Transport properties and electronic states of the thermoelectric oxide NaCo$_2$O$_4$

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Physical properties of the thermoelectric oxide NaCo$_2$O$_4$ are briefly reviewed. The high thermoelectric properties of this material are attributed to the substantially enhanced effective mass, which comes from the large entropy of Co$^{2+}$ in the low spin state. The large entropy confined in the CoO$_2$ block causes a spin-density-wave transition at 22 K upon Cu substitution for Co, which can be regarded as “order from disorder”.

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 ($\kappa$). 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 cobalt oxide NaCo$_2$O$_4$ exhibits high thermoelectric performance [3]. Fujita et al. showed that the dimensionless figure of merit $S^2T/\rho\kappa$ of a NaCo$_2$O$_4$ single crystal exceeds unity at $T=1000$ K [4]. Ohtaki et al. measured $S^2T/\rho\kappa \sim 0.8$ 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.

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 heavy-fermion compounds. In fact the material dependence of the thermopower quite resembles that of heavy-fermion compounds. In fact the material dependence of the thermopower quite resembles that of heavy-fermion compounds. In fact the material dependence of the thermopower quite resembles that of heavy-fermion compounds. In fact the material dependence of the thermopower quite resembles that of heavy-fermion compounds. In fact the material dependence of the thermopower quite resembles that of heavy-fermion compounds. In fact the material dependence of the thermopower quite resembles that of heavy-fermion compounds. In fact the material dependence of the thermopower quite resembles that of heavy-fermion compounds.

Figure 2(a) shows the resistivity and the thermopower of a NaCo$_2$O$_4$ single crystal along the a-axis (parallel to the CoO$_2$ block) direction. The magnitude of the resistivity is as low as 200 $\mu$cm at 300 K, which corresponds to nearly the best conductivity among transition-metal oxides. The thermopower is 100 $\mu$V/K at 300 K, which is as large as that of degenerate semiconductors. As a result, the power factor $S^2/\rho$ is as large as (or even larger than) $S^2/\rho$ of the state-of-the-art thermoelectric material Bi$_2$Te$_3$.

Figure 2(b) shows the magnetic susceptibility $\chi$ and the specific heat $C$ of a polycrystalline sample of NaCo$_2$O$_4$. The susceptibility is relatively large ($4 \times 10^{-3}$ emu/Co mol at 4 K), and weakly temperature dependent. We attribute the weakly temperature dependent susceptibility to a kind of spin fluctuation, as is seen in the valence fluctuation systems. In fact, Co-site substitution causes non-trivial change in the susceptibility. Nonmagnetic Zn substitution induces a Curie term, whereas magnetic Cu substitution decreases the magnitude of the susceptibility, which cannot be interpreted by the local spin picture.

The electron specific heat coefficient $\gamma$ is evaluated by the value of $C/T$ as $T \rightarrow 0$. $C/T$ approaches 35-50 mJ/Co mol K$^2$, which is two orders of magnitude larger than the value of conventional metals. The large values of $\gamma$ and $\chi$ clearly indicate that the density of states (and also

II. Physical Properties of NaCo$_2$O$_4$

In Fig.1 is schematically shown the crystal structure of NaCo$_2$O$_4$, where edge-shared distorted octahedra of oxygen ions form a two-dimensional triangular lattice. A cobalt ion is in the center of the distorted octahedra to form a two-dimensional triangular lattice, while a sodium ion is in a prism site between CoO$_2$ blocks. An important feature in this structure is that sodium ions randomly occupy the regular site by 50%, and the sodium content changes from 50 to 75%. In this sense NaCo$_2$O$_4$ should be written as Na$_x$Co$_2$O$_2$ ($x=0.5$). Nevertheless we will call it NaCo$_2$O$_4$, because the best thermoelectric properties are realized near the 50% Na occupancy [3].
the effective mass) is substantially enhanced in NaCo$_2$O$_4$.
Note that the band calculation by Singh [11] also predicts
the large density of states, though it is difficult to explain
the anomalous impurity effects discussed later.

III. Comparison with Ce-based intermetallics

The microscopic theory for the high thermoelectric
performance of NaCo$_2$O$_4$ is still lacking, but we think
that the following features are now established. (1) The
mixture of Co$^{3+}$ and Co$^{4+}$ in the low spin state can carry
a large entropy of $k_B \log 6$, which gives a thermopower
of 150 $\mu V/K$ in the high-temperature limit [12]. (2)
NaCo$_2$O$_4$ shows no structural, electric, and magnetic
transitions from 2 to 1000 K. (3) From (1)(2), the large
entropy cannot be released through phase transitions,
and inevitably point to the conducting carriers to form a
“heavy-fermion”-like electron [6]. (4) Although an exact
one-to-one correspondence is not realized, the calculated
Fermi surface of NaCo$_2$O$_4$ is made from two orbitals of
different nature [11], just like Ce 4$f$ and $sp$ bands in the
Ce-based intermetallics [7, 8].

In the heavy-fermion compounds, $\gamma$ is proportional to
the susceptibility $\chi$, and $\chi/\gamma$ (the Wilson ratio) is inde-
pendent of materials. In Fig. 3, various $\gamma$’s are plotted as
a function of $\chi$, where the data for NaCo$_2$O$_4$ is just close
to the data for the valence-fluctuation compound CePd$_3$
[13]. We should note that CePd$_3$ has nearly the same val-
ues of $S$ (80 $\mu V/K$ at 300 K) and $\rho$ (150 $\mu Ocm$ at 300 K).
Unfortunately it has much higher thermal conductivity
than NaCo$_2$O$_4$, which greatly reduces the thermoelectric
performance.

According to the classical Boltzmann theory, the dif-
susive term of the thermopower of a metal is understood
as transport entropy per carrier, implying that a large
effective mass can lead to a large thermopower. Figure 3 indicates that the effective mass of NaCo$_2$O$_4$ is more
than 10 times larger than the bare electron mass, which
is in a quantitative agreement with the reflectivity edge and
the magnitude of the Hall effect [8]. Considering
a striking similarity to the heavy fermion compounds,
we attribute the large mass of NaCo$_2$O$_4$ to the coherent
state between the conduction carrier and the spin fluc-
tuation. Very recently Valla et al. have performed a
photoemission experiment for the layered cobalt oxides,
and have successfully observed the coherent state at low
temperatures [14].

IV. Cu substitution effects: Order from disorder

Figure 4(a) shows the specific heat for the Cu-
substituted sample NaCo$_{1.8}$Cu$_{0.2}$O$_4$ as a function of tem-
perature, where the specific heat jump at 22 K is clearly seen [6]. The entropy change of the 22-K transition is as
small as 77 mJ/Kmole, corresponding to 0.01$k_B$ per Co.
Actually only 5% of Co$_3$O$_4$ impurity exhibits a specific
heat jump of the same order at 30 K. A phase transition
accompanied by a small entropy change is an off-diagonal
long range order, which induces a small entropy change
of the order of $Nk_B T/E_F$. This order is suppressed by
FIG. 4: (a) Specific heat coefficient $C$, (b) Temperature derivative of the resistivity ($dp/dT$) and temperature coefficient of the thermopower $S/T$ for the Cu-substituted NaCo$_{1.8}$Cu$_{0.2}$O$_4$. Inset: The specific heat in magnetic fields.

external fields, as shown in the inset of Fig. 4(a).

Figure 4(b) shows the $T$-linear term of the thermopower ($S/T$) and the temperature derivative of the resistivity $dp/dT$. 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 of the $a_{1g}$ band is hexagon-like [1], which is unstable against CDW or SDW formation with the nesting vector along the Γ-K direction. We think that the 22-K transition is SDW-like, because CDW is insensitive to magnetic field. Actually we can find many similarities between the 22-K transition and the SDW transition in Cr [15].

NaCo$_2$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” [4]. In other words, instabilities against various phases are competing or disordered in NaCo$_2$O$_4$, and any phase transitions are prohibited down to low temperatures. This does not mean that NaCo$_2$O$_4$ is far from the instability of phase transitions, but rather, is very susceptible to various transitions against various perturbations. In fact, Na$_{1.5}$Co$_2$O$_4$ exhibits a spin-glass behavior at 3 K [16] and a ferromagnetic transition at 22 K [17], possibly owing to the structure instability of the γ phase, and (Bi,Pb)-Sr-Co-O shows a ferromagnetic transition at 4 K due to the lattice misfit [18].

Let us qualitatively discuss why the SDW-like state is favored in NaCo$_{2-x}$Cu$_x$O$_4$. SDW and CDW are closely related to the nesting of the and the topology of the Fermi surface, and occur when the correlation effect is weak enough to hold one-electron picture based on the band calculation. We think that Cu suppresses the mass enhancement without significant change in the carrier concentration [1]. If so, 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

We have reviewed the anomalous properties of NaCo$_2$O$_4$, which are promising for thermoelectric applications. We have explained the thermoelectric properties of NaCo$_2$O$_4$ in terms of the layered structure consisting of the strongly correlated CoO$_2$ layer. Carries in oxides are often coupled with the optical phonons, the spin degrees of freedom and the orbital degrees of freedom. These couplings induce exotic electronic states such as polarons, heavy fermions, spin liquids and orbital liquids. Furthermore, the geometry and the dimensionality are easy to change in certain classes of oxides, where layered, ladder and chain structures can be controlled. Therefore I believe that many functional materials including thermoelectric materials will still sleep unknown. I hope that NaCo$_2$O$_4$ is just the beginning, and that a thermoelectric oxide of higher performance will appear in near future.

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