Low thermal conductivity of the layered oxide (Na,Ca)Co$_2$O$_4$: Another example of a phonon glass and an electron crystal

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The thermal conductivity of polycrystalline samples of (Na,Ca)Co$_2$O$_4$ is found to be unusually low, 20 mW/cmK at 280 K. On the assumption of the Wiedemann-Franz law, the lattice thermal conductivity is estimated to be 18 mW/cmK at 280 K, and it does not change appreciably with the substitution of Ca for Na. A quantitative analysis has revealed that the phonon mean free path is comparable with the lattice parameters, where the point-defect scattering plays an important role. Electronically the same samples show a metallic conduction down to 4.2 K, which strongly suggests that NaCo$_2$O$_4$ exhibits a glass-like poor thermal conduction together with a metal-like good electrical conduction. The present study further suggests that a strongly correlated system with layered structure can act as a material of a phonon glass and an electron crystal.

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Thermoelectric materials have recently attracted a renewed interest as an application to a clean energyconversion system. The conversion efficiency of a thermoelectric material is characterized by the figure of merit $Z = S^2/\rho\kappa$, where $S$, $\rho$ and $\kappa$ are the thermopower, the resistivity and the thermal conductivity, respectively. At a temperature, $T$, a dimensionless value of $ZT$ is required to be more than unity for a good thermoelectric material, which is, however, difficult to realize. We have found a large thermopower (100 $\mu$V/K at 300 K) and a low resistivity (200 $\mu$Ohm at 300 K) for NaCo$_2$O$_4$ single crystals. These parameters suggest that NaCo$_2$O$_4$ is a potential thermoelectric material. An important finding is that the transport properties are difficult to understand in the framework of a conventional one-electron picture based on band theories. We have proposed that strong electron-electron correlation plays an important role in the enhancement of the thermopower. Very recently Ando et al. have found that the electron specific-heat coefficient of NaCo$_2$O$_4$ is as large as 48 mJ/molK$^2$, which is substantially enhanced from the free-electron value, possibly owing to the strong correlation.

In addition to a large thermopower and a low resistivity, a thermoelectric material is required to show a low thermal conductivity. In view of this, a filled skutterudite, Ce(Fe,Co)$_3$Sb$_2$ shows quite interesting properties. The most remarkable feature of this compound is that “filled” Ce ions make the lattice thermal conductivity several times lower than that for an unfilled skutterudite CoSb$_3$. The Ce ions are weakly bound in an oversized atomic cage so that they will vibrate independently from the other atoms to cause large local vibrations. This vibration and the atomic cage are named “rattling” and a “rattling site”, respectively. As a result, the phonon mean free path can be as short as the lattice parameters. Namely this compound has a poor thermal conductivity like a glass and a good electric conduction like a crystal, which Slack named a material of “phonon glass and an electron crystal”. It should be mentioned that rattling is not the only reason for the low thermal conductivity, where point defects and/or solid solutions significantly reduce the thermal conductivity of La$_2$(Fe,Co)$_3$Sb$_2$ ($x < 1$) and Co$_{1-x}$M$_x$Sb$_3$ ($M$ = Fe, Ni, and Pt). Nevertheless a search for materials having rattling sites is a recent trend for thermoelectric material hunting. Through this search, BaGa$_{16}$Ge$_{20}$ and Tl$_2$MTe$_5$ ($M$ = Sn and Ge) have been discovered as potential thermoelectric materials with low thermal conductivity.

A preliminary study of the thermal conductivity of polycrystalline NaCo$_2$O$_4$, which has no rattling sites, revealed a low value of 15-20 mW/cmK at 300 K. This is indeed unexpectedly low, because a material consisting of light atoms such as oxygens will have a high thermal conductivity. In fact, polycrystalline samples of a high-temperature superconducting copper oxide show a higher conductivity. In another attempt, BaGa$_{16}$Ge$_{20}$ and Tl$_2$MTe$_5$ ($M$ = Sn and Ge) have been discovered as potential thermoelectric materials with low thermal conductivity.
In this paper, we report on measurements and quantitative analyses on the thermal conductivity of polycrystalline samples of \((\text{Na, Ca})\text{Co}_2\text{O}_4\) from 15 to 280 K. The observed thermal conductivity is like that for a disordered crystal, and is insensitive to the substitution of Ca for Na. These results imply that the phonon mean free path is as short as the lattice parameters, and a semi-quantitative analysis reveals that the point-defect scattering due to the solid solution of Na ions and vacancies effectively reduces the lattice thermal conductivity down to 15-20 mW/cmK. On the other hand, the electrical resistivity remains metallic down to 4.2 K, which means that the electron mean free path is much longer than the lattice parameters. Thus NaCo$_2$O$_4$ can be a material of a phonon glass and an electron crystal, whose conduction mechanisms are qualitatively different from those of the “rattler” model of the filled skutterudite.

Polycrystalline samples of \(\text{Na}_{1.2-x}\text{Ca}_x\text{Co}_2\text{O}_4\) \(x=0, 0.05, 0.10\) and 0.15 were prepared through a solid-state reaction. Starting powders of NaCO$_3$, CaCO$_3$ and Co$_3$O$_4$ were mixed and calcined at 860°C for 12 h. The product was finely ground, pressed into a pellet, and sintered at 920°C for 12 h. Since Na tends to evaporate during calcination, we added 20% excess Na. Namely we expected samples of the nominal composition of \(\text{Na}_{1.2-x}\text{Ca}_x\text{Co}_2\text{O}_4\) to be \(\text{Na}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_4\), which we will denote as \((\text{Na, Ca})\text{Co}_2\text{O}_4\).

The thermal conductivity was measured using a steady-state technique in a closed refrigerator pumped down to $10^{-6}$ Torr. The sample was pasted on a copper block with silver paint (Dupont 4922) to make a good thermal contact with a heat bath, and on the other side of the sample a chip resistance heater (120 Ω) was pasted to supply heat current. Temperature gradient was monitored by a differential thermocouple made of Chromel-Constantan, while temperature was monitored with a resistance thermometer (Lakeshore CERNOX 1050).

Figure 1 shows the thermal conductivity of \((\text{Na, Ca})\text{Co}_2\text{O}_4\). The substitution of Ca for Na only slightly decreases the thermal conductivities of \((\text{Na, Ca})\text{Co}_2\text{O}_4\). This makes a remarkable contrast to the change of the resistivity with the Ca substitution. The magnitude (20 mW/cmK at 280 K) is as low as that of a conventional thermoelectric material such as Bi$_2$Te$_3$, which is consistent with the previous study.

Let us make a rough estimate of the phonon mean free path \(\ell_{\text{ph}}\) for NaCo$_2$O$_4$ at 280 K. In the lowest order approximation, the lattice thermal conductivity \(\kappa_{\text{ph}}\) is expressed by

$$\kappa_{\text{ph}} = \frac{1}{3}cv\ell_{\text{ph}},$$

where \(c\) and \(v\) are the lattice specific heat and the sound velocity. Since we consider a moderately high temperature region where phonons are sufficiently excited, we assume \(c = 3Nk_B\) (\(N\) is the number of atoms per unit volume). The sound velocity is associated with the Debye temperature \(\theta_D\) as

$$\theta_D = \frac{h v_B}{k_B (6\pi^2 N)^{1/3}}.$$

We employ \(\theta_D = 350\) K from the recent specific-heat data and get \(\ell_{\text{ph}} = 6.7\) Å for 20 mW/cmK, which is comparable with the in-plane lattice parameter (3 Å). This picture is intuitively understood from the fact that the Na layer is highly disordered. Note that the observed data of 20 mW/cmK includes the electron thermal conductivity, and thus the obtained value of 6.7 Å gives the upper limit of the phonon mean free path.

Figure 2 summarizes the thermoelectric parameters of NaCo$_2$O$_4$. In Fig. 2(a) are shown the thermal conductivity (the same data as \(x=0\) in Fig. 1) and the figure of merit calculated using the resistivity and the thermopower of the same sample. We also plot the electron thermal conductivity \((\kappa_{\text{el}})\) estimated from the resistivity on the assumption of the Wiedemann-Franz law as \(\kappa_{\text{el}} = L_0 T/\rho\) \((L_0 = \pi^2 k_B^2 /3e^2\) is the Lorentz number). \(\kappa_{\text{el}}\) is 10% of \(\kappa\), and the heat conduction is mainly determined by the phonons. The figure of merit is \(10^{-4}K^{-1}\) above 100 K, which is largest among oxides but does not yet reach the criteria of ZT = 1. Much progress is thus needed to realize oxide thermoelectrics.

In Fig. 2(b), the resistivity and the thermopower are plotted as a function of temperature, which reproduce the pioneering work on the Na-Co-O system by Molenda et al.\cite{1} The temperature dependence of the resistivity is essentially the same as that for the in-plane resistivity of the single crystals, though the magnitude is much higher owing to the grain-boundary scattering. It should be noted that the resistivity exhibits metallic conduction down to 4.2 K without any indication of the localization. This implies that the electron mean free path is much longer than the lattice parameters. Previously we showed that the electron mean free path of the single crystal is as long as 230 Å at 4.2 K along the in-plane direction.\cite{2}

We can therefore say that the phonon mean free path is much shorter than the electron mean free path. This is nothing but a material of a phonon glass and an electron crystal.

Here we will compare the measured thermal conductivity with the phonon-scattering theory by Callaway.\cite{3} The total scattering rate \(\tau^{-1}\) is given as the sum of three scattering rates as

$$\tau^{-1} = \tau_{\text{pd}}^{-1} + \tau_{\text{ph-\text{ph}}}^{-1} + \tau_0^{-1} = \frac{\omega^4}{A} + \frac{B\omega^2}{L} + \frac{v}{L},$$

where \(\tau_{\text{pd}}^{-1}\), \(\tau_{\text{ph-\text{ph}}}^{-1}\) and \(\tau_0^{-1}\) are the scattering rates for the point-defect scattering, the phonon-phonon scattering, and the boundary scattering, respectively. For a phonon frequency \(\omega\), the three scattering rates are written as \(A\omega^4\), \(B\omega^2\) and \(v/L\), where \(A\), \(B\) and \(L\) are characteristic parameters. According to Ref.\cite{3} \(A\) is expressed as \(A = \Omega_0 \sum f_i (1 - M_i/M)^2/4\pi v^3\), where \(\Omega_0\) is the unit
cell volume, $M_i$ is the mass of an atom, $f_i$ is the fraction of an atom with mass $M_i$, and $M = \sum f_i M_i$ is the average mass. We calculated $A$ for (Na,Ca)Co$_2$O$_4$ by following the method in Ref. 1 where Na (23g/mol), Ca (40g/mol) and □ (vacancy) make a solid solution in the ratio of Na:Ca:□=1:(1-$x$):x:1. $B$ is a temperature-dependent parameter, which is proportional to $T$ at high temperatures ($B \sim CT$). It should be noted that the phonon-phonon scattering gives $\kappa \propto 1/\sqrt{CT}$ at high temperatures in the presence of a large $A$. As clearly shown in Fig. 1, $\kappa$ for (Na,Ca)Co$_2$O$_4$ increases with $T$, implying that the phonon-phonon scattering is negligibly small. Thus $L$ corresponding to an inelastic scattering length is the only fitting parameter.

In Fig. 3, the measured $\kappa_{ph}$ ($= \kappa - \kappa_{el}$) of NaCo$_2$O$_4$ is compared with two theoretical curves. Sample #1 is the same sample as shown in Fig. 1, and Sample #2 is another sample prepared in a different run. Curve A is the calculation using the phonon-scattering theory, where $L=0.2$ $\mu$m is used. As expected, the point-defect scattering quite effectively reduces the thermal conductivity by two or three orders of magnitude. The Ca substitution effect is also consistently explained as shown in the inset, where data points (as indicated by open circles) in different runs are added to show the reproducibility. Although the solid solution of Na and □ dominates $\kappa_{ph}$, the theory predicts a small correction due to the substitution of Ca (as indicated by the solid line), which is in good agreement with the observation. This directly indicates that the point-defect scattering plays an important role in reducing $\kappa_{ph}$. A problem is the physical meaning of $L=0.2$ $\mu$m: It is much longer than the electron mean free path (10-10$^2$ $\AA$), but much shorter than the grain size (10 $\mu$m). Possible candidates are the average distance of stacking faults and/or interlayer disorder.

The absence of the phonon-phonon scattering means that the phonon lifetime is extremely short and is rather characteristic of the thermal conductivity of a glass. Curve B is the calculation of the minimum thermal conductivity $\kappa_{min}$ by Cahill et al. which has been compared with $\kappa_{ph}$ for a glass. Although the calculated $\kappa_{min}$ is one order of magnitude smaller than the measured $\kappa_{ph}$, such a deviation is also seen in other disordered crystals. Note that $\kappa_{ph} \propto T^3$ is not seen for NaCo$_2$O$_4$ at low temperatures, which is a hallmark of disordered crystals. Since $\kappa_{ph} \propto T^3$ is usually seen below 10 K, this is possibly because the measurement temperature was high. NaCo$_2$O$_4$ consists of the sandwich structure of the amorphous and crystalline layers, and the heat conduction process is perhaps in between that for a mixed crystal and an amorphous solid. Thus it should be further explored which curve is more likely to capture the essential feature of the heat conduction in NaCo$_2$O$_4$.

We propose that a layered material consisting of a strongly correlated conducting layer and disordered insulating layer can be a promising thermoelectric material. If the heavy-fermion system is realized in the strongly correlated layer, $S^2/\rho$ can be increased through the mass enhancement due to the spin fluctuation. Recently we proposed that the effective mass of NaCo$_2$O$_4$ is enhanced as much as that for CePd$_3$. Meanwhile, in the disordered insulating layer, the lattice thermal conductivity can be minimized by the disorder that causes little effect on the electric conduction. In this context, it will work as a material of a phonon glass and an electron crystal.

This scenario might be compared with the thermoelectric superlattices extensively studied by Dresselhaus et al. At present, no band calculation of NaCo$_2$O$_4$ is available, but the band calculation of isostructural LiCo$_2$O$_4$ shows that the valence bands do not show any sub-band structure expected from the 2D quantum confinement. This means that the electronic states of NaCo$_2$O$_4$ are not very anisotropic in a one-electron picture. This situation is essentially identical to the band picture of high-temperature superconductors. We think that the enhancement of the thermopower of NaCo$_2$O$_4$ should not be attributed to the quantum confinement of the semiconductor superlattices, but to the strong correlation.

In summary, we prepared polycrystalline samples of (Na,Ca)Co$_2$O$_4$ and measured the thermal conductivity from 15 to 280 K. We have found that the phonon mean free path is 6.7 $\AA$ at 280 K, which is much shorter than the electron mean free path. This means that (Na,Ca)Co$_2$O$_4$ acts as a materials of a phonon glass and an electron crystal, though it has no rattling sites. We have compared the experimental data with the phonon-scattering theory and the minimum thermal conductivity, and have found that the point-defect scattering plays an important role.

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Another possibility is that the phonon in NaCo,

FIG. 1. The thermal conductivity of (Na,Ca)CO$_2$O$_4$ plotted as a function of temperature. The inset shows the schematic picture of the crystal structure of NaCo$_2$O$_4$.

FIG. 2. The thermoelectric parameters of polycrystalline NaCo$_2$O$_4$. (a) The thermal conductivity ($\kappa$) and the figure of merit ($Z$); (b) The resistivity ($\rho$) and the thermopower ($S$). Note that the electron thermal conductivity ($\kappa_{el}$) evaluated through the Wiedemann-Franz law is shown by the solid curve, where $L_0$ is the Lorentz number ($=\pi^2 k_B^2/3e^2$).
FIG. 3. The lattice thermal conductivity ($\kappa_{ph}$) of NaCo$_2$O$_4$. The open and closed circles represent $\kappa_{ph}$ measured for Sample #1 and #2, where the electron thermal conductivity was estimated through the Wiedemann-Franz law. Curve A is the calculation proposed by Callaway. Curve B is the minimum thermal conductivity proposed by Cahill et al. The inset shows $\kappa_{ph}$ of (Na,Ca)Co$_2$O$_4$ at 200 K. The solid line is the same calculation as Curve A.