PHYSICAL REVIEW B

CONDENSED MATTER AND MATERIALS PHYSICS

THIRD SERIES, VOLUME 61, NUMBER 19 **15 MAY 2000-I**

BRIEF REPORTS

Brief Reports are accounts of completed research which, while meeting the usual **Physical Review B** *standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Low thermal conductivity of the layered oxide (Na,Ca)Co_2O_4: Another example of a phonon glass and an electron crystal

K. Takahata, Y. Iguchi, D. Tanaka, and T. Itoh
Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan

I. Terasaki*
Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan
and Precursory Research for Embryonic Science and Technology, Japan Science Technology, Tokyo 102-0074, Japan

(Received 3 August 1999; revised manuscript received 28 December 1999)

The thermal conductivity of polycrystalline samples of (Na,Ca)Co_2O_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/cm K 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 $NaCo_2O_4$ exhibits a glasslike 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.

Thermoelectric materials have recently attracted a renewed interest as an application to a clean energy-conversion system.[1] The conversion efficiency of a thermoelectric material is characterized by the figure of merit $Z=S^2/\rho\kappa$, where S, ρ, and κ 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 μV/K at 300 K) and a low resistivity (200 $\mu\Omega$ cm at 300 K) for $NaCo_2O_4$ single crystals.[2] These parameters suggest that $NaCo_2O_4$ 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.[2–4] Very recently, Ando *et al.*[5] have found that the electron specific-heat coefficient of $NaCo_2O_4$ is as large as 48 mJ/mol K^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)$_4$Sb$_{12}$ shows quite interesting properties.[6–9] 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 $CoSb_3$.[6] 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.[9] 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 conduction like a glass and a good electric conduction like a crystal, which Slack[10] named a material of ''a 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$_x$(Fe,Co)$_4$Sb$_{12}$ ($x<1$) (Ref. 11) and $Co_{1-x}M_xSb_3$ ($M=$Fe, Ni, and Pt).[12,13] Nevertheless, a search for materials having rattling sites is a

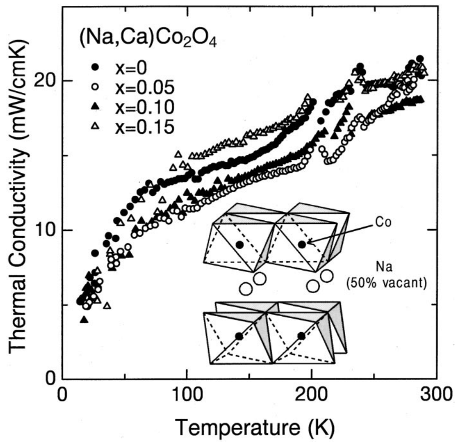

FIG. 1. The thermal conductivity of $(Na,Ca)Co_2O_4$ plotted as a function of temperature. The inset shows the schematic picture of the crystal structure of $NaCo_2O_4$.

recent trend for thermoelectric-material hunting. Through this search, $BaGa_{16}Ge_{30}$ (Ref. 14) and Tl_2MTe_5 ($M=Sn$ and Ge) (Refs. 15 and 16) have been discovered as potential thermoelectric materials with low thermal conductivity.

A preliminary study of the thermal conductivity of polycrystalline $NaCo_2O_4$, which has *no rattling sites*, revealed a low value of 15–20 mW/cm K at 300 K.[17] 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 value of 40–50 mW/cm K at 300 K.[18,19] This is qualitatively understood from its crystal structure as schematically shown in the inset of Fig. 1. $NaCo_2O_4$ is a layered oxide, which consists of the alternate stack of the CoO_2 layer and the Na layer. The CoO_2 layer is responsible for the electric conduction, whereas the Na layer works only as a charge reservoir to stabilize the crystal structure. The most important feature is that the Na ions randomly occupy 50% of the regular sites in the Na layer. The Na layer is highly disordered like an amorphous solid, and it looks like a glass for the in-plane phonons. Thus significant reduction of the thermal conductivity is likely to occur in the sandwich structure made of the crystalline metallic layers and the amorphous insulating layers.[20]

In this paper, we report on measurements and quantitative analyses on the thermal conductivity of polycrystalline samples of $(Na,Ca)Co_2O_4$ 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 semiquantitative 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/cm K. 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 $NaCo_2O_4$ 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.[7–9]

Polycrystalline samples of $Na_{1.2-x}Ca_xCo_2O_4$ ($x=0$, 0.05, 0.10, and 0.15) were prepared through a solid-state reaction. Starting powders of $NaCO_3$, $CaCO_3$, and Co_3O_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 $Na_{1.2-x}Ca_xCo_2O_4$ to be $Na_{1-x}Ca_xCo_2O_4$, which we will denote as $(Na,Ca)Co_2O_4$.

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 (120Ω) 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 $(Na,Ca)Co_2O_4$. The substitution of Ca for Na only slightly decreases the thermal conductivities of $(Na,Ca)Co_2O_4$. This makes a remarkable contrast to the change of the resistivity with the Ca substitution.[3,4] The magnitude (20 mW/cm K at 280 K) is as low as that of a conventional thermoelectric material such as Bi_2Te_3,[21] which is consistent with the previous study.[17]

Let us make a rough estimate of the phonon mean free path (l_{ph}) for $NaCo_2O_4$ at 280 K. In the lowest-order approximation, the lattice thermal conductivity κ_{ph} is expressed by[22]

$$\kappa_{ph}=\frac{1}{3}cvl_{ph},$$

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 θ_D as

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

We employ $\theta_D=350$ K from the recent specific-heat data,[5] and get $l_{ph}=6.7$ Å for 20 mW/cm K, 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/cm K include 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 $NaCo_2O_4$. 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 (κ_{el}) estimated from the resistivity on the assumption of the Wiedemann-Franz law as $\kappa_{el}=L_0T/\rho$ ($L_0=\pi^2k_B^2/3e^2$ is the Lorentz number). κ_{el} is 10% of κ, 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,[1] but

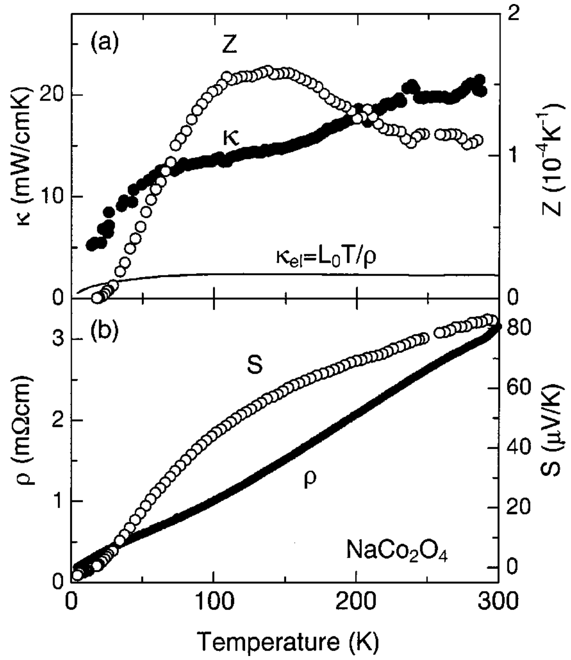

FIG. 2. The thermoelectric parameters of polycrystalline $NaCo_2O_4$. (a) The thermal conductivity (κ) and the figure of merit (Z); (b) the resistivity (ρ) and the thermopower (S). Note that the electron thermal conductivity (κ_{el}) evaluated through the Wiedemann-Franz law is shown by the solid curve, where L_0 is the Lorentz number ($=\pi^2 k_B^2/3e^2$).

does not yet reach the criteria of $ZT=1$. Much progress is thus needed to realize oxide thermoeletcrics.

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.*[23] 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.[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.[10]

Here we will compare the measured thermal conductivity with the phonon-scattering theory by Callaway.[24,25] The total scattering rate τ^{-1} is given as the sum of three scattering rates as

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

where τ_{pd}^{-1}, $\tau_{\mathrm{ph\text{-}ph}}^{-1}$, and τ_0^{-1} are the scattering rates for the point-defect scattering, the phonon-phonon scattering, and the boundary scattering, respectively. For a phonon frequency ω, 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. 26, A is expressed as $A=\Omega_0\Sigma f_i(1-M_i/M)^2/4\pi v^3$, where Ω_0 is the unit-cell volume, M_i is

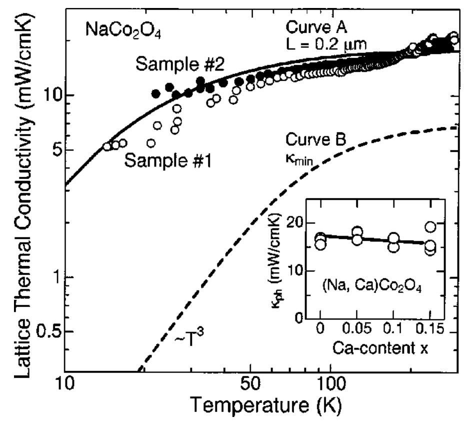

FIG. 3. The lattice thermal conductivity (κ_{ph}) of $NaCo_2O_4$. The open and closed circles represent κ_{ph} measured for sample no. 1 and no. 2, where the electron thermal conductivity was estimated through the Wiedemann-Franz law. Curve A is the calculation proposed by Callaway (Refs. 24 and 25) Curve *B* is the minimum thermal conductivity proposed by Cahill *et al.* (Ref. 28). The inset shows κ_{ph} of $(Na,Ca)Co_2O_4$ at 200 K. The solid line is the same calculation as curve *A*.

the mass of an atom, f_i is the fraction of an atom with mass M_i, and $M=\Sigma f_i M_i$ is the average mass. We calculated A for $(Na,Ca)Co_2O_4$ by following the method in Ref. 11, where Na (23 g/mol), Ca (40 g/mol), and □ (vacancy) make a solid solution in the ratio of Na:Ca:□$=(1-x):x:1$. 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 $\kappa\propto 1/\sqrt{ACT}$ at high temperatures in the presence of a large A.[25] As clearly shown in Fig. 1, κ for $(Na,Ca)Co_2O_4$ 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 κ_{ph} ($=\kappa-\kappa_{\mathrm{el}}$) of $NaCo_2O_4$ is compared with two theoretical curves. Sample no. 1 is the same sample as shown in Fig. 1, and sample no. 2 is another sample prepared in a different run. Curve *A* is the calculation using the phonon-scattering theory,[24,25] where $L=0.2$ μm 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 κ_{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 κ_{ph}. A problem is the physical meaning of $L=0.2$ μm: It is much longer than the electron mean free path (10–10^2 Å), but much shorter than the grain size (10 μm). 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,[27] and is rather characteristic of the thermal conductivity of a glass. Curve *B* is the calculation of the minimum thermal conductivity κ_{min} by Cahill *et al.*,[28] which has been compared with κ_{ph} for a glass.

Although the calculated κ_{min} is one order of magnitude smaller than the measured κ_{ph}, such a deviation is also seen in other disordered crystals. Note that $\kappa_{ph} \propto T^3$ is not seen for $NaCo_2O_4$ 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. $NaCo_2O_4$ 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 $NaCo_2O_4$.

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/ρ can be increased through the mass enhancement due to the spin fluctuation.[1,29] Recently, we proposed that the effective mass of $NaCo_2O_4$ is enhanced as much as that for CeP_3.[20] 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.*[30,31] At present, no band calculation of $NaCo_2O_4$ is available, but the band calculation of isostructural $LiCoO_2$ shows that the valence bands do not show any subband structure expected from the 2D quantum confinement.[32] This means that the electronic states of $NaCo_2O_4$ 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 $NaCo_2O_4$ should not be attributed to the quantum confinement of the semiconductor superlattices, but to the strong correlation.

In summary, we prepared polycrystalline samples of $(Na,Ca)Co_2O_4$ and measured the thermal conductivity from 15 to 280 K. We have found that the phonon mean free path is 6.7 Å at 280 K, which is much shorter than the electron mean free path. This means that $(Na,Ca)Co_2O_4$ 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.

The authors would like to thank J. Takeya and Y. Ando for technical help in thermal-conductivity measurements. They also thank T. Kawata, T. Kitajima, T. Takayanagi, T. Takemura, and T. Nonaka for their collaboration.

*Author to whom correspondence should be addressed. Electronic address: terra@mn.waseda.ac.jp

[1] For a recent review, see G. D. Mahan, Solid State Phys. **51**, 81 (1998).

[2] I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B **56**, 12 685 (1997).

[3] T. Itoh, T. Kawata, T. Kitajima, and I. Terasaki, *Proceedings of the 17th International Conference on Thermoelectrics (ICT '98), Nagoya, Japan, 1998* (The Institute of Electrical and Electronics Engineers, Piscataway, 1998), p. 595.

[4] T. Kawata, Y. Iguchi, T. Itoh, K. Takahata, and I. Terasaki, Phys. Rev. B **60**, 10 584 (1998).

[5] Y. Ando, N. Miyamoto, K. Segawa, T. Kawata, and I. Terasaki, Phys. Rev. B **60**, 10 580 (1998).

[6] D. T. Morelli and G. P. Meisner, J. Appl. Phys. **77**, 3777 (1995).

[7] B. C. Sales, D. Mandrus, and R. K. Williams, Science **272**, 1325 (1996).

[8] B. C. Sales, D. Mandrus, B. C. Chakoumakos, V. Keppens, and J. R. Thompson, Phys. Rev. B **56**, 15 081 (1997).

[9] V. Keppens, D. Mandrus, B. C. Sales, B. C. Chakoumakos, P. Dai, R. Coldrea, M. B. Maple, D. A. Gajewski, E. J. Freeman, and S. Bennington, Nature (London) **395**, 876 (1998).

[10] G. A. Slack, in *CRC Handbook of Thermoelectronics*, edited by D. M. Rowe (CRC Press, Boca Raton, 1995), p. 407.

[11] G. P. Meisner, D. T. Morelli, S. Hu, J. Yang, and C. Uher, Phys. Rev. Lett. **80**, 3551 (1998).

[12] S. Katsuyama, Y. Shichijo, M. Ito, K. Majima, and H. Nagai, J. Appl. Phys. **84**, 6708 (1998).

[13] H. Anno, K. Matsubara, Y. Notohara, T. Sakakibara, and H. Tashiro, J. Appl. Phys. **84**, 3780 (1999).

[14] G. S. Nolas, J. L. Cohn, G. A. Slack, and S. B. Schujman, Appl. Phys. Lett. **73**, 178 (1998).

[15] J. W. Sharp, B. C. Sales, D. G. Mandrus, and B. C. Chakoumakos, Appl. Phys. Lett. **74**, 3794 (1999).

[16] B. C. Sales, B. C. Chakoumakos, D. Mandrus, and J. W. Sharp, J. Solid State Chem. **146**, 528 (1999).

[17] H. Yakabe, K. Kikuchi, I. Terasaki, Y. Sasago, and K. Uchinokura, in *Proceedings of the 16th International Conference on Thermoelectricity (ICT '97), Dresden, Germany, 1997* (The Institute of Electrical and Electronics Engineers, Piscataway, 1998), p. 523.

[18] J. L. Cohn, C. P. Popoviciu, Q. M. Lin, and C. W. Chu, Phys. Rev. B **59**, 3823 (1999).

[19] M. Ikebe, H. Fujishiro, T. Naito, and K. Noto, J. Phys. Soc. Jpn. **63**, 3107 (1994).

[20] I. Terasaki, in *Proceedings of the 18th International Conference on Thermoelectricity (ICT '99), Baltimore, Maryland, 1999* (The Institute of Electrical and Electronics Engineers, Piscataway, 2000).

[21] T. Caillat, M. Carle, P. Pierrat, H. Scherrer, and S. Scherrer, J. Phys. Chem. Solids **53**, 1121 (1992).

[22] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Hot-Saunders, Philadelphia, 1976), p. 22.

[23] J. Molenda, C. Delmas, and P. Hargenmuller, Solid State Ionics **9&10**, 431 (1983).

[24] J. Callaway, Phys. Rev. **113**, 1046 (1959).

[25] J. Callaway and H. C. von Baeyer, Phys. Rev. **120**, 1149 (1960).

[26] P. G. Klemens, Phys. Rev. B **119**, 507 (1960).

[27] Another possibility is that the phonon in $NaCo_2O_4$ is quite harmonic. In this case, there are little dissipation channels, and κ_{ph} would be much higher.

[28] D. G. Cahill, S. K. Watson, and R. O. Pohl, Phys. Rev. B **46**, 6131 (1992).

[29] B. C. Webb, A. J. Sievers, and T. Mihalisin, Phys. Rev. Lett. **57**,

1951 (1986).
[30] L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B **47**, 12 727 (1993).
[31] M. S. Dresselhaus, *Proceedings of the 17th International Conference on Thermoelectrics (ICT '98)* (Ref. 3), p. 29 and references therein.
[32] M. K. Aydinol, A. P. Kohan, G. Ceder, K. Cho, and J. Joannopoulos, Phys. Rev. B **56**, 1354 (1997).