# Large magnetothermal conductivity in $GdBaCo_2O_{5+x}$ single crystals

X. F. Sun,[1,2,*] A. A. Taskin,[2] X. Zhao,[3] A. N. Lavrov,[4] and Yoichi Ando[5]
[1]*Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*
[2]*Central Research Institute of Electric Power Industry, Komae, Tokyo 201-8511, Japan*
[3]*Department of Astronomy and Applied Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*
[4]*Institute of Inorganic Chemistry, Lavrentyeva-3, Novosibirsk 630090, Russia*
[5]*Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan*
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To study the effects of paramagnetic spins on phonons, both the in-plane and the *c*-axis heat transport of $GdBaCo_2O_{5+x}$ single crystals are measured at low temperature down to 0.36 K and in magnetic field up to 16 T. It is found that the phonon heat transport is very strongly affected by the magnetic field and nearly five times increase of the thermal conductivity in several tesla field is observed at 0.36 K. It appears that phonons are resonantly scattered by paramagnetic spins in zero field and the application of magnetic field removes such strong scattering, but the detailed mechanism is to be elucidated.

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## I. INTRODUCTION

In magnetic materials, coupling of spins with other elementary excitations is a matter of fundamental importance. In particular, the spin-phonon interaction causing unusual physical properties in correlated oxides has been an issue of significant interest both by its own right and because it provides a useful means to gain insight into frustrated magnetism as well as multiferroics.[1–5] The low-temperature thermal conductivity is one of the most effective probes for studying the spin-phonon coupling,[6] especially in insulators where magnetic excitations along with phonons are the main heat carriers. Even if the long-range magnetic order is not established in a crystal or the contribution of magnons to the thermal conductivity is limited at low temperatures, the presence of localized spins still can play an important role in the heat transport as was observed long time ago in some ionic compounds doped with magnetic impurities.[6–8] However, in strongly correlated materials, the low-*T* behavior of thermal conductivity can be so complicated that it is difficult to selectively study the effect of spin-phonon interaction, especially when the electron transport, which can also depend on magnetic field, is contributing to the thermal conductivity. In order to gain insight into the impact of spin-phonon coupling and its underlying mechanism, one needs a material in which the spin-phonon coupling can be treated independently.

For this purpose, recently synthesized layered cobaltite $GdBaCo_2O_{5+x}$ (GBCO), which has attracted a great deal of attention due to its rich phase diagram and fascinating physical properties (see Ref. 9 and references therein), would be an ideal system for studying the spin-phonon coupling. This compound is a good electrical insulator at low temperatures for a wide range of oxygen content, and hence there is no need to consider the electronic heat conduction. Although GBCO shows a long-range magnetic ordering of Co spins, their Ising-like spin anisotropy prevents the low-energy magnon excitations, while the Gd ions remain paramagnetic and behave as almost free spins down to very low temperatures. Furthermore, a lattice disorder in GBCO can be easily introduced by merely changing its oxygen content.

In this work, we perform detailed studies of the low-*T* heat transport of GBCO single crystals with various oxygen contents. It is found that both the in-plane and the *c*-axis thermal conductivities ($\kappa_{ab}$ and $\kappa_c$) show extremely strong magnetic-field dependence at low temperatures. The $\kappa(H)$ isotherms at 1–2 K show a diplike feature at low fields where the heat conduction is reduced by as much as 50%, while at subkelvin temperatures the magnetic field induces a steplike enhancement of $\kappa$ by nearly five times. The magnetic-field dependences of the thermal conductivity indicate that phonons are strongly scattered by the Gd spins that are susceptible to the Zeeman effect in magnetic fields. The large magnetothermal effect illuminates the important role of free spins in the heat transport of strongly-correlated oxide materials.

## II. EXPERIMENTS

High-quality $GdBaCo_2O_{5+x}$ single crystals are grown using a floating-zone technique[9–11] and carefully annealed to tune their oxygen contents to $x=0.50$, 0.30, and 0.00. The thermal conductivity along both the *ab* plane and the *c* axis is measured from 0.36 to 5 K in a $^3$He refrigerator by using a "one heater, two thermometers" technique and from 5 to 300 K in a $^4$He cryostat by using the Chromel/Constantan thermocouple. Details of the measurements of the temperature and magnetic-field dependence of $\kappa$ were described in previous publications.[12–14] All the parallelepiped crystals are precisely cut along three crystallographic axes with an error of less than 1°. The heat capacity is measured by the relaxation method in the temperature range from 2 to 300 K using a commercial physical property measurement system (Quantum Design).

## III. RESULTS AND DISCUSSIONS

Before presenting the heat transport results of GBCO crystals, we show in Fig. 1 the representative heat capacity

 

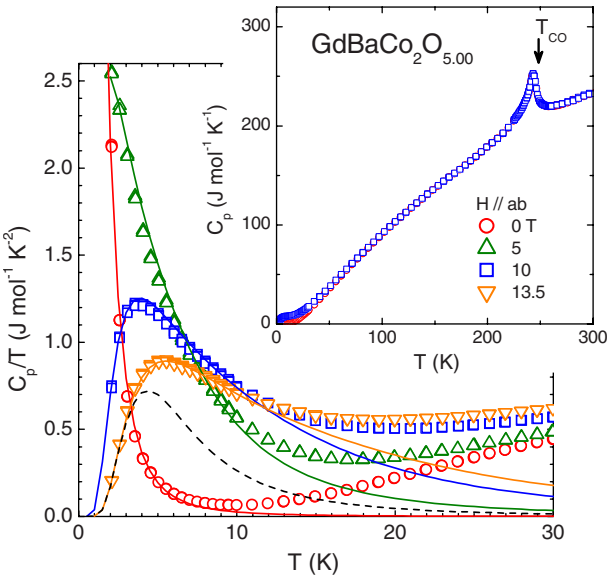


FIG. 1. (Color online) The low-temperature specific heat of $GdBaCo_2O_{5.00}$ in magnetic fields of 0, 5, 10, and 13.5 T applied along the *ab* plane. Solid lines show calculated Schottky contributions of paramagnetic $Gd^{3+}$ ions assuming $S=7/2$ (see text). The dashed line indicates the Schottky contribution of paramagnetic ions with $S=1/2$ at $H=13.5$ T. The inset shows the heat capacity in the temperature range of 2–300 K measured at $H=0$ and 10 T. The arrow indicates the charge ordering transition.

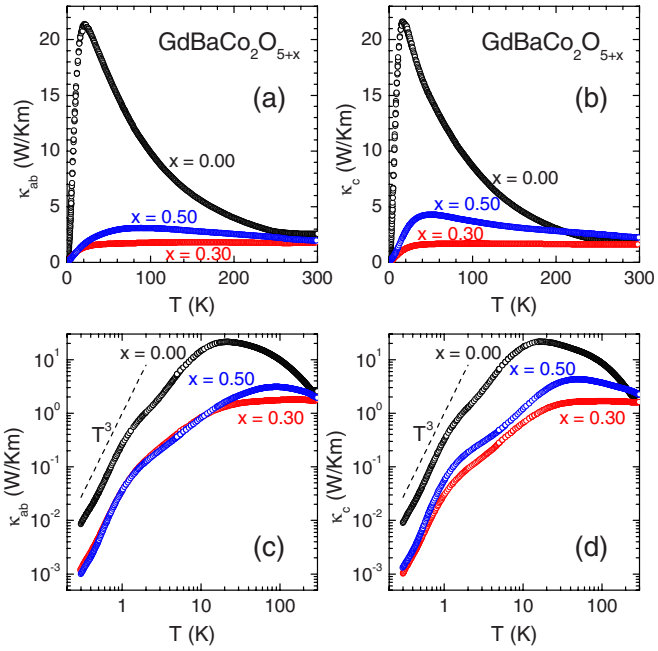


FIG. 2. (Color online) Temperature dependences of the thermal conductivity along the *ab* plane and the *c* axis in zero magnetic field for $GdBaCo_2O_{5+x}$ single crystals with various oxygen contents. The data are displayed in both linear and logarithmic plots. The dashed lines indicate the $T^3$ dependence.

data, which prove to be very informative regarding the magnetic excitations. In GBCO, regardless of the oxygen content, the spins of cobalt ions undergo magnetic ordering at rather high temperatures,[9,10] but Gd ions, in contrast, remain paramagnetic down to very low temperatures as suggested by magnetization measurements.[9] In order to confirm this, we have measured the heat capacity of an $x=0.00$ single crystal in different magnetic fields. As can be seen in the inset of Fig. 1, the $C_p(T)$ curve is insensitive to the magnetic field, except for the low-$T$ part: the peak around 248 K, which corresponds to the charge ordering transition at this temperature,[15] is not affected by applying a high magnetic field either. At low temperatures, on the other hand, the specific heat $C_p/T$ shows a pronounced Schottky anomaly with a maximum that shifts to a higher temperature with increasing magnetic field. All the data measured in $H=0$, 5, 10, and 13.5 T are well fitted by a simple Schottky contribution of paramagnetic $Gd^{3+}$ ions with a spin value of 7/2, which is determined by the area under the peak (the Schottky contribution of paramagnetic ions with $S=1/2$ at $H=13.5$ T is shown for comparison), and the $g$ factor of $1.64\pm0.04$, which is determined by the peak position. We should note also that there is a finite splitting of the Gd spin levels even in the absence of an external magnetic field that can be a result of a weak magnetic interaction of Gd ions with each other or with the cobalt sublattices.

Figure 2 shows the temperature dependences of $\kappa_{ab}$ and $\kappa_c$ of $GdBaCo_2O_{5+x}$ single crystals in zero field. First of all, as we already pointed out, the insulating ground state and the Ising-like spin anisotropy of GBCO leave little room for carriers other than phonons to contribute to the heat transport, at least at low temperatures. As can be seen in Fig. 2, the $x=0.00$ crystals show a large phonon peak at $\sim$20 K, indicating the negligible imperfection of the crystal lattice. In contrast, for $x=0.30$ and 0.50, the phonon conductivity is dramatically weakened at low temperatures and the phonon peak is wiped out almost completely, which is not surprising since the oxygen nonstoichiometry brings strong lattice disorder. Between the latter two compositions, the $x=0.50$ crystals have better heat conductivity, presumably due to the oxygen ions being ordered into chains at this oxygen content.[9,10] The worst heat conduction is observed in $x=0.30$ crystals, which have the largest degree of oxygen-induced lattice disorder.[9]

The temperature dependences of $\kappa$ in Fig. 2 are actually more complicated than those in conventional insulators. At high temperatures, for example, the $\kappa(T)$ data for the good phonon conductor $x=0.00$ cannot be described by the usual phonon umklapp scattering,[6,16] which suggests the existence of a more complicated scattering mechanism or some other kind of heat carrier. In fact, the specific heat data in Fig. 1 indicate that above $\sim$100 K, magnon excitations of the Co spin lattice become important and may affect the high-$T$ heat transport properties. On the opposite side, the lowest-$T$ behavior of the heat conduction also seems to differ from the boundary scattering limit of phonons expected for conventional insulators,[6] in which case the magnitude of the phonon thermal conductivity should depend only on the sample size, and not on impurities, defects, or oxygen concentration (the dispersion of acoustic phonons and the sound velocity do not change much upon changing the oxygen content). Although both $\kappa_{ab}$ and $\kappa_c$ below 1 K are rather close to $\sim T^3$, the heat conductivity of the $x=0.00$ sample is nearly 1 order of mag-

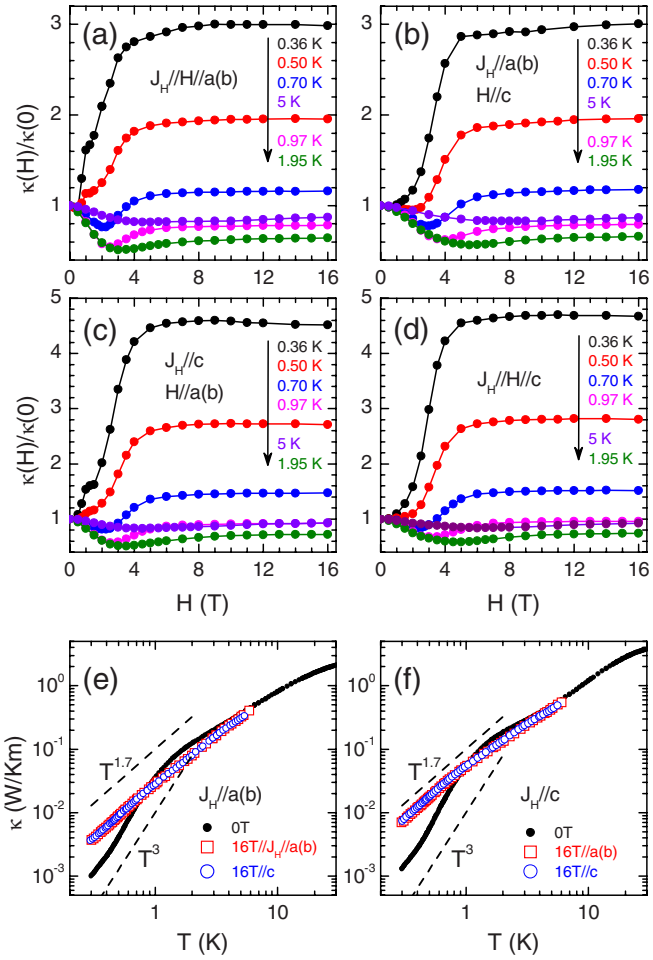


FIG. 3. (Color online) [(a)–(d)] Magnetic-field dependences of the low-$T$ thermal conductivity of the $GdBaCo_2O_{5+x}$ single crystal with $x=0.50$. Directions of the heat current ($J_H$) and the magnetic field ($H$) are shown in each panel. [(e) and (f)] Temperature dependences of $\kappa_{ab}$ and $\kappa_c$ in 0 and 16 T magnetic fields. The dashed lines indicate the $T^3$ and $T^{1.7}$ dependences.

nitude larger than that of $x=0.30$ and 0.50 samples. Note that the $\kappa_c$ data for different oxygen contents were collected on one and the same sample that was annealed each time to obtain the required $x$; the samples for $\kappa_{ab}$ differ in size by less than 20%. In addition, the low-$T$ parts of the $\kappa(T)$ data are not smooth: regardless of the oxygen content, all the crystals exhibit clear wiggles in their $\kappa(T)$ curves below 2 K, which suggests the existence of some kind of resonant phonon scattering.[6]

Upon applying the magnetic field at low temperatures, we have found remarkably strong changes in the heat conductivity of all crystals. For instance, at the lowest temperature 0.36 K, both $\kappa_{ab}$ and $\kappa_c$ of the parent compound $x=0.50$ show a steplike enhancement by several times with increasing field and saturates above ~5 T [Figs. 3(a)–3(d)]. At higher temperatures, a diplike feature appears at low field, while the subsequent enhancement at higher field gradually weakens with increasing temperature. At the "high" temperature of 5 K, the magnetic-field dependence is already rather weak and only a broad and shallow dip remains. Here, the most impressive result is the magnitude of the field-induced

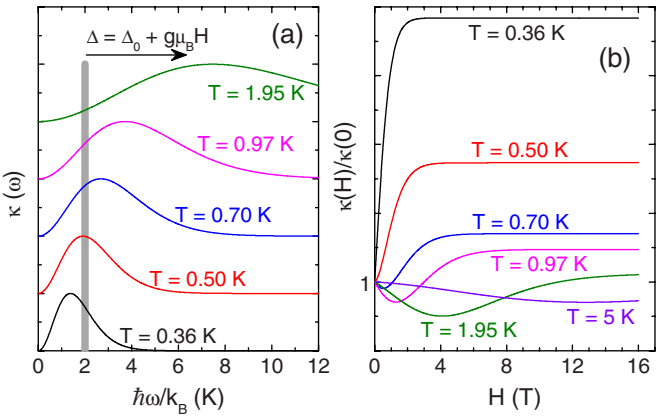


FIG. 4. (Color online) (a) Schematic picture of the phonon conductivity spectrum $\kappa(\omega)$ at several temperatures (the curves are normalized by their peak values and shifted vertically for clarity). The phonons can be strongly scattered by magnetic ions if their energy is close to the energy splitting of the spin states, which gives rise to a "resonant scattering band" centered at $\Delta=\Delta_0+g\mu_B H$, where $\Delta_0$ is the zero-field splitting and $g\mu_B H$ is the Zeeman splitting. (b) Simulated $\kappa(H)$ by assuming that the phonons within the resonant scattering band do not carry heat.

changes in $\kappa$: the low-field suppression can be as *large* as a factor of 2, and the high-field enhancement can be nearly 400%. While the magnitude of the high-field enhancement in $\kappa$ depends on the direction of the heat current [Figs. 3(a)–3(f)], it is surprisingly insensitive to the field direction, which confirms that magnon excitations in the long-range ordered spins cannot be relevant to the low-$T$ heat transport.

A clue given by the diplike feature in $\kappa(H)$ is that the low-$T$ heat transport may be governed by the phonon scattering by free spins,[6–8] as we previously observed in $Pr_{1.3}La_{0.7}CuO_4$.[12] Qualitatively, the $\kappa(H)$ behavior shown in Fig. 3 can be well understood in terms of magnetic scattering of phonons: (i) In zero field, the phonons are presumably scattered by the spins of Gd ions that behave like $S=7/2$ free spins judging from the low-$T$ magnetization and specific heat data.[9,10] To be capable of scattering phonons, the Gd spins should not be completely free, but the spin states should be slightly split, which has been confirmed by the heat capacity data. (ii) In magnetic fields, the energy splitting of the spin states is increased by the Zeeman effect. The phonon scattering off these spins is most effective in suppressing the heat transport when the energy splitting is equal to $\sim 3.8k_BT$, where the phonon conductivity spectrum (defined below) peaks; therefore, the spin-phonon scattering generates a diplike feature in $\kappa(H)$ at this energy and the dip position shifts to higher fields with increasing temperature.[6] (iii) In the high-field limit, the spin energy splitting becomes too large to exchange energy with phonons and the spin-phonon scattering is completely quenched, enhancing $\kappa$ above its zero-field value.

To illustrate the above picture, in Fig. 4 we show schematically the relation between the energy splitting of spin states and the peak in the phonon conductivity spectrum from the Debye model. The "phonon conductivity spectrum"

$\kappa(\omega)$ represents the contribution to thermal conductivity from the phonons with an energy $\hbar\omega$ and is proportional to $\omega^4 \exp(\hbar\omega/k_BT)/T^2[\exp(\hbar\omega/k_BT)-1]^2$ which peaks at energy $\hbar\omega \sim 3.8k_BT$.[6] Although Gd ions have the spin state $S=7/2$ that splits into eight energy states in magnetic fields, allowing multiple transitions, for simplicity we take just a single band, corresponding to the spin transition with the lowest energy, $\Delta m=1$. The energy of this transition changes with the magnetic field as $\Delta=\Delta_0+g\mu_BH$, and the phonons in a certain energy range around this $\Delta$ are considered to be resonantly scattered upon the spin transition. Figure 3(b) shows simulated $\kappa(H)$ behaviors, where one can see the variations of $\kappa$ as the position of the resonant scattering band is changed by the magnetic field. Upon calculating these $\kappa(H)$, we simply assume that those phonons whose energy lies in a resonant scattering band centered around $\Delta$ cannot contribute to the heat transport, and the rest of the phonons have the same relaxation time (which is the case at very low temperature).[17] It is reassuring that such a crude picture with only two adjustable parameters, $\Delta_0$ ($\approx$2 K) and the width of the resonant band, can capture most of the qualitative experimental features of $\kappa(H)$. Indeed, both the steplike enhancement and the diplike feature are essentially reproduced.

Nonetheless, there is an obvious difficulty in the above simple picture; namely, the magnitude of the observed changes in $\kappa(H)$ requires the resonance scattering band to be extremely wide; indeed, the observed fivefold increase in $\kappa$ implies that at least 80% of phonon conductivity spectrum are affected by the spin scattering. Apparently, including other resonance bands related to higher-energy spin transitions of Gd ions with $\Delta m>1$ does not help, since the Zeeman splitting $\Delta m g\mu_BH$ should quench these transitions at several times lower fields than we observe in the experiment. A possible explanation for the extremely wide scattering band is the local fluctuation of the zero-field splitting $\Delta_0$, which would be quite natural if $\Delta_0$ is determined by the dipole-dipole interactions within the disordered Gd subsystem. Depending on the local environment, Gd ions feel different local fields and thus should exhibit a continuous spectrum of spin-transition energies, rather than a single resonance line.[18]

We have done the same experiments on $x=0.30$ and 0.00 crystals and show the representative $\kappa(H)$ isotherms in Fig. 5. Obviously, the main features, including both the high-field steplike enhancement and low-field diplike feature, are the same as those for $x=0.50$ crystals. The essential similarity of the $\kappa(H)$ behaviors for different oxygen contents seems reasonable if the phonon scattering by Gd moments is playing the key role, since the oxygen content apparently has no major impact on the magnetic state of the Gd ions. This result clearly indicates the separable effects of free spins and impurities and/or defects on the low-$T$ heat transport of GBCO. It is worth noting that the quantitative $x$ dependence of $\kappa(H)/\kappa(0)$ is rather complicated, namely, the magnitude of $\kappa(H)/\kappa(0)$ is slightly enhanced upon increasing $x$ from 0.00 to 0.30, while it becomes much more pronounced upon further increasing $x$ to 0.50. Obviously, for quantitative description of the all experimental observations, not only the spin-phonon scattering but also the oxygen-induced lattice disorder must be taken into consideration.

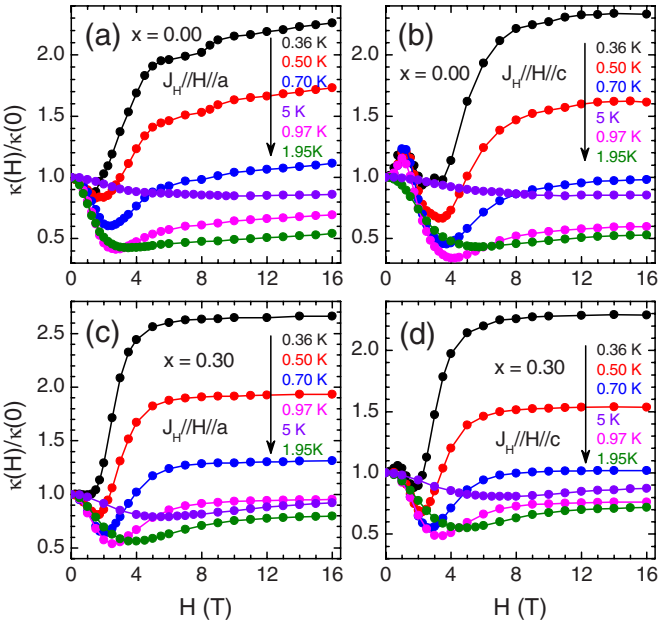


FIG. 5. (Color online) Representative data for the magnetic-field dependences of the low-$T$ thermal conductivity of $GdBaCo_2O_{5+x}$ single crystals with $x=0.00$ and 0.30.

Although the detailed mechanism of the large magnetothermal effect in GBCO calls for further investigation, one can already capture some important information from the above experimental results. First, the phonon heat transport can be strongly dependent on the magnetic field even at very low temperature for the materials containing paramagnetic moments, such as high-$T_c$ cuprates[12] and other strongly correlated compounds. Second, if the paramagnetic moments have a small enough splitting between the spin states, the spin-phonon scattering can survive down to very low temperature and prevent phonons from entering the boundary scattering limit. This makes the data analysis of the low-$T$ thermal conductivity very difficult, especially when the boundary scattering limit is required for separating the electron and phonon terms.[19–22]

## IV. SUMMARY

In summary, a surprisingly strong magnetic-field dependence of thermal conductivity is observed in GBCO single crystals down to very low temperatures. The main features of the magnetothermal conductivity, i.e., a high-field enhancement and a low-field dip, can be well understood in terms of the phonon scattering by the nearly free Gd spins. The present finding demonstrates the potentially significant role of the spin-phonon coupling in correlated oxides.

## ACKNOWLEDGMENTS

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*xfsun@ustc.edu.cn

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