# Thermal conductivity of pure and Zn-doped $LiCu_2O_2$ single crystals

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We report a study of the low-temperature thermal conductivity ($\kappa$) of pure and Zn-doped $LiCu_2O_2$ single crystals. The $\kappa(T)$ of pure $LiCu_2O_2$ single crystal shows a double-peak behavior, with two peaks located at 48 K and 14 K, respectively. The different dependences of the peaks on the Zn concentration indicate that the high-$T$ peak is likely due to the phonon transport while the low-$T$ one is attributed to the magnon transport in the spin spiral ordering state. In addition, the magnetic field can gradually suppress the low-$T$ peak but does not affect the high-$T$ one; this further confirms that the low-$T$ peak is originated from the magnon heat transport.

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## I. INTRODUCTION

$LiCu_2O_2$ is the first example of Cu-based multiferroic material and is particularly attractive because of its one-dimensional spin structure.[1–11] It promises a routine to find multiferroicity in some low-dimensional quantum magnets that exhibit the magnetic frustration effect.[12–14] It is known that $LiCu_2O_2$ crystallizes in an orthorhombic unit cell with space group $Pnma$ and lattice parameters $a = 5.734(4)$Å, $b = 2.856(2)$Å, and $c = 12.415(6)$Å at room temperature.[1] There are an equal number of $Cu^+$ and $Cu^{2+}$ ions in distinctly nonequivalent crystallographic positions, only the latter of which carry spin $S = 1/2$. The $Cu^{2+}$ ions are sitting on the center of edge-sharing $CuO_4$ plaquettes and form edge-shared chains running along the $b$ axis with the Cu-O-Cu bond angle of 94°.[1] The competition of the nearest-neighboring ferromagnetic (FM) interaction and the next-nearest-neighboring antiferromagnetic (AF) interaction of $Cu^{2+}$ spins leads to magnetic frustration and a spiral (helicoidal) magnetic order below ∼24 K.[1] More exactly, two AF transitions were found at $T_{N1} = 24.6$ K and $T_{N2} = 23.2$ K with a sinusoidal spin order at $T_{N2} < T < T_{N1}$ and an incommensurate cycloidal spin order at $T < T_{N2}$.[3–7] A spontaneous polarization along the $c$ axis emerges at the second phase transition[1] and was discussed to be originated from the inverse DM interaction of neighboring spins or the nonrelativistic exchange.[3,7] Furthermore, the magnetic field applied along the $b$ axis leads to the $Cu^{2+}$ spin spiral plane flipping from the $bc$ to the $ab$ plane and consequently results in the flip of the polarization from the $c$ to the $a$ direction.[1]

The low-temperature thermal conductivity is an effective probe for studying the transport properties of phonons and magnetic excitations, which might be of particularly interesting for the low-dimensional quantum magnets.[15–17] It is well known that the elementary excitations in magnetic long-range ordered states, magnons, can contribute to the heat transport properties by acting as either heat carriers or phonon scatterers.[18] In low-dimensional spin systems, even without exhibiting long-range ordering, the magnetic excitations can effectively transport heat because of the strong quantum fluctuations.[15] For example, the recent experiments revealed extremely large magnetic heat conductivity in one-dimensional spin 1/2 systems, such as $SrCuO_2$, $Sr_2CuO_3$, $CaCu_2O_3$, and $(Sr,Ca,La)_{14}Cu_{24}O_{41}$.[19–23] These results were theoretically well understood as the ballistic transport of spinons or magnons. On the other hand, the thermal conductivity can effectively detect the transitions of magnetic structure, like spin flop, reorientation or polarization.[24] In particular, the low-$T$ thermal conductivity was found to display drastic changes across these kinds of transition in some other families of multiferroic materials, for example, $HoMnO_3$ and $GdFeO_3$.[25,26]

Although the low dimensionality of the magnetic structure $LiCu_2O_2$ was already known for a long time, the heat transport properties have not been investigated for this material. In this work, we study the temperature and magnetic-field dependences of thermal conductivity ($\kappa$) of $LiCu_2O_2$ single crystals to probe the nature of magnetic excitations and the coupling between spin and lattice. It is found that the $\kappa(T)$ data show two peaks at 48 K and 14 K, which are above and below the long-range magnetic transition temperatures, respectively. The Zn substitution for Cu is found to be able to effectively suppress the two peaks but show quite different doping dependences. The magnetic field applied in the $ab$ plane only suppresses the low-$T$ peak. These results manifest that the low-$T$ peak is likely due to the magnons contribution to the heat transport acting as heat carriers, while the high-$T$ peak is phonon peak.

## II. EXPERIMENTS

High-quality single crystals of $LiCu_{2-x}Zn_xO_2$ with the nominal compositions $x = 0$, 0.02, 0.04, 0.10, and 0.20 are grown by a self-flux method. Correspondingly, the actual Zn contents of these crystals are $x = 0$, 0.013, 0.027, 0.064, and 0.177, measured by the inductively coupled plasma atomic-emission spectroscopy (ICP-AES) (with 10% uncertainty of measurements). The as-grown $LiCu_2O_2$ single crystals have plate-like shape with typical size as large as $10 \times 8 \times 0.5$ mm$^3$. Upon doping Zn, the sizes of crystals decrease gradually to about $5 \times 3 \times 0.5$ mm$^3$ for $x = 0.177$. The quality of the crystals, judged from the x-ray diffraction results, does not decay significantly. The largest surfaces of single crystals are confirmed to be the $ab$ planes by the x-ray diffraction and Laue back reflection.

 

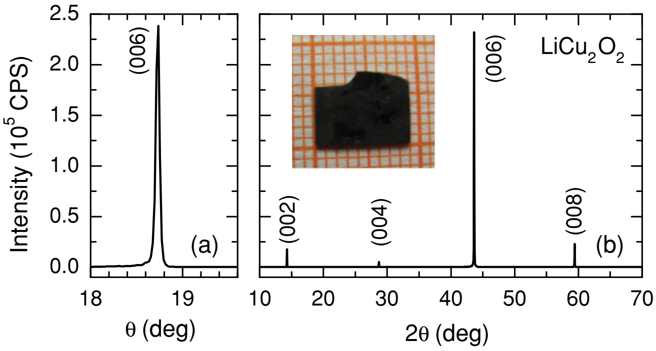


FIG. 1. (Color online) (a) X-ray rocking curve of the (006) reflection of a $LiCu_2O_2$ single crystal. The FWHM of the peak is only 0.05°. (b) X-ray (00*l*) diffraction pattern of the same crystal. Inset: The photograph of this crystal.

The magnetic susceptibility ($\chi$) is measured using a superconducting quantum interference device magnetometer (SQUID, Quantum Design). The specific heat is measured by the relaxation method in a physical property measurement system (PPMS, Quantum Design) from 2 to 300 K. The in-plane thermal conductivity is measured in PPMS with "one heater, two thermometers" configuration or in a $^4$He cryostat using a Chromel-Constantan thermocouple.[25–27]

### III. RESULTS AND DISCUSSION

$LiCu_2O_2$ single crystals have plate-like shape and shinning surfaces. Using x-ray diffraction, it is found that the large surface of the crystals are the *ab* plane, so it is easy to get the (00*l*) diffraction pattern. Figure 1 shows the x-ray diffraction results of a representative $LiCu_2O_2$ single crystal, including the (00*l*) diffraction pattern and the rocking curve of (006) peak. Figure 1(b) does not show any sign of other phases, indicating the high purity of this sample. The full-width at half-maximum (FWHM) of the (006) reflection is as small as 0.05°, indicating the perfect crystallinity of this sample. X-ray Laue back reflection is also used to determine the crystallographic axes. A fine twin structure of the *ab* plane is found, which is in agreement with the previous observation through a polarized optical microscope.[1] The origin is that the *a*-axis lattice constant is nearly the twice of the *b*-axis length. Because of the existence of twin structure, it is impossible to measure the in-plane anisotropy of the transport properties of $LiCu_2O_2$ single crystals, although all the samples are cut along the *a* (or *b*) axis.

The magnetic susceptibility and specific heat are measured to characterize our crystals. It has been known that the main feature of $\chi(T)$ for pure $LiCu_2O_2$ is a broad maximum at ∼36 K, which is a characteristic of quasi-one-dimensional magnet, and the onsets of long-range magnetic orders at $T_{N1}$ and $T_{N2}$ induce a sharp anomaly at the temperature derivative of the magnetic susceptibility, $d\chi(T)/dT$, for magnetic field along the *c* axis and the *ab* plane, respectively.[2] These results are well reproduced in our crystals, as shown in Figs. 2(a) and 2(b). Furthermore, upon doping Zn, the peak positions of $d\chi(T)/dT$ gradually move to lower temperatures, indicating the suppression of long-range magnetic order with increasing nonmagnetic impurities.[10,11] Figure 2(c) shows

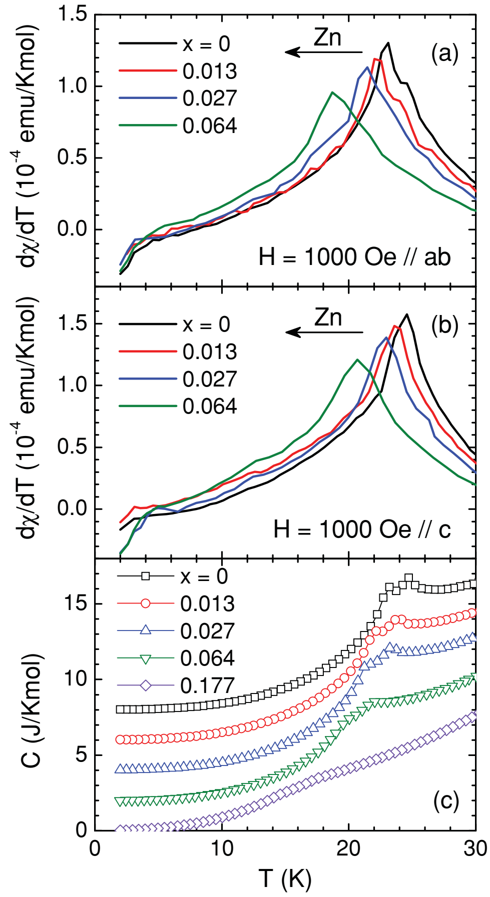


FIG. 2. (Color online) (a,b) Temperature dependences of $d\chi/dT$ for $LiCu_{2-x}Zn_xO_2$ single crystals along the *ab* plane and the *c* axis measured with 1000 Oe magnetic field. (c) Low-temperature specific heat of $LiCu_{2-x}Zn_xO_2$ single crystals. For clarity, the data are shifted upward by 2 J/Kmol one by one.

the low-temperature specific heat of pure and Zn-doped $LiCu_{2-x}Zn_xO_2$ single crystals. For pure sample, the $C(T)$ curve shows two small but clear peaks at $T_{N1} = 24.7$ K and $T_{N2} = 23.2$ K, respectively, which are known to be due to the magnetic phase transitions from paramagnetic state to a sinusoidal spin ordering and then to a helicoidal spin ordering.[3–7] Upon doping Zn, these two peaks shift to lower temperatures and become weaker and their positions have good correspondence with those in $d\chi(T)/dT$. When $x$ arrives 0.177, the two peaks in $C(T)$ are not distinguishable from each other and evolute to a hump-like anomaly at ∼17 K. This evolution of the specific heat with Zn doping is compatible with some earlier reports,[10,11] in which it was discussed that Zn doping results in either the phase transition of short-range or significant inhomogeneity.

Figure 3 shows the low-temperature thermal conductivity of pure and Zn-doped $LiCu_2O_2$ single crystals. The thermal conductivity of pure crystal is rather large but its temperature dependence is apparently different from that of usual insulators.[18] With lowering temperature, the $\kappa$ increases quickly and achieves a high value of 57 W/Km at 48 K. A remarkable feature of $\kappa(T)$ is the appearance of two peaks at 48 K and 14 K. It is notable that the minimum between two peaks is located at ∼22 K, having a good correspondence to

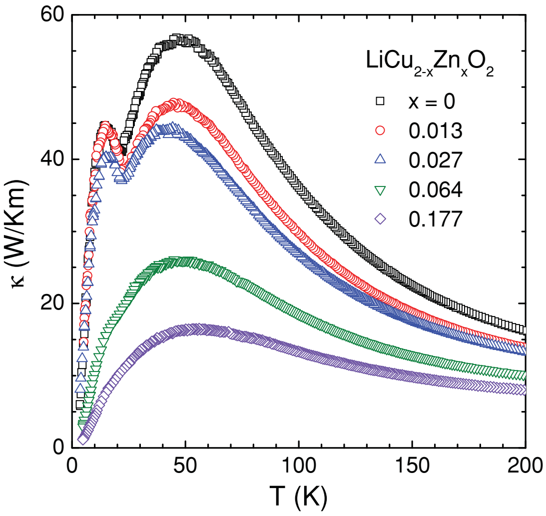


FIG. 3. (Color online) Thermal conductivity of pure and Zn-doped $LiCu_2O_2$ single crystals.

the positions of specific-heat peaks. This suggests a possible origin of the double peaks of $\kappa(T)$, that is, their appearance is due to the formation of a minimum, caused by strong phonon scattering by the spin fluctuations at the critical regions of magnetic transitions.[28] This phenomenon was also found in some multiferroic materials exhibiting strong spin-phonon coupling, such as $HoMnO_3$.[25] Although this explanation does not bring obvious contradict with the impurity (Zn) doping effect, however, it meets with difficulty in understanding the magnetic-field dependence of thermal conductivity, as shown below.

It is found that the two $\kappa(T)$ peaks show rather different dependences on the concentration of Zn. While the high-$T$ peak weakens gradually with increasing $x$, the low-$T$ one shows a weak $x$ dependence for low doping levels $x \leqslant 0.027$ but it is so strongly damped for $x \geqslant 0.064$ that it is almost smeared out completely. Note that the evolution of low-$T$ peak seems to have some direct relationship to the Zn-doping effect on the specific-heat data. As can be seen in Fig. 2, the two specific-heat peaks are also smeared out for $x \geqslant 0.064$, which manifests that the long-range spin orderings are destroyed by such high impurity dopings. This comparison naturally suggests that the low-$T$ peak of $\kappa(T)$, which locates at temperature just below the phase transition of long-range spin ordering, is likely due to the heat transport by the magnons in the antiferromagnetically ordered state.

As far as the high-$T$ peak of $\kappa(T)$ is concerned, one possible origin is the phonon peak as in usual insulators.[18] The magnitude of phonon peak is known to be strongly dependent on the impurities and point defects in crystals. Apparently, the strong impurity dependence of high-$T$ peak of $LiCu_2O_2$ is compatible with such standard behavior. However, one may note that the position of this "phonon peak" is located at a bit too high temperature, compared to many other materials which present phonon peaks below 20 K.[18] Therefore, we need to consider another possible origin of the high-$T$ peak due to the magnetic excitations transporting heat, as evidenced in many low-dimensional spin systems, such as $SrCuO_2$, $Sr_2CuO_3$, $CaCu_2O_3$, $Sr_{14}Cu_{24}O_{41}$, $La_2CuO_4$.[19–22,29–31] In these materials, the magnetic term of thermal conductivity can be much larger than the phononic term and is also sensitive to the impurities. In particular, the magnetic excitations heat transport in quasi-one-dimensional spin-1/2 materials was predicted to be the ballistic type. One direct experimental evidence for the ballistic transport was the nonmagnetic impurity doping effect, in which the mean-free path of magnetic excitations was found to be very close to the average distance between spin defects.[20] In this regard, the magnetic heat transport in these low-dimensional spin systems is usually obtained from the strong anisotropy of thermal conductivity;[16,17] that is, one can get the purely magnetic thermal conductivity by subtracting the phonon term, which is estimated from the thermal conductivity perpendicular to the one-dimensional spin chain or the two-dimensional spin network. It will be interesting to get the magnetic heat transport in $LiCu_2O_2$ by using the same method and compare the Zn-doping effect with that in other spin-1/2 chain compounds. However, because of the in-plane twin structures of $LiCu_2O_2$ crystals, one cannot separate the heat transport along the $a$ and the $b$ axes. In addition, the heat transport along the $c$ axis is also found to be impossible to measure reliably because of the easy cleavage of the $LiCu_2O_2$ crystals along the $ab$ plane. It is therefore not feasible for us now to get the magnetic heat transport along the spin chains in these $LiCu_2O_2$ crystals. An effective way to detwin the $LiCu_2O_2$ crystals is called for the investigation on the possible role of the magnetic excitations transporting heat.

The effect of magnetic field on the thermal conductivity is studied for in-plane fields up to 14 T. First of all, as shown in Fig. 4(a), the high-$T$ peak is completely independent of the magnetic field, which would not be unreasonable if the high-$T$ peak is a pure phononic behavior. For some well-studied low-dimensional magnetic materials, it is also found in recent experiments that the magnetic heat transport is insensitive to the external magnetic field, which is however due to the large exchange coupling in these materials, typically being of the order of magnitude of 100 meV.[22,32] The exchange coupling in $LiCu_2O_2$ is known to be more than one order of magnitude smaller[2] and is therefore not much larger than the energy caused by the magnetic field in order of 10 T. In this sense, the insensitivity of the high-$T$ thermal conductivity to the magnetic field may not support the conjecture that the magnetic excitations are responsible for transporting heat above the magnetic phase transitions and the formation of high-$T$ peak. Second, the "dip" between two $\kappa(T)$ peaks does not show any change in applied magnetic field, which immediately rule out the possibility that the "dip" is caused by strong spin-phonon scattering. In contrast, it has already been found in many AF materials that the strong magnetic field can suppress the spin fluctuations and recover the thermal conductivity if the spin-phonon coupling is considerably strong.[25]

On the other hand, the low-$T$ peak is gradually suppressed by the magnetic field, similar to those in many antiferromagnetically ordered materials.[33] The detailed field dependences of $\kappa$ are shown in Fig. 4(b), in which two $\kappa(H)$ isotherms at 5 and 18 K are included. It is clear that the thermal conductivity is monotonically decreased with increasing field, without showing any signature of saturation or drastic transition up

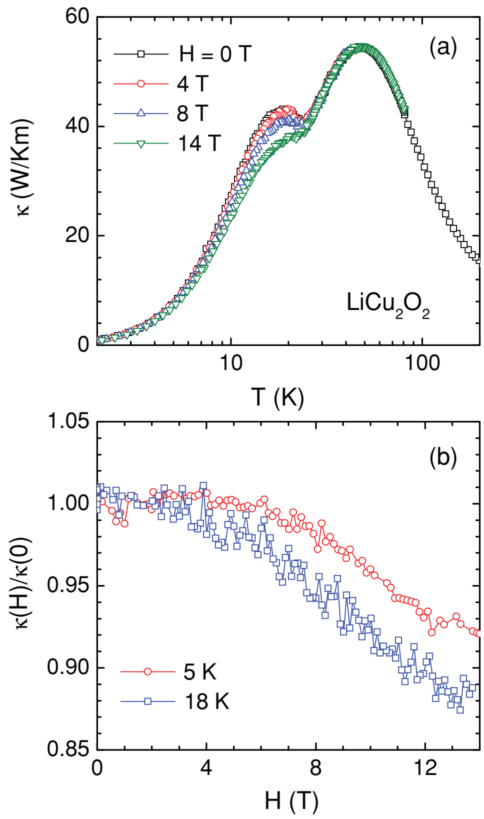


FIG. 4. (Color online) (a) Temperature dependences of thermal conductivity of $LiCu_2O_2$ single crystal in 0–14 T. The direction of magnetic field is along that of the heat current. (b) Low-temperature $\kappa(H)$ isotherms at 5 K and 18 K.

to 14 T. This kind of field dependence is expectable for the magnon heat transport since the magnons tend to be less populated with increasing magnetic field. In addition, the field dependence at 18 K, which is near the low-$T$ peak of $\kappa(T)$, is stronger than that at 5 K. It is also understandable because the magnetic heat conductivity is apparently much larger at 18 K. This result shows clear evidence that below the long-range-order transition temperature the magnons act as heat carriers in $LiCu_2O_2$. Note that both the $\kappa(T)$ and $\kappa(H)$ behaviors indicate that the magnon heat transport seems to be weakened with lowering temperature. This is mainly due to the decrease of magnon population and is reasonable for $LiCu_2O_2$ since there is a 1.4 meV gap in the magnetic excitation spectrum, found by the electron spin resonance experiments.[8] It can be seen that the heat transport properties of $LiCu_2O_2$ are rather conventional,[33] without showing any peculiar behavior of the low-dimensional quantum magnets. The reason is likely related to the rather strong spin frustration in this material.

It has been known that the in-plane magnetic field can rotate the spin directions and produce some spin-flop-like transitions at 2 T.[1] However, the $\kappa(H)$ curves do not show any anomaly across these transitions, in contrast to some observations in other compounds.[24–26] One reason for the drastic change of $\kappa$ at the spin-flop transition is that the magnons are significantly populated because of the closure of the anisotropy gap.[24] Therefore, it is not clear whether the magnon spectrum is gapless at the spin reorientation transition in this spirally ordered antiferromagnet.

## IV. SUMMARY

The Zn-doping and magnetic-field dependences of thermal conductivity of $LiCu_2O_2$ single crystals are carefully studied. The $\kappa(T)$ data show a double-peak phenomenon. The higher-$T$ peak at 48 K is due to the phonon heat transport, while the lower-$T$ peak at 14 K is a result of magnon heat transport showing up in the magnetic long-range-ordered state. The present results indicate that the magnetic heat transport of $LiCu_2O_2$ behaves similarly as that in the three-dimensional antiferromagnets. The absence of the characteristic transport properties of that in the low-dimensional quantum spin systems may be related to the complexity of spin structure and spin frustration.

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