Anomalous Pd substitution effects in the thermoelectric oxide NaCo$_{2-x}$Pd$_x$O$_4$

R Kitawaki and I Terasaki*

Department of Applied Physics, Waseda University, Tokyo 169-8555, JAPAN
(Dated: March 22, 2022)

We prepared a set of polycrystalline samples of the thermoelectric oxide NaCo$_{2-x}$Pd$_x$O$_4$ ($x=0$, 0.05, 0.1 and 0.2), and investigated the Pd substitution effects on transport phenomena. The effects are so drastic that only 5-10% Pd ions reduce the resistivity and the Seebeck coefficient to one-third of the values for $x=0$, and increase the magnitude of the Hall coefficient by three times. A semi-quantitative analysis has revealed that the $x=0.2$ sample has much smaller effective mass and carrier concentration than the $x=0.05$ sample. This is difficult to explain within a rigid-band picture, and is qualitatively consistent with a strong-correlation picture applied to the Ce-based heavy fermion systems.

I. INTRODUCTION

A thermoelectric material converts heat into electricity and vice versa through the Seebeck and Peltier effects, which is characterized by a low resistivity ($\rho$), a large Seebeck coefficient ($S$), and a low thermal conductivity ($\kappa$). Thermoelectric devices are attracting renewed interests in recent years, because they are direct energy conversion devices without any wastes, and can work for a long time without maintenance.

Terasaki et al. [1] discovered high thermoelectric properties in NaCo$_2$O$_4$ in 1997. A single crystal of this material showed low resistivity (200 $\mu\Omega$cm) and large Seebeck coefficient (100 $\mu$V/K) at room temperature. Fujita et al. [2] reported a low value of $\kappa$ (50 mW/cmK) for single-crystal NaCo$_2$O$_4$ at 800 K, which strongly suggests that NaCo$_2$O$_4$ is a potential thermoelectric material at high temperature.

In spite of low thermoelectric performance for conventional oxides, the thermoelectric properties of NaCo$_2$O$_4$ are exceptionally high. Thus a central issue is to elucidate the mechanism of the thermoelectric properties of NaCo$_2$O$_4$. We have proposed that the strong (electron-electron) correlation plays an important role in this compound, as is similar to the case of the Ce-based intermetallic compounds (so-called valence fluctuation/heavy-fermion systems) [3]. Koshibae et al. [4] evaluated $S$ induced from the correlated electrons to be 150 $\mu$V/K in the high-temperature limit by using the extended Heikes formula, which roughly agrees with experiments. On the other hand, Singh [5] predicted a large value of $S=100$ $\mu$V/K at 300 K on the basis of the band calculation.

We have studied various substitution effects to examine whether or not the band picture is broken down by the correlation. Upon the Na-site substitution, the transport properties were rather insensitive, where the Ca substitution reduced carrier concentration slightly [6]. Most of the impurities substituted for Co acted as a strong scatterer, and increased resistivity with a strong upturn at low temperatures [6]. Exceptions were found in Cu- and Pd-substitutions for Co. The Cu substitution improved the thermoelectric performance [7], which was successfully explained in analogy to the Ce-based intermetallic compounds [8]. The Pd substitution is another anomalous case, where it decreases both the resistivity and the Seebeck coefficient. In this paper we report on a semi-quantitative analysis of the Pd substitution effect in NaCo$_{2-x}$Pd$_x$O$_4$, which strongly supports our strong correlation picture rather than the simple band picture.

II. EXPERIMENTAL

Polycrystalline samples of Na$_{1.2}$Co$_{2-x}$Pd$_x$O$_4$ ($x=0$, 0.05, 0.1 and 0.2) were prepared by a solid-state reaction. Stoichiometric amounts of Na$_2$CO$_3$, Co$_3$O$_4$ and PdO were mixed, and the mixture was 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. We expected samples of the nominal composition of Na$_{1.2}$Co$_{2-x}$Pd$_x$O$_4$ to be NaCo$_{2-x}$Pd$_x$O$_4$.

The resistivity was measured by a four-terminal method from 4.2 to 300 K in a liquid He cryostat. The Seebeck coefficient was measured using a steady-state technique with a typical temperature gradient of 0.5 K/cm from 4.2 to 300 K in a liquid He cryostat. The thermopower of the voltage leads was carefully subtracted. The Hall coefficient ($R_H$) was measured in a closed refrigerator from 15 to 200 K. A CERNOX resistive thermometer was placed at 45 cm above the magnet core, which successfully suppressed the magnetoresistance of the thermometer to keep the accuracy of the measured temperature within 0.01% at 7 T. An AC-bridge nano-ohmmeter was used to measure the resistivity by sweeping magnetic field from -7 to 7 T in 20 minutes at constant temperatures. An unwanted signal occurring from a misalignment of the voltage pads was carefully removed by subtracting negative-field data from positive-field data. The Hall voltage was linear in magnetic field, and $R_H$ was determined by the data at $\pm$7 T.

The X-ray diffraction (XRD) of the samples was measured using a standard diffractometer with Fe K$_\alpha$ radia-
tion as an X-ray source in the $\theta - 2\theta$ scan mode. Figure 1 shows typical XRD patterns of NaCo$_{2-x}$Pd$_x$O$_4$. Almost all the peaks are indexed as the $\gamma$ phase [7]. For $x = 0$, a small amount of Co$_3$O$_4$ indicated by ‘*’ appears. For $x=0.2$, a tiny trace of PdO indicated by ‘x’ and an unidentified phase indicated as ‘□’ appears instead of the peaks of Co$_3$O$_4$. Although Pd did not fully substitute for Co in a strict sense, the volume fraction of the impurity phases (3%) is small enough to retain high signal-noise ratio of the XRD pattern. In the next section we will see a systematic evolution of the transport parameters with the Pd substitution, which allows us to conclude that Pd in NaCo$_{2-x}$Pd$_x$O$_4$ surely modified the electronic states of the host.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the resistivity of the prepared samples of NaCo$_{2-x}$Pd$_x$O$_4$ plotted as a function of temperature ($T$). The resistivity decreases systematically with the Pd content $x$, whose magnitude decreases from 3 m$\Omega$cm for $x=0$ to 0.7 m$\Omega$cm for $x=0.2$ at room temperature. This is a quite unusual substitution effect. NaCo$_3$O$_4$ is a layered oxide consisting of the conductive CoO$_2$ layer and the insulating Na layer, where an impurity in the conductive layer would normally act as a scattering center. Thus one can expect that the impurity induces a residual resistivity in conventional metals, and in fact the Mn- Fe- Ru- and Rh-substitutions dramatically increase the residual resistivity in NaCo$_3$O$_4$ [11].

The inset of figure 2(a) shows the low-temperature resistivity of the same samples as a function of ($T/100$ K)$^2$, where no resistivity upturn is seen. This indicates that the Pd substitution makes no localization down to 4.2 K, and that the scattering cross section of Pd is negligibly small. We should further note that all the resistivities strongly depend on temperature down to 4.2 K, which suggests that the carriers are predominantly scattered through the electron-electron interaction, not through the electron-phonon interaction. Thus the electron-electron correlation still dominates in the most conductive sample of $x = 0.2$, the low-temperature resistivity for which is roughly proportional to $T^2$ that is usually expected for the electron-electron scattering.

Figure 2(b) shows the Seebeck coefficient of NaCo$_{2-x}$Pd$_x$O$_4$ plotted as a function of temperature. As is similar to the resistivity, the Seebeck coefficient decreases with $x$, where $S$ for $x = 0.2$ (20 $\mu$V/K at 300 K) is about quarter of that for $x = 0$. This is another quite anomalous substitution effect. Since the Seebeck coefficient is independent of scattering time in the lowest order approximation, it is insensitive to the disorder and/or impurities in usual cases. However, the substituted Pd not only decreases the magnitude of $S$, but also modifies the temperature dependence. As is shown in the inset of figure 2(b), $S$ goes to negative at low temperatures. We do not understand the mechanism of the sign change at present. Suffice it to say that similar sign change is observed in CeM$_2$Si$_2$ ($M$=Au, Pd, Rh and Ru) [11], whose

![ FIG. 1: The X-ray diffraction patterns of polycrystalline NaCo$_{2-x}$Pd$_x$O$_4$.](image)

![ FIG. 2: (a) The resistivity ($\rho$), (b) the Seebeck coefficient ($S$) and (c) the Hall coefficient ($R_H$) of polycrystalline NaCo$_{2-x}$Pd$_x$O$_4$ plotted as a function of temperature ($T$).](image)
origin is not fully understood either.

Figure 2 (c) shows the temperature dependence of the Hall coefficient of NaCo$_{2-x}$Pd$_x$O$_4$. The sign is negative for all the samples, and the temperature dependence becomes weaker with $x$. The magnitude of $R_H$ significantly increases from $5 \times 10^{-4}$ cm$^3$/C for $x = 0$ to $3 \times 10^{-3}$ cm$^3$/C for $x = 0.2$ at 15 K. We should emphasize that a value of $3 \times 10^{-3}$ cm$^3$/C is considerably large, implying that the k-space volume surrounded by the Fermi surface is sufficiently small. The Hall coefficient for a two-band model is written as $R_H = (n_p - n_e)/e(n_p + n_e)^2$, where $n_p$ and $n_e$ are the carrier concentrations for the hole band and the electron band, respectively (for simplicity, the same mobility is assumed). Since this expression clearly shows $|1/eR_H| > n_e$, the electron concentration is smaller than $2-3 \times 10^{21}$ cm$^{-3}$. We can also point out that $n_e$ and $n_p$ should be of the order of $10^{21} - 10^{22}$ cm$^{-3}$, considering that the formal valence of Co does not change so much from +3.5. Thus we conclude that the minority carrier concentration must be small for $x = 0.2$, and that the electric conduction is dominated by a single band. We note that $|R_H|$ for $x = 0.2$ is as large as $|R_e|$ of optimally-doped high-temperature superconductors, which has been analysed with a single band [12]. $R_H$ for $x = 0.2$ is as weakly dependent on temperature as $R_H$ for high-temperature superconductors, which is further consistent with the single-band picture, because a temperature-dependent $R_H$ is often due to different mobilities in multi-bands.

Now we will discuss the Pd-substitution effect more quantitatively. As mentioned above, the large value of $|R_H|$ is likely to allow us to apply a single-band picture, although the signs of $S$ and $R_H$ are different. Then we can evaluate the carrier concentration ($n$), the effective mass ($m$) and the scattering time ($\tau$) for the single band. In the lowest order approximation, $\rho$, $R_H$ and $S$ are expressed as functions of $n$, $m$ and $\tau$ as

$$\rho = \frac{m}{n e^2 \tau} \quad (1)$$

$$|R_H| = \frac{1}{n e} \quad (2)$$

$$|S| = \frac{\pi k_B^2 m}{2h^2 e \tau} \quad \frac{T}{n} \quad (3)$$

where $d_c (=0.54 \text{ nm})$ is the inter-layer spacing, and $e (>0)$ is the unit charge. For the expression of $S$, we assumed the two-dimensional Fermi surface [3].

Unfortunately equations (1)-(3) are valid only in the limited temperature range, where $T$-linear $S$ and $T$-independent $R_H$ are expected. Thus we conclude that the data below 100 K is unsuitable for the analysis. The upper limit is set to be 160 K, the highest measured temperature for $R_H$ of $x = 0$. Consequently we have chosen 100 and 160 K as two representative temperatures.

Figure 3 shows thus evaluated $n$, $m/m_0$ and $\tau$ using equations (1)-(3) and the data in figure 2, where $m_0$ is the free electron mass. In spite of the rough assumptions, the parameters are reasonably evaluated: $n$ and $m$ are found to be essentially independent of temperature, and is highly dependent on $x$. On the other hand, $\tau$ is highly dependent on temperature, but is weakly dependent on $x$. These are indeed what we expect in a simple metal of a single band. Apparent $T$-dependence in $m$ and $n$ for $x = 0$ is due to the fact that the single-band analysis is not guaranteed for $x = 0$ because of the small $|R_H|$. Nonetheless the three parameters are systematically varied from $x = 0.2$ down to $x = 0$, which strongly suggests that the single-band picture is more or less valid for all the samples. In particular, we think that the data for $x \geq 0.05$ are reasonably evaluated.

Let us take a closer look at the $x$ dependence of $n$, $m$ and $\tau$. Reflecting that the substituted Pd does not cause the residual resistivity, $\tau$ is evaluated to be essentially independent of $x$, which indicates that the scattering cross section of Pd is negligibly small. The magnitude is of the order of $10^{-15}$ s, which is as large as $\tau$ of usual metals. The evaluated magnitudes of $n$ and $m$ for $x = 0$ are satisfactory, although the single-band analysis is less reliable than for $x > 0$. A value of $m/m_0 = 10 - 30$ is consistent with the specific-heat measurement [14], and $n = 10^{22}$ cm$^{-3}$ is of the same order of the value estimated from the formal valence of Co (3.5+). An important finding is that the $x$ dependence of $m$ and $n$ is surprisingly

![FIG. 3: The carrier concentration ($n$), the effective mass normalized by the free electron mass ($m/m_0$) and the scattering time ($\tau$) of polycrystalline NaCo$_{2-x}$Pd$_x$O$_4$ plotted as the function of Pd content $x$.](image-url)
large. In going from $x = 0.05$ to $x = 0.2$, $n$ decreases by 1.5-2 times, and $m$ decreases by 4-5 times. As a result, $n/m$ is found to increase by 3 times from $x=0.05$ to 0.2, which is the origin for the decrease in $\rho$ and $S$ with $x$.

We should note that the rapid decrease in $m$ is seriously incompatible to the band picture. According to the band structure by Singh [3], the band dispersion near the Fermi energy is smooth without any singularities. Thus the band mass is unlikely to change by 4-5 times in the rigid-band picture. Furthermore the $a_{1g}$ band (responsible for the large $S$) forms the cylindrical Fermi surface, which makes the density of states at the Fermi energy nearly independent of $x$ in the rigid-band picture. Thus the rapid decrease in $n$ with $x$ is also incompatible to the band picture.

On the contrary, the strong correlation scenario can, at least qualitatively, explain the rapid change in $n$ and $m$. In the previous paper, we compared the physical properties of the Cu substituted samples with the Ce-based compounds [9]. According to this, two valence bands near the Fermi level for NaCo$_2$O$_4$ are well compared with those of the Ce-based compounds. One is the $a_{1g} + e_g$ band responsible for the electric conduction, corresponding to the $sp$ conduction band. The other is the $a_{1g}$ band responsible for the large density of states, corresponding to the Ce $4f$ band. Unlike the Ce-based compound, both bands cross the Fermi level to form two kinds of the Fermi surface. Therefore, the rapid decrease in $m$ accompanied by the rapid decrease in $n$ can occur, when the Fermi surface of the $a_{1g}$ band disappears (or decouples with the $a_{1g} + e_g$ band) upon the Pd substitution. A possible candidate for the disappearance is a pseudogap opening. The Cu substitution induces the spin-density-wave like transition at 22 K, below which the $a_{1g}$ Fermi surface seems to be gapped [4].

Finally, we will briefly comment on some remaining issues. (i) Thermoelectric power factor $S^2/\rho$, a measure of thermoelectric performance, is proportional to $m/n$, according to equations (1) and (3). In this case, good conduction adversely affects the thermoelectric properties. In fact, the Pd substitution decreases the thermoelectric performance of NaCo$_2$O$_4$. (ii) The magnetoresistance of the Pd-substituted samples is positive. We previously reported that NaCo$_2$O$_4$ shows negative magnetoresistance, which is attributed to the pseudogap in the $a_{1g}$ band [3]. In this sense the positive magnetoresistance is consistent with the disappearance of the $a_{1g}$ band, but the field dependence is too complicated to analyze. The angular dependence/anisotropy should be measured by using single crystals. Unfortunately we have not yet succeeded in preparing Pd-substituted single crystals. (iii) We failed to address how Pd modifies the electronic states at a microscopic level. Our measurement is limited to the transport properties, and a microscopic probe such as photoemission is necessary. Nevertheless we expect the small scattering cross section for Pd. Probably Pd exists as Pd$^{2+}$ with the highest occupied orbital of $d_{z^2}$, which is orthogonal to the valence bands of NaCo$_2$O$_4$ of $t_{2g}$.

(iv) We do not understand why the sign of $S$ and $R_H$ differs. A number of materials show different signs of $R_H$ and $S$, most of which are due to the multi-bands. In the present case, however, we assumed that the single band gives the positive $S$ and the negative $R_H$. A similar sign difference is seen in the Kondo semiconductor CeNiSn below the pseudogap temperature [5, 6], and high-temperature superconductors [7]. In general, the signs of $S$ and $R_H$ are determined through different averaging of the energy bands, which can be different even in a single band [8].

IV. SUMMARY

In summary, we prepared a set of polycrystalline samples of Na$_{1.2}$CoO$_{2-x}$Pd$_x$O$_4$ ($x = 0, 0.05, 0.1$ and $0.2$). The substituted Pd decreases both the resistivity and the Seebeck coefficient, and increases the absolute value of the Hall coefficient. These results indicate that Pd decreases the carrier concentration and the effective mass significantly, while it does not influence the scattering time. Though microscopic details are still unknown, the present study reinforces our scenario that interplay between the two bands is a key to the high thermoelectricity in NaCo$_2$O$_4$, just as in the case of heavy-fermion systems.

Acknowledgements

The authors would like to appreciate K. Takahata for fruitful discussions and valuable comments. We would also like to thank W. Kobayashi and A. Satake for collaboration.

[1] Terasaki I, Sasago Y and Uchinokura K 1997 Phys. Rev. B56 R12685
[2] Fujita K, Mochida T and Nakamura K 2001 Jpn. J. Appl. Phys. 40 4644
[3] Terasaki I 2001 Mater. Trans. JIM 42 951
[4] Kosbibae W, Tsutsui K and Maekawa S 2000 Phys. Rev. B60 6869
[5] Singh D J 2000 Phys. Rev. B61 13397
[6] Kawata T, Iguchi Y, Itoh T, Takahata K, and Terasaki I 1999 Phys. Rev. B60 10584
[7] Terasaki I 2000 Proc. of the 19th International Conference on Thermoelectrics (ICT 2000), 182; cond-mat/0108485
[8] Terasaki I, Ishii Y, Tanaka D, Takahata K and Iguchi Y 2001 Jpn. J. Appl. Phys. 40 L65
[9] Terasaki I, Tsukada I and Iguchi Y 2002 Phys. Rev. B65
[10] Jansen V M and Hoppe R 1974 Z. Anorg. Alleg. Chem. 408 104
[11] Amato A and Sierro J 1985 J Mag. Mag. Mater. 47& 48 526
[12] Ando Y, Hanaki Y, Ono S, Murayama T, Segawa K, Miyamoto N and Komiya S 2000 Phys. Rev. B61 R14956
[13] Mandal J B, Das A N and Ghosh B 1996 J. Phys. Condens. Matter 8 3047
[14] Ando Y, Miyamoto N, Segawa K, Kawata T, and Terasaki I 1999 Phys. Rev. B60 10580
[15] Takabatake T, Echizen Y, Yoshino T, Kobayashi K, Nakamoto G, Fujii H and Sera M 1999 Phys. Rev. B59 13878
[16] Takabatake T, Teshima F, Fujii H, Nishigori S, Suzuki T, Fujita T, Yamaguchi Y, Sakurai J and Jaccard D 1990 Phys. Rev. B41 9607
[17] Terasaki I, Sato Y, Miyamoto S, Tajima S and Tanaka S 1995 Phys. Rev. B 52 16246
[18] Allen P B, Pickett W E and Krakauer H 1988 Phys. Rev. B 37 7482