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

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Abstract

We prepared a set of polycrystalline samples of the thermoelectric oxide $\text{NaCo}_{2-x}\text{Pd}_x\text{O}_4$ ($x = 0, 0.05, 0.1, \text{ and } 0.2$), and investigated the Pd substitution effects on transport phenomena. The effects are so drastic that just 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.

1. Introduction

A thermoelectric material converts heat into electricity and vice versa through the Seebeck and Peltier effects; it is characterized by a low resistivity (ρ), a large Seebeck coefficient (S), and a low thermal conductivity (κ). Thermoelectric devices have been attracting renewed interest in recent years, because they are devices that achieve direct energy conversion without any waste, and can work for a long time without maintenance.

Terasaki *et al* [1] discovered highly thermoelectric properties in NaCo_2O_4 in 1997. A single crystal of this material showed low resistivity ($200 \mu\Omega \text{ cm}$) and large Seebeck coefficient ($100 \mu\text{V K}^{-1}$) at room temperature. Fujita *et al* [2] reported a low value of κ ($50 \text{ mW cm}^{-1} \text{ K}^{-1}$) for single-crystal NaCo_2O_4 at 800 K, which strongly suggests that NaCo_2O_4 can be applied to thermoelectric power generation at high temperature.

In spite of poor thermoelectric performance of conventional oxides, the thermoelectric properties of NaCo_2O_4 are exceptionally strong. Thus a central issue is elucidating the

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mechanism of the thermoelectric properties of NaCo_2O_4 . We have proposed that the strong (electron–electron) correlation plays an important role in this compound, similarly to the case for 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 $150 \mu\text{V K}^{-1}$ 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 $S = 100 \mu\text{V K}^{-1}$ 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. The transport properties were rather insensitive to Na-site substitution, while Ca substitution reduced the carrier concentration slightly [6]. Most of the impurities substituted for Co acted as strong scatterers, and increased the resistivity, with a strong upturn at low temperatures [7]. Exceptions were found in Cu and Pd substitutions for Co. The Cu substitution improved the thermoelectric performance [8], which was successfully explained by analogy to the Ce-based intermetallic compounds [9]. The Pd substitution is another anomalous case: 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 $\text{NaCo}_{2-x}\text{Pd}_x\text{O}_4$, which strongly supports our strong-correlation picture rather than the simple band picture.

2. Experimental details

Polycrystalline samples of $\text{Na}_{1.2}\text{Co}_{2-x}\text{Pd}_x\text{O}_4$ ($x = 0, 0.05, 0.1, \text{ and } 0.2$) were prepared by solid-state reaction. Stoichiometric amounts of Na_2CO_3 , Co_3O_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 calcining, we added 20% excess Na. We expected samples of the nominal composition of $\text{Na}_{1.2}\text{Co}_{2-x}\text{Pd}_x\text{O}_4$ to be $\text{NaCo}_{2-x}\text{Pd}_x\text{O}_4$.

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^{-1} 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, keeping 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 the magnetic field from -7 to 7 T in 20 min at constant temperatures. An unwanted signal arising 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 from the data at ± 7 T.

The x-ray diffraction (XRD) of the samples was measured using a standard diffractometer with Fe $K\alpha$ radiation as an x-ray source in the θ - 2θ scan mode. Figure 1 shows typical XRD patterns of $\text{NaCo}_{2-x}\text{Pd}_x\text{O}_4$. Almost all the peaks are indexed to the γ -phase [10]. For $x = 0$, a small amount of Co_3O_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_3O_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 a 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 $\text{NaCo}_{2-x}\text{Pd}_x\text{O}_4$ certainly modified the electronic states of the host.

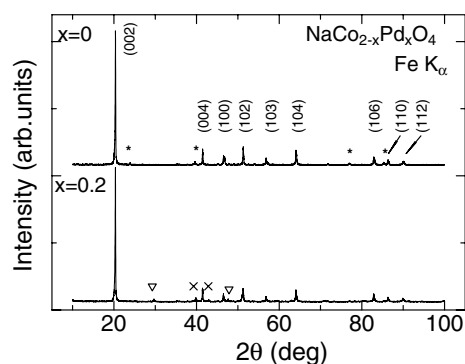


Figure 1. The XRD patterns of polycrystalline $\text{NaCo}_{2-x}\text{Pd}_x\text{O}_4$.

3. Results and discussion

Figure 2(a) shows the resistivity of the prepared samples of $\text{NaCo}_{2-x}\text{Pd}_x\text{O}_4$ plotted as a function of temperature (T). The resistivity decreases systematically with the Pd content x ; its magnitude decreases from $3 \text{ m}\Omega \text{ cm}$ for $x = 0$ to $0.7 \text{ m}\Omega \text{ cm}$ for $x = 0.2$ at room temperature. This is a quite unusual substitution effect. NaCo_2O_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 centre. Thus one can expect the impurity to induce a residual resistivity in conventional metals, and in fact the Mn, Fe, Ru, and Rh substitutions dramatically increase the residual resistivity in NaCo_2O_4 [7].

The inset of figure 2(a) shows the low-temperature resistivity of the same samples as a function of $(T/100 \text{ K})^2$, where no resistivity upturn is seen. This indicates that the Pd substitution causes 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 with $x = 0.2$, the low-temperature resistivity for which is roughly proportional to T^2 as is usually expected for electron–electron scattering.

Figure 2(b) shows the Seebeck coefficient of $\text{NaCo}_{2-x}\text{Pd}_x\text{O}_4$ plotted as a function of temperature. Like the resistivity, the Seebeck coefficient decreases with x : S for $x = 0.2$ ($20 \mu\text{V K}^{-1}$ 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 negative at low temperatures. We do not understand the mechanism of the sign change at present. Suffice it to say that a similar sign change is observed in CeM_2Si_2 ($M = \text{Au}, \text{Pd}, \text{Rh}, \text{and Ru}$) [11], whose origin is not fully understood either.

Figure 2(c) shows the temperature dependence of the Hall coefficient of $\text{NaCo}_{2-x}\text{Pd}_x\text{O}_4$. The sign is negative for all the samples, and the temperature dependence becomes weaker with x . The magnitude of R_H significantly increases from $5 \times 10^{-4} \text{ cm}^3 \text{ C}^{-1}$ for $x = 0$ to $3 \times 10^{-3} \text{ cm}^3 \text{ C}^{-1}$ for $x = 0.2$ at 15 K. We should emphasize that a value of $3 \times 10^{-3} \text{ cm}^3 \text{ C}^{-1}$ is large, implying that the k -space volume surrounded by the Fermi surface is fairly small.

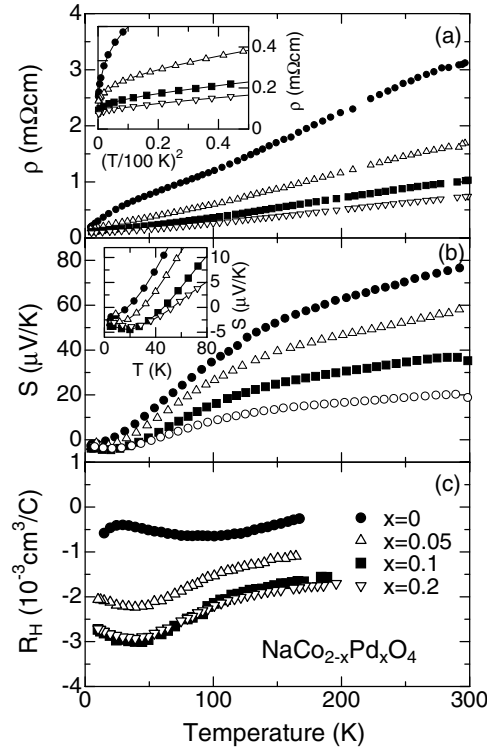


Figure 2. (a) The resistivity (ρ), (b) the Seebeck coefficient (S), and (c) the Hall coefficient (R_H) of polycrystalline $\text{NaCo}_{2-x}\text{Pd}_x\text{O}_4$ plotted as a function of temperature (T).

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, it is assumed that the mobilities are the same). Since this expression clearly shows that $|1/eR_H| > n_e$, the electron concentration is smaller than $(2-3) \times 10^{21} \text{ cm}^{-3}$. We can also note 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 $|R_H|$ 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 (τ) for the single band. In the lowest-order approximation, ρ , R_H , and S are expressed as functions of n , m , and τ as

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

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

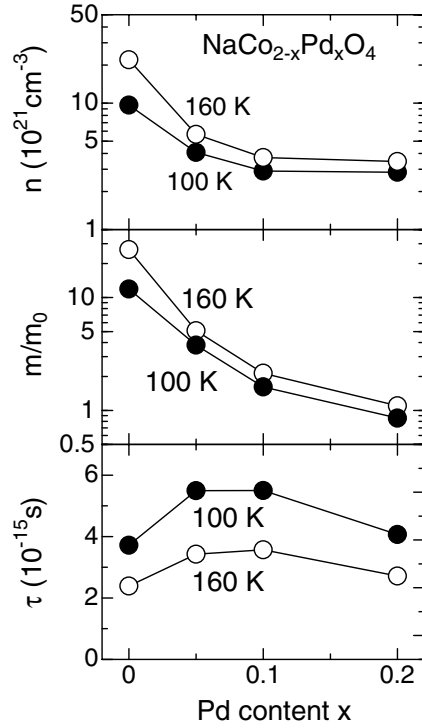


Figure 3. The carrier concentration (n), the effective mass normalized by the free electron mass (m/m_0), and the scattering time (τ) of polycrystalline $\text{NaCo}_{2-x}\text{Pd}_x\text{O}_4$ plotted as a function of Pd content x .

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

where d_c ($=0.54$ nm) is the inter-layer spacing, and e (>0) is the unit charge. For the expression for S , we assumed a two-dimensional Fermi surface [13].

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 are unsuitable for the analysis. The upper limit is set to 160 K, the highest measured temperature for R_H for $x = 0$. Consequently we have chosen 100 and 160 K as two representative temperatures.

Figure 3 shows n , m/m_0 , and τ evaluated thus 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 highly dependent on x . On the other hand, τ is highly dependent on temperature, but is weakly dependent on x . These are indeed the outcomes that we expect in a simple metal of single-band type. The apparent T -dependence of 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 systematically vary from $x = 0.2$ down to 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 τ . Reflecting that the substituted Pd does not cause the residual resistivity, τ 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 τ for 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 $m/m_0 = 10\text{--}30$ is consistent with the specific heat measurement [14], and $n = 10^{22}$ cm $^{-3}$ is of the same order as the value estimated from the formal valence of Co (3.5+). An important finding is that the x -dependences of m and n are surprisingly large. In going from $x = 0.05$ to 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 three times from $x = 0.05\text{--}0.2$, which is the origin for the decrease in ρ and S with x .

We should note that the rapid decrease in m is seriously incompatible with the band picture. According to the band structure given by Singh [5], 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 a 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 with the band picture.

In contrast, the strong-correlation scenario can, at least qualitatively, explain the rapid change in n and m . In our previous paper, we compared the physical properties of the Cu-substituted samples with those of the Ce-based compounds [9]. According to this, two valence bands near the Fermi level for NaCo $_2$ O $_4$ compare well 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 case for the Ce-based compound, both bands cross the Fermi level to form two kinds of 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 from the $a_{1g} + e_g$ band) upon Pd substitution. A possible candidate for causing 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 [9].

Finally, we will briefly comment on some remaining issues.

- (i) The thermoelectric power factor S^2/ρ , 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, Pd substitution degrades 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 analyse. 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 a 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} type.
- (iv) We do not understand why the signs of S and R_H differ. A number of materials show different signs of R_H and S , most of which are due to multi-bands. In the present case, however, we assumed that a 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 [15, 16], and in high-temperature superconductors [17]. In general, the signs of S and R_H are determined through different averagings of the energy bands, which can be different even in a single band [18].

4. Summary

In summary, we prepared a set of polycrystalline samples of $\text{Na}_{1.2}\text{Co}_{2-x}\text{Pd}_x\text{O}_4$ ($x = 0, 0.05, 0.1$, 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 in which interplay between the two bands is a key to the high thermoelectricity in NaCo_2O_4 , just as in the case of heavy-fermion systems.

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