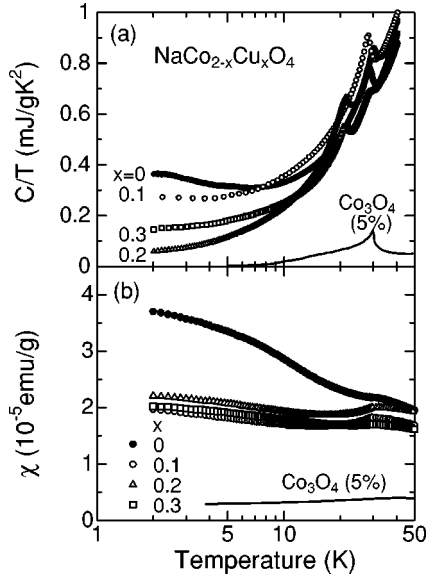


FIG. 3. (a) The specific heat  $C$  and (b) the susceptibility  $\chi$  of polycrystalline samples of  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ . Note that  $C/T$  is plotted in order to emphasize the electron specific-heat coefficient  $\gamma$ . The samples include 5% of unreacted  $\text{Co}_3\text{O}_4$ , and the data for 5%  $\text{Co}_3\text{O}_4$  taken from Refs. 20 and 21 are plotted by the solid curves.

that the 22-K anomaly comes from a (second-order) phase transition.

Figure 3(b) shows the susceptibility ( $\chi$ ) of  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ . The substituted Cu also decreases the susceptibility, indicating the decrease of the density of states and/or the mass-enhancement factor. A broad hump near 30 K is due to the antiferromagnetic transition of the unreacted  $\text{Co}_3\text{O}_4$ , as shown by the solid curve.<sup>21</sup> Interestingly, there is no anomaly near 22 K in the susceptibility, suggesting that the transition at 22 K is not the magnetic transition of impurity phases. We further note that the Curie-like contribution is absent in the susceptibility at low temperatures, which shows that magnetic impurities are unlikely to exist other than  $\text{Co}_3\text{O}_4$ . Quantitatively, the decrease of  $\chi$  by Cu is more moderate than that of  $C/T$ .  $C/T$  decreases by a factor of 10 from  $x=0$  to 0.2, whereas  $\chi$  decreases only by a factor of 2. This implies that the 22-K transition causes a dramatic reduction of the electron entropy possibly owing to a (pseudo)gap formation, while it does not alter the uniform susceptibility (i.e., the magnetic excitation in the long-wavelength limit). The nature of the 22-K transition will be discussed in the next section.

Figure 4(a) shows the Hall coefficient ( $R_H$ ) of  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ . The sign is negative below 100 K, and the magnitude is as small as  $4\text{--}6 \times 10^{-4} \text{ cm}^3/\text{C}$ . The Cu substitution does not change the magnitude very much, indicating that the carrier concentration is nearly unchanged. By contrast, it changes the temperature dependence in a complicated way, which implies that several kinds of carriers are responsible for the electric conduction. The band calculation by Singh<sup>22</sup> reveals that the two bands of different symmetries cross the Fermi level for  $\text{NaCo}_2\text{O}_4$ . (See the next section.)

Contrary to the Hall effect, the magnetoresistance is weakly dependent on the Cu substitution, as shown in Fig.

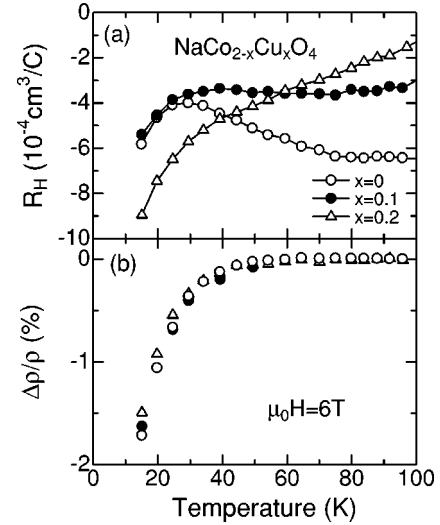


FIG. 4. (a) The Hall coefficient  $R_H$  and (b) the magnetoresistance  $\Delta\rho/\rho$  of polycrystalline samples of  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ .

4(b). By taking a closer look at the  $x$  dependence, one can see that the negative magnetoresistance is gradually suppressed by the substituted Cu. This implies that the kink of the resistivity is more or less smeared against magnetic field, which suggests that the magnetic field suppresses the 22-K transition.

#### IV. DISCUSSION

Before going into details, we will begin with a brief review on the electronic states of  $\text{NaCo}_2\text{O}_4$ . As is well known, the fivefold-degenerate  $d$  orbitals split into twofold- ( $e_g$ ) and threefold- ( $t_{2g}$ ) degenerate levels in an oxygen octahedron. In the real triangular  $\text{CoO}_2$  block, the octahedron is compressed along the  $c$  direction, and the degeneracy is further quenched, where the lower  $t_{2g}$  levels split into  $e_g$  and  $a_{1g}$  levels. The lower  $e_g$  levels correspond to the orbital spread along the  $\text{CoO}_2$  block to make a relatively broad band, while the  $a_{1g}$  orbital is spread along the  $c$  direction to make a nearly localized narrow band. Since each Co ion is  $3.5+$  with  $(3d)^{5.5}$ , the highest occupied orbital is  $a_{1g}$  in the atomic limit, and the main part of the Fermi surface consists of the narrow  $a_{1g}$  band. In the real band calculation, however, there is significant hybridization between the  $a_{1g}$  and  $e_g$  levels, and the broader  $e_g + a_{1g}$  band touches the Fermi level to make small Fermi surfaces.<sup>22</sup>

We have proposed that the electronic structure of  $\text{NaCo}_2\text{O}_4$  is similar to that of the Ce-based intermetallics, a prime example of valence-fluctuation/heavy-fermion compounds.<sup>13</sup>  $\gamma$  and  $\chi$  of  $\text{NaCo}_2\text{O}_4$  are as large as those of  $\text{CePd}_3$ . In this context, the large thermopower of  $\text{NaCo}_2\text{O}_4$  is explained in terms of a diffusive contribution of a metal with a heavily enhanced effective mass, and is roughly proportional to  $\gamma$ . In the heavy-fermion compounds, the broad conduction band crosses the Fermi energy, and the narrow (localized)  $f$  band is located below the Fermi energy. For  $\text{NaCo}_2\text{O}_4$ , the broad  $e_g + a_{1g}$  band and the narrow  $a_{1g}$  band do exist, but both cross the Fermi energy to form two kinds

of Fermi surface. Thus it is not trivial whether or not the two Fermi surfaces behave heavy-fermion-like in the charge transport. At least we can say that the two Fermi surfaces play different roles, where the Cu substitution induces different effects:  $\rho$  is weakly dependent on the Cu content  $x$ , whereas  $S$ ,  $\chi$ , and  $\gamma$  are strongly dependent on  $x$ .  $S$ ,  $\chi$ , and  $\gamma$  are basically proportional to the density of states in the lowest order, which is determined by the large Fermi surface of the  $a_{1g}$  symmetry. In contrast, the carriers on the  $e_g + a_{1g}$  band can be highly mobile, because the band is spread along the in-plane direction. In short, the  $a_{1g}$  and  $e_g + a_{1g}$  bands are responsible for the large thermopower and good electrical conduction, respectively.

Existence of the  $a_{1g}$  and  $e_g + a_{1g}$  bands was suggested from the angular dependence of the x-ray-absorption spectroscopy experiments,<sup>23,24</sup> where the valence bands of  $\text{NaCo}_2\text{O}_4$  consist of the  $a_{1g}$  and  $e_g + a_{1g}$  bands. The valence band of the less conductive Bi-Sr-Co-O is mainly composed only of the  $a_{1g}$  band, which is consistent with our speculation that the  $e_g + a_{1g}$  band is responsible for the metallic nature of  $\text{NaCo}_2\text{O}_4$ . The large Fermi surface suggested by the band calculation was not seen in the angle photoemission spectra for Bi-Sr-Co-O, which indicates that the band calculation should be modified by additional effects such as the electron-electron or electron-phonon effects.

#### A. Phase transition at 22 K

As shown in the previous section, the Cu substitution causes the phase transition at 22 K, which is probed by the jump of the specific heat, the dip in the thermopower, and the kink in the resistivity. Figure 5(a) shows the specific heat for the  $x=0.2$  sample [the same data as in Fig. 3(a)] as a function of temperature in linear scale in order to see the 22-K anomaly clearly. One feature to point out is that the entropy change of this transition is surprisingly small. As shown in Fig. 5(a), we estimated the entropy change by the area surrounded with  $C/T$  and the dotted line, which is approximately 77 mJ/Kmol, corresponding to  $0.01k_B$  per Co. Actually only 5% of the  $\text{Co}_3\text{O}_4$  impurity exhibits a specific-heat jump of the same order at 30 K.

There are two possibilities for the origin of the small entropy change. One is that the 22-K transition is something related to the impurity phase of the order of 1%. Although we cannot exclude this possibility completely, we will take the other possibility that the small entropy change is an intrinsic nature in bulk, because (i) the field dependence of  $C/T$  is different between the 22-K transition and the magnetic transition in  $\text{Co}_3\text{O}_4$  at 30 K as shown in Fig. 5(b), (ii) a possible impurity phase is a Cu-based magnetic material, which is inconsistent with no anomaly in  $\chi$  at 22 K, and (iii) the thermopower and the resistivity systematically change at the same temperature. The most familiar phase transition accompanied by a small entropy change is perhaps a superconducting transition. More generally, off-diagonal long-range order induces a small entropy change of the order of  $Nk_B T/E_F$ .

Figure 5(c) shows the  $T$ -linear term of the thermopower ( $S/T$ ) and the temperature derivative of the resistivity

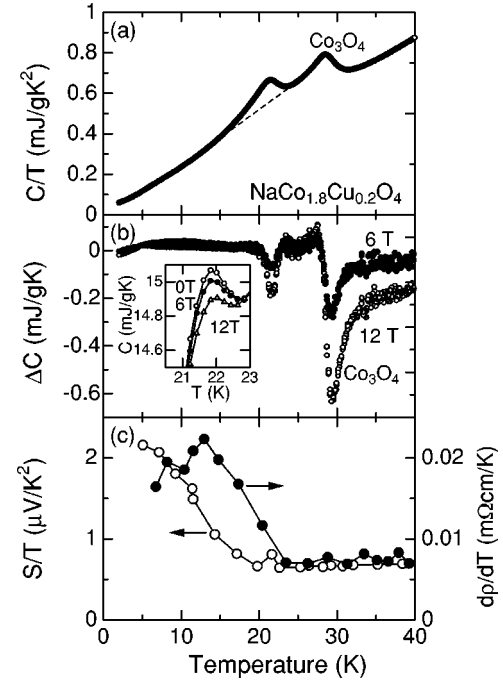


FIG. 5. Phase transition at 22 K for the Cu-substituted sample ( $x=0.2$ ). (a) Specific heat, (b) magnetospecific heat  $\Delta C(H) \equiv C(H) - C(0)$ , and (c) temperature derivative of the resistivity  $d\rho/dT$  and the  $T$ -linear coefficient of the thermopower  $S/T$ . The inset shows the magnetic-field dependence of the specific heat.

$d\rho/dT$ , both of which are inversely proportional to the Drude weight.<sup>25</sup> Their temperature dependencies are quite similar to each other, where the magnitude increases up to almost twice below 22 K. This indicates that the Drude weight decreases by 50% at low temperatures, implying the existence of a (pseudo)gap. As an off-diagonal long-range order with a gapped state, one would think of the charge-density wave (CDW) or spin-density wave (SDW) or both. The calculated Fermi surface<sup>22</sup> of the  $a_{1g}$  band is hexagon-like, which is unstable against CDW or SDW formation with the nesting vector along the  $\Gamma$ - $K$  direction. We think that the 22-K transition is SDW-like, because a CDW is insensitive to magnetic field.<sup>26</sup> Actually we can find many similarities between the 22-K transition and SDW transition: The entropy change is observed to be quite small in Cr,<sup>27</sup> YbBiPt,<sup>28</sup> and  $(\text{TMTSF})_2\text{PF}_6$ .<sup>29</sup> The resistivity shows a hump,<sup>27,28</sup> and the thermopower shows a dip at the transition.<sup>30</sup>

It is not surprising that the 22-K transition has little effect on the magnetic susceptibility. Since an SDW state is an antiferromagnetically ordered state, the magnetic excitation is gapless in principle. In fact, the SDW state of Cr exhibits a very tiny (1%–2%) change in the susceptibility at the transition temperature,<sup>27</sup> while it causes a clear hump in the resistivity.<sup>31</sup> The metallic conduction below 22 K implies that a part (approximately 50%) of the Fermi surface remains, which could smear the SDW transition. To clarify the nature of the transition, a local magnetic probe such as NMR or  $\mu\text{SR}$  (muon spin relaxation) should be employed.

#### B. Effects on the Hall coefficient and thermopower

Next we will discuss how we can understand the Cu-substitution effects on  $R_H$  and  $S$ . We should note here that



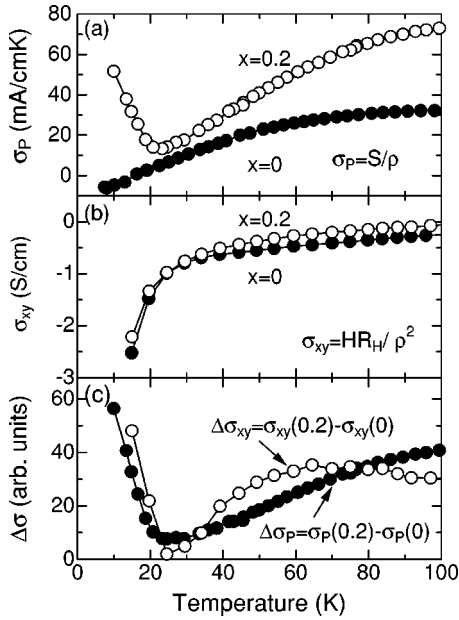


FIG. 6. (a) Peltier conductivity  $\sigma_P = S/\rho$ , (b) Hall conductivity  $\sigma_{xy} = HR_H/\rho^2$  for the  $x=0$  and  $x=0.2$  samples, and (c) the relative change in  $\sigma_P$  and  $\sigma_{xy}$  from  $x=0$  to 0.2.

the sum rules of transport parameters for a multiband system are expressed in the form of conductivities, not in the form of  $R_H$  or  $S$ . Let us denote the conductivities for the  $a_{1g}$  and  $e_g + a_{1g}$  bands as  $\sigma^a$  and  $\sigma^e$ , respectively. The total conductivity  $\sigma$  is then written as

$$\sigma = \sigma^e + \sigma^a. \quad (1)$$

Similarly, the total Hall conductivity  $\sigma_{xy}$  and the total Peltier conductivity  $\sigma_P$  are written as

$$\sigma_{xy} = \sigma_{xy}^e + \sigma_{xy}^a, \quad (2)$$

$$\sigma_P = \sigma_P^e + \sigma_P^a, \quad (3)$$

where the Peltier conductivity<sup>32</sup> is defined as  $\sigma_P \equiv S\sigma = S/\rho$ .

Figure 6(a) shows the temperature dependence of  $\sigma_P = S/\rho$  for  $x=0$  and 0.2. The Cu substitution enhances the Peltier conductivity over the measured temperature range from 4 to 100 K, indicating that the mobility is enhanced by Cu. The enhancement below 22 K is more remarkable in  $\sigma_P$  than in  $S$ , which indicates that the mobility is rapidly enhanced below the 22-K transition. Figure 6(b) shows the temperature dependence of  $\sigma_{xy} = HR_H/\rho^2$  for  $x=0$  and 0.2. The complicated change seen in  $R_H$  is converted into a simpler change in  $\sigma_{xy}$ . Although the Cu-substitution effects in  $\rho$  are quite small,  $1/\rho^2$  term moderates the difference in  $R_H$ . One can see that  $\sigma_{xy}$  is also increased by Cu over the temperature range from 15 to 100 K, as is similar to the case of  $\sigma_P$ .

Let us assume that the substituted Cu affects only the  $a_{1g}$  band. Then a difference between  $x=0$  and 0.2 is reduced to a change in  $\sigma_P^a$  and  $\sigma_{xy}^a$ . Figure 6(c) shows  $\Delta\sigma_P = \sigma_P(x=0.2) - \sigma_P(x=0)$ ,  $\Delta\sigma_{xy} = \sigma_{xy}(x=0.2) - \sigma_{xy}(x=0)$ . Most unexpectedly, the change in the Peltier conductivity  $\Delta\sigma_P$  and

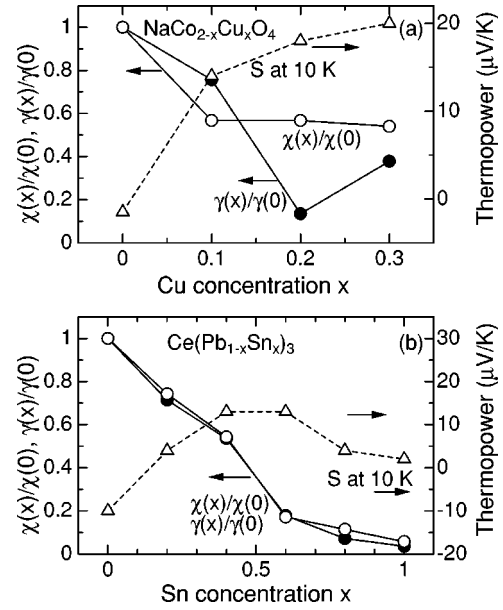


FIG. 7. (a) Cu dependence of  $\chi$ ,  $\gamma$ , and  $S$  of  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ . (b) Sn dependence of  $\chi$ ,  $\gamma$ , and  $S$  of  $\text{Ce}(\text{Pb}_{1-y}\text{Sn}_y)_3$ .

the change in the Hall conductivity  $\Delta\sigma_{xy}$  show nearly the same temperature dependence. In particular, a clear enhancement below 22 K indicates that the phase transition causes an equal impact on  $S$  and  $R_H$  in the form of the Peltier and Hall conductivities.

On the assumption that only the  $a_{1g}$  band is modified by Cu, we will consider the change in the  $a_{1g}$  band in terms of the carrier concentration  $n$ , the effective mass  $m$ , and the scattering time  $\tau$ . Then  $\sigma_P^a$  and  $\sigma_{xy}^a$  are roughly expressed as  $\sigma_P^a \sim \langle n/m^* \rangle$  and  $\sigma_{xy}^a \sim \langle \tau/m^* \rangle$ , where the average of  $\langle \dots \rangle$  is defined as  $(4\pi^3)^{-1} \int (v_F)^2 \tau \dots d^3k$ . A close similarity between  $\Delta\sigma_P$  and  $\Delta\sigma_{xy}$  implies that  $\Delta\langle \tau \rangle$  and  $\Delta\langle n \rangle$  are nearly independent of temperature. The  $T$  independent  $\Delta\langle \tau \rangle$  means the scattering time averaged in the  $a_{1g}$  Fermi surface is dominated by impurity scattering, which is consistent with the localized picture of the  $a_{1g}$  band. The positive values of  $\Delta\sigma_{xy}$  and  $\Delta\sigma_P$  suggest the increase of  $\langle 1/m^* \rangle$ . This indicates that the mass enhancement is suppressed (the mobility is enhanced) by Cu over the measured temperature range, regardless of the 22-K transition, which is consistent with the decrease in  $\gamma$  and  $\chi$  by Cu.

### C. Comparison with Ce-based compounds

Based on the heavy-fermion scenario, it seems inconsistent that the substituted Cu causes the decrease in  $\gamma$  (Fig. 3) together with the increase in  $S$  (Fig. 2). As shown in Fig. 7(a),  $\gamma$ ,  $\chi$  and  $S$  are plotted as a function of the Cu content  $x$ . Note that  $\gamma$  was estimated as  $C/T$  at 2 K, and  $\chi$  was estimated as the raw value of  $\chi$  at 2 K.  $S$  was estimated as the value at 10 K, where a linear behavior of  $S$  with  $T$  is expected for conventional metals. Although  $\gamma$  and  $\chi$  decrease with  $x$ ,  $S$  significantly increases with  $x$ , where  $S \propto \gamma T$  is no longer valid.

We should emphasize that the relationship between  $\gamma$  and  $S$  is complicated also in the Ce-based compounds. Figure

7(b) shows  $\gamma$ ,  $\chi$ ,<sup>33</sup> and  $S$  (Ref. 34) for  $\text{Ce}(\text{Pb}_{1-y}\text{Sn}_y)_3$  as a function of the Sn content  $y$ .  $\text{CePb}_3$  is in the heavy-fermion regime (low Kondo temperature) and  $\text{CeSn}_3$  is in the valence-fluctuation regime (high Kondo temperature). Thus the solid solution between Pb and Sn changes the material from the heavy-fermion to the valence-fluctuation compound, which is evidenced by the fact that  $\chi$  and  $\gamma$  monotonically decrease with  $y$ . On the other hand,  $S$  exhibits complicated  $y$  dependence.  $S$  is negative for  $y=0$ , increases with  $y$  up to 0.4, and eventually decreases from  $y=0.6$  to 1.0.

This is intuitively understood as follows. When the Kondo temperature is sufficiently low as in the case of  $\text{CePb}_3$ , the Ruderman-Kittel-Kasuya-Yosida interaction survives at low temperatures, and often causes a magnetic transition. Since the magnetic transition releases the entropy of the spin sector, the entropy per carrier (equivalently the diffusive term of the thermopower) would be suppressed against the fluctuation of the magnetic transition. On the other hand, when the Kondo temperature is high enough, the mass enhancement is severely suppressed to give a small thermopower again. Thus the thermopower would take a maximum at an intermediate value of the Kondo temperature. This is indeed what we see in Fig. 7(b), similar to the general trend of the 20-K thermopower of  $\text{CeM}_2\text{X}_2$  found by Jaccard *et al.*<sup>35</sup> We should note the reason why the SDW formation for  $x>0.1$  affects only the thermopower, and not the specific heat. Since the thermopower is the entropy per carrier, it could be affected by either carrier density or carrier entropy. Thus a small entropy change due to the SDW does not affect the specific heat, but the SDW (pseudo)gap decreases the carrier density to enhance the thermopower.

In this context, the  $\text{NaCo}_2\text{O}_4$  is located near the heavy-fermion regime, and the substituted Cu causes a decrease in the mass enhancement accompanied by an increase in  $S$ , which is consistent with the increase in the Peltier and Hall conductivities seen in the previous subsection. Although there is no microscopic relationship between  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$  and  $\text{Ce}(\text{Pb}_{1-y}\text{Sn}_y)_3$ , a close resemblance in Fig. 7 suggests that the unsubstituted  $\text{NaCo}_2\text{O}_4$  corresponds to  $y\sim 0.2$ , while  $\text{NaCo}_{1.8}\text{Cu}_{0.2}\text{O}_4$  corresponds to  $y\sim 0.4-0.6$ . We further note that the Pd-substituted  $\text{NaCo}_2\text{O}_4$  shows *negative* thermopower below 50 K, which might correspond to  $y<0.2$ .<sup>36</sup>

#### D. Order from disorder

Although the microscopic theory for the high thermoelectric performance of  $\text{NaCo}_2\text{O}_4$  is still lacking, the following features are established. (i) The mixture of  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  in the low spin state can carry a large entropy of  $k_B \ln 6$ .<sup>37</sup> (ii)  $\text{NaCo}_2\text{O}_4$  shows no structural, electric, and magnetic transitions from 2 to 1000 K.<sup>4,3</sup> (iii) From (i) and (ii), the large entropy cannot be released through phase transitions, and inevitably points to the conducting carriers forming a “heavy-fermion”-like electron.

In this respect,  $\text{NaCo}_2\text{O}_4$  is very close to the instability for various phase transitions arising from the large entropy per site. The Cu substitution enhances the instability, and eventually causes the SDW-like transition at 22 K. This type of transition is called “order from disorder,”<sup>38</sup> which has been

extensively investigated experimentally as well as theoretically. In other words, instabilities against various phases are competing or disordering in  $\text{NaCo}_2\text{O}_4$ , and any phase transitions are prohibited down to low temperatures. This does not mean that  $\text{NaCo}_2\text{O}_4$  is far from the instability of phase transitions, but rather, is very susceptible to various transitions against various perturbations. In fact,  $\text{Na}_{1.5}\text{Co}_2\text{O}_4$  exhibits a glassy behavior at 3 K due to a structural instability of the  $\gamma$  phase,<sup>39</sup> and (Bi,Pb)-Sr-Co-O shows a ferromagnetic transition at 4 K due to the lattice misfit.<sup>40</sup>

Among various possible transitions, it is not trivial whether or not an SDW-like state is favored by impurities. As an SDW-formation mechanism, we should note here that the SDW and CDW are closely related to the nesting and topology of the Fermi surface. They are properties of a metal, and occur when the correlations are weak enough to validate the one-electron picture based on band calculations. As often mentioned in the present paper, the experimental results consistently suggest that Cu suppresses the mass enhancement without significant change in the carrier concentration. If so, the decrease in  $\chi$  implies that the substituted Cu enhances the screening of the magnetic fluctuation, which might recover the band picture to cause the CDW/SDW instability of the  $a_{1g}$  Fermi surface.

#### V. SUMMARY AND FUTURE ISSUES

In this paper, we have discussed the Cu-substitution effects on the thermoelectric and thermodynamic properties of  $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ . The substituted Cu induces a phase transition at 22 K, which is characterized by the kink in the resistivity, the hump in the thermopower, and the jump in the specific heat. We have analyzed the nature of the transition, and finally proposed a spin-density-wave-like state as a possible origin, because (i) it accompanies a small entropy change of the order of  $10^{-2}k_B$  per Co, (ii) the transition is sensitive to the magnetic field, and (iii) the large Fermi surface of the  $a_{1g}$  character is gapped. The impurity-induced transition is often called “order from disorder,” which implies that phase transitions are somehow suppressed in the unsubstituted  $\text{NaCo}_2\text{O}_4$ .

One might find that the observed pseudogap behavior induced by Cu is remarkably similar to the pseudogap seen in the underdoped high-temperature superconductors (HTSC).<sup>41,42</sup> One can see a reduction in the resistivity, an enhancement in the thermopower, a decrease in the specific heat, and a decrease in the susceptibility below a pseudogap temperature  $T^*$ . Thus there is no reason to deny that the pseudogap might be generic in the strongly correlated transition-metal oxides, although the shape of the Fermi surface, the carrier concentration (the filling factor), and the spin structure are completely different between HTSC and  $\text{NaCo}_2\text{O}_4$ .

Above the transition temperature, the thermoelectric properties are at least qualitatively compared with those of heavy-fermion valence-fluctuation compounds, where mobile holes on the  $e_g + a_{1g}$  band and the nearly localized holes of the  $a_{1g}$  band correspond to the carrier and the  $f$  electrons. In this analogy, the substituted Cu increases the interaction between

the  $e_g + a_{1g}$  and  $a_{1g}$  bands to decrease the effective-mass enhancement.

In this paper we have reviewed the phenomenology of the Cu-substitution effects, but failed to address the microscopic origin and/or the electronic states of the substituted Cu. This is because our experiments were concerned only with the thermodynamic and transport properties of bulk materials. Nonetheless we can say that the scattering cross section will be small for the  $d_{x^2-y^2}$  and  $d_{z^2}$  levels of the impurity in  $\text{NaCo}_2\text{O}_4$ , because the valence bands of  $\text{NaCo}_2\text{O}_4$  consist of  $t_{2g}$ . Thus the substituted Cu (possibly divalent<sup>43</sup>) will not increase  $\rho$  seriously, because  $\text{Cu}^{2+}$  has the highest occupied

orbital of  $d_{x^2-y^2}$  that is orthogonal to  $t_{2g}$ . In addition, strong Jahn-Teller effects of  $\text{Cu}^{2+}$  may cause local distortion of the  $\text{CoO}_2$  block, which serves as a kind of chemical pressure to increase  $S$ .<sup>13</sup> To proceed further, site-selective probes such as NMR, photoemission, and scanning-tunneling microscopy/scanning-tunneling-spectroscopy should be employed.

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