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

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(Dated: January 17, 2022)

Various physical quantities are measured and analysed for the Cu-substituted thermoelectric oxide NaCo$_{2-x}$Cu$_x$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 fluctuation. The Cu substitution induces a phase transition at 22 K that is very similar to a spin-density-wave transition.

I. INTRODUCTION

Recently layered cobalt oxides have been extensively investigated as a promising candidate for a thermoelectric material. The thermoelectric material is a material that shows large thermopower ($S$), low resistivity ($\rho$) and low thermal conductivity ($\kappa$) and a quantity of $Z \equiv S^2/\rho \kappa$ called the figure of merit characterizes the thermoelectric conversion efficiency. 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 NaCo$_2$O$_4$ exhibits good thermoelectric performance [3]. Fujita et al. showed that the dimensionless figure of merit $ZT$ of a NaCo$_2$O$_4$ single crystal exceeds unity at $T = 1000$ K [4]. Ohtaki et al. measured $ZT \sim 0.8$ at 1000 K even in the polycrystalline samples of NaCo$_2$O$_4$. Thus this compound is quite promising for thermoelectric power generation at high temperature.

Following NaCo$_2$O$_4$, other layered cobalt oxides, Ca-Co-O [5, 6, 7, 8], Bi-Sr-Co-O [9, 10, 11], Ti-Sr-Co-O [12] have been found to show good thermoelectric performance. In particular, Funahashi et al. showed that $ZT > 1$ at 1000 K for Ca-Co-O. The most important feature is that the CdI$_2$ type triangular Co$_2$ 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, similarly to the case of heavy-fermion compounds. In fact the material dependence of the thermopower quite resembles that of CeM$_2$X$_2$ [13].

A prime example for the difficulties of the one-electron picture is observed in the Cu substitution effects in NaCo$_2$O$_4$ [4]. The thermopower of NaCo$_{2-x}$Cu$_x$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 zero-th order of scattering time. Indeed this is what was observed in high-temperature superconductors [13]. Importantly, correlation effects can explain the large impurity effect on the thermopower, similarly to the case of dilute magnetic alloys [15]. In this paper, we report on measurement of specific heat, susceptibility, Hall coefficient, and transverse magnetoresistance for NaCo$_{2-x}$Cu$_x$O$_4$ polycrystalline samples, and discuss the Cu substitution effects quantitatively.

II. EXPERIMENTAL

Polycrystalline samples of Na$_{3.2}$Co$_{2-x}$Cu$_x$O$_4$ ($x = 0, 0.01, 0.02$ and $0.03$) were prepared through a solid-state reaction. A stoichiometric amount of Na$_2$CO$_3$, Co$_3$O$_4$ and CuO was mixed and calcined at $860$°C for $12$ h in air. The product was finely ground, pressed into a pellet, and sintered at $920$°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...
The x-ray diffraction (XRD) was measured using a standard diffractometer with Fe Kα radiation as an x-ray source in the θ−2θ 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 gradient of 0.5 K/cm. The Hall coefficient ($R_H$) and the transverse magnetoresistance were measured from 15 to 100 K in a closed 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 addenda heat capacity. The susceptibility was measured with a SQUID susceptometer in a magnetic field of 1 T.

**III. RESULTS**

Figure 1(a) shows the x-ray diffraction patterns of the prepared samples of NaCo$_{2-x}$Cu$_x$O$_4$. Almost all the peaks are indexed as the γ phase [17, 18], though a small amount (approximately less than 5%) of unreacted Co$_3$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 NaCo$_{2-x}$Cu$_x$O$_4$. All the samples are metallic down to 4.2 K without any indication of localization. It should be noted that the increased resistance due to the substituted Cu is of the order of 10μΩcm for 1 at.% Cu, which is anomalously small in the layered transition-metal oxides [18]. Another important feature is that the resistivity for the Cu substituted samples show a kink near 22 K as indicated by the dotted line. Since the temperature dependence is 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 NaCo$_{2-x}$Cu$_x$O$_4$. Thermopower increases with increasing $x$ with a dip near 22 K and a peak.

![FIG. 1: The x-ray diffraction patterns of the polycrystalline samples of NaCo$_{2-x}$Cu$_x$O$_4$. The Fe Kα is used as an x-ray source.](image)

![FIG. 2: (a) The resistivity and (b) the thermopower of polycrystalline samples of NaCo$_{2-x}$Cu$_x$O$_4$.](image)
is nearly the same as the kink temperature for the resistances. It should be emphasized that the dip temperature for NaCo$_2$O$_4$ is a meaningful temperature, which corresponds to S/T that is an essential parameter similarly to the electron specific heat coefficient $\gamma$. The samples include 5\% of unreacted Co$_3$O$_4$, and the data for 5\% Co$_3$O$_4$ taken from Refs.\cite{20, 21} are plotted by the solid curves.

Figure 3(a) shows the specific heat $C$ for NaCo$_{2-x}$Cu$_x$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 the decrease of 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 the 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 Co$_3$O$_4$, as shown by the solid curve\cite{21}. As mentioned above, the $x$-ray diffraction patterns reveal less than 5 at.\% of unreacted Co$_3$O$_4$, which is consistent with the peak height of the specific heat at 30 K. We should emphasize here that the existence of Co$_3$O$_4$ does not seriously affect the estimation of $\gamma$, because the $C/T$ value for Co$_3$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 that the 22-K anomaly comes from a (2nd order) phase transition.

Figure 3(b) shows the susceptibility ($\chi$) of NaCo$_{2-x}$Cu$_x$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 Co$_3$O$_4$, as shown by the solid curve\cite{21}. 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 Co$_3$O$_4$. Quantitatively, the decrease of $\chi$ by Cu is more moderate than that of $C/T$. $C/T$ decreases by a factor of ten from $x$ = 0 to 0.2, whereas $\chi$ decreases only by a factor of two. 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 magnetic excitation at $k = 0$. The nature of the 22-K transition will be discussed in the next section.

Figure 4(a) shows the Hall coefficient ($R_H$) of NaCo$_{2-x}$Cu$_x$O$_4$. The sign is negative below 100 K, and the magnitude is as small as 4-6\times10^{-4} cm$^3$/C. The Cu substitution does not change the magnitude so much, indicating that the carrier concentration is nearly unchanged. By contrast, it changes the temperature dependence in a complicated way, which implies that plural kinds of carriers are responsible for the electric conduction. The band calculation by Singh\cite{22} reveals that the two bands of different symmetries cross the Fermi level for NaCo$_2$O$_4$. (See the next section)

Contrary to the Hall effect, the magnetoresistance is weakly dependent on the Cu substitution, as shown in Fig. 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.
the main part of the Fermi surface consists of the narrow e_g band in NaCo_2-xCu_xO_4. As a prime example of valence-fluctuation/Heavy-fermion compounds, the broad conduction band crosses the Fermi energy, and the narrow (localized) f band is located below the Fermi energy. For NaCo_2O_4, the broad e_g + a_1g band and the narrow a_1g band do exist, but both of which cross the Fermi energy to form two kinds of the Fermi surfaces. 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: ρ is weakly dependent on the Cu content x, whereas S, χ and γ are strongly dependent on x. S, χ and γ are basically proportional to the density of states in the lowest order, which are 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 it 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 a good electric 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 experiment [23, 24], where the valence bands of NaCo_2O_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 NaCo_2O_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.

IV. DISCUSSION

Before going into details, we will begin with a brief review on the electronic states of NaCo_2O_4. As is well known, the five-fold degenerate d orbitals split into two-fold (e_g) and three-fold (t_2g) degenerate levels in an oxygen octahedron. In the real triangular 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 CoO_2 block to make a relatively broad band, whilst 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, 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 [22].

We have proposed that the electronic structure of NaCo_2O_4 is similar to that of the Ce-based intermetallics, a prime example of valence-fluctuation/Heavy-fermion compounds [13]. γ and χ of NaCo_2O_4 are as large as those of CePd_3. In this context, the large thermopower of NaCo_2O_4 is explained in terms of a diffusive contribution of a metal with a heavily enhanced effective mass, and is roughly proportional to γ. 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 NaCo_2O_4, the broad e_g + a_1g band and the narrow a_1g band do exist, but both of which cross the Fermi energy to form two kinds of the Fermi surfaces. 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: ρ is weakly dependent on the Cu content x, whereas S, χ and γ are strongly dependent on x. S, χ and γ are basically proportional to the density of states in the lowest order, which are 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 it 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 a good electric conduction, respectively.

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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 in Fig. 4(a)) as a function of temperature in linear scale in order to see the 22-K anomaly clearly. One thing 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 0.01 k_B per Co. Actually only 5% of CoO_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 CoO_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 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 \( d\rho/dT \), both of which are inversely proportional to the Drude weight \( \Delta \sigma \). Their temperature dependences 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 charge density wave (CDW) or spin density wave (SDW). The calculated Fermi surface \( \xi_{12} \) of the \( \alpha_{12} \) 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 CDW is insensitive to magnetic field \( \xi_{12} \).

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 \( \xi_{12} \), YbBiPt \( \xi_{12} \), and \((\text{TMTSF})_2\text{PF}_6 \)
\( \xi_{12} \). The resistivity shows a hump \( \xi_{12} \), and the thermopower shows a dip at the transition \( \xi_{12} \). It is not surprising that the 22-K transition has little effects 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 \( \xi_{12} \), while it causes a clear hump in the resistivity \( \xi_{12} \). 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 \( \mu \)SR should be employed.

\section*{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 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 $[32]$ is defined as $\sigma_P \equiv S\sigma = S/\rho$. Figure 3(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 the mobility is rapidly enhanced below the 22-K transition. Figure 3(b) shows the temperature dependence of $\sigma_{xy} = H R_H/\rho^2$ 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 $\rho$ is quite small, $1/\rho^2$ term moderate 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 3(c) shows $\Delta \sigma_P = \sigma_P(x = 0.2) - \sigma_P(x = 0)$ and $\Delta \sigma_{xy} = \sigma_{xy}(x = 0.2) - \sigma_{xy}(x = 0)$. Most unexpectedly, the change in the Peltier conductivity $\Delta \sigma_P$ and 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 $\sigma_P^a \sim (n/m)^{3/2}$ and $\sigma_{xy}^a \sim (\tau/m^*)$, where the average of $\langle \cdots \rangle$ is defined as $\langle \cdots \rangle = \int (\nu_F)^2 \tau \cdots d^3k$. A close similarity between $\Delta \sigma_P$ and $\Delta \sigma_{xy}$ implies that $\langle \tau \rangle$ and $\langle n \rangle$ are nearly independent of temperature. The $T$-independent $\langle \tau \rangle$ 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 $\Delta \sigma_P$ suggests that the increase of $1/(m^*)$. 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.) Although $\gamma$ and $\chi$ decreases with $x$, $S$ significantly increases with $x$, where $S \propto \gamma$ 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 $\gamma$, $\chi$, and $S$ for Ce(Pb$_{1-y}$Sn$_y$)$_3$ as a function of the Sn content $y$. CePb$_3$ is in the heavy fermion regime (low Kondo temperature) and 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 CePb$_3$, the RKKY interaction survives at low temperatures, and often causes a magnetic transition. Since
the magnetic transition release 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), and similar to the general trend of the 20-K thermopower of CeM2X2 found by Jaccard et al. [33].

In this context, the NaCo2O4 is located near the heavy-fermion regime, and the substituted Cu caused the decrease in the mass enhancement accompanied by the 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 NaCo2−xCuO4 and Ce(Pb1−ySny)2, a close resemblance in Fig. 7 suggests that the unsubstituted NaCo2O4 corresponds to y ≈ 0.2, while NaCo1.8Cu0.2O4 corresponds to y ≈ 0.4−0.6. We further note that the Pd substituted NaCo2O4 shows negative thermopower below 50 K, which might correspond to y < 0.2 [36].

D. Order from disorder

Although the microscopic theory for the high thermoelectric performance of NaCo2O4 is still lacking, the following features are established. (1) The mixture of Co3+ and Co4+ in the low spin state can carry a large entropy of kB log 6 [37]. (2) NaCo2O4 shows no structural, electric, and magnetic transitions from 2 to 1000 K [3, 4]. (3) From (1)/(2), the large entropy cannot be released through phase transitions, and inevitably adhere to the conducting carriers to form a “heavy-fermion”-like electron.

In this respect, NaCo2O4 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” [38], which has been extensively investigated experimentally as well as theoretically. In other words, instabilities against various phases are competing or disordering in NaCo2O4, and any phase transitions are prohibited down to low temperatures. This does not mean that NaCo2O4 is far from the instability of phase transitions, but rather, is very susceptible to various transitions against various perturbations. In fact, Na1.5CoO4 exhibits a glassy behavior at 3 K due to structure instability of the γ phase [39], and (Bi,Pb)-Sr-Co-O shows a ferromagnetic transition at 4 K due to the lattice misfit [40].

Among various possible transitions, it is not trivial whether an SDW-like state is favored by impurities or not. As an SDW-formation mechanism, we should note here that SDW and CDW are closely related to the nesting of the and the topology of the Fermi surface. They are a property for a metal, and occur when the correlation effect is weak enough to hold one-electron picture based on the band calculation. 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 χ 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 a1g Fermi surface.

V. SUMMARY AND FUTURE ISSUES

In this article, we have discussed the Cu substitution effects on the thermoelectric and thermodynamic properties of NaCo2−xCuO4. 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 analysed 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 10−2kB per Co, (ii) the transition is sensitive to the magnetic field, (iii) the large Fermi surface of the a1g character is gapped. The impurity induced transition is often called “order from disorder”, which implies that phase transitions are somehow suppressed in the unsubstituted NaCo2O4.

Above the transition temperature, the thermoelectric properties are at least qualitatively compared with those of heavy-fermions valence-fluctuation compounds, where mobile holes on the eg + a1g band and the nearly localized holes of the a1g band correspond to the carrier and the f electrons. In this analogy, the substituted Cu increase the interaction between the eg + a1g and a1g bands to decrease the effective-mass enhancement.

In this article 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 d2−yg and d2 levels of the impurity in NaCo2O4, because the valence bands of NaCo2O4 consist of t2g. Thus the substituted Cu (possibly divalent [41]) will not increase ρ seriously, because Cu2+ has the highest occupied orbital of d2−yg that is orthogonal to t2g. Thus the substitution effect of Cu2+ may cause local distortion of the CoO2 block, which serves as a kind of chemical pressure to increase S [4]. To proceed further, site-selective probes such as NMR, photoemission, and STM/STS should be employed.
Acknowledgments

The authors would like to thank T. Motohashi, H. Yamauuchi, N. Murayama, K. Koumoto, and T. Mizokawa for fruitful discussion.

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