Thermal conductivity of pure and Zn-doped LiCu$_2$O$_2$ single crystals

X. G. Liu,$^1$ X. M. Wang,$^1$ W. P. Ke,$^1$ W. Tao,$^1$ X. Zhao,$^2$ and X. F. Sun$^1$

$^1$Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People’s Republic of China
$^2$School of Physical Sciences, University of Science and Technology of China, Hefei, Anhui 230026, People’s Republic of China

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We report a study of the low-temperature thermal conductivity ($\kappa$) of pure and Zn-doped LiCu$_2$O$_2$ single crystals. The $\kappa(T)$ of pure LiCu$_2$O$_2$ single crystal shows a double-peak behavior, with two peaks locating 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$_2$O$_2$ is the first example of Cu-based multiferroic material and is particularly attractive because of its one-dimensional spin structure.$^1$ It promises a new routine to find multiferroicity in some low-dimensional quantum magnets that exhibit the magnetic frustration effect.$^{12-14}$ It is known that LiCu$_2$O$_2$ 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$^{2+}$ 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 $94^\circ$. The competition of the nearest-neighbor ferromagnetic (FM) interaction and the next-nearest-neighbor antiferromagnetic (AF) interaction of Cu$^{2+}$ spins leads to magnetic frustration and a spiral (helicoidal) magnetic order below $\sim 24$ 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 $T < T_{N2}$.$^{12,13}$ A spontaneous polarization along the $c$ axis emerges at the second phase transition$^{14}$ and was discussed to be originated from the inverse DM interaction of neighboring spins or the nonrelativistic exchange.$^{15}$ 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.$^{16}$

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.$^{19}$ For example, the recent experiments revealed extremely large magnetic heat conductivity in one-dimensional spin 1/2 systems, such as SrCuO$_2$, Sr$_2$CuO$_3$, CaCu$_2$O$_3$ and (Sr,Ca,La)$_{24}$Cu$_{24}$O$_{41}$.$^{20-22}$ 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$_2$O$_2$ has already known for 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$_2$O$_2$ single crystals for probing 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$_x$O$_2$ 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

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and 0.177, measured by the inductively-coupled plasma atomic-emission spectroscopy (ICP-AES) (with 10% uncertainty of measurements). The as-grown LiCu$_2$O$_2$ single crystals have plate-like shape with typical size as large as 10 × 8 × 0.5 mm$^3$. Upon doping Zn, the sizes of crystals decrease gradually to about 5 × 3 × 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.

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 \[2,3\].

III. RESULTS AND DISCUSSION

LiCu$_2$O$_2$ single crystals have plate-like shape and shining 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$_2$O$_2$ 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. 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$_2$O$_2$ 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$_2$O$_2$ is a broad maximum at $\sim 36$ 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. Figure 2(c) shows the low-temperature specific heat of pure and Zn-doped LiCu$_{2-x}$Zn$_x$O$_2$ 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. 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 evolve to a hump-like anomaly at $\sim 17$ K. This evolution of the specific heat with Zn doping is compatible with some earlier reports 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$_2$O$_2$ single crystals. The thermal conductivity of pure crystal is rather large but its temperature dependence is apparently different from that of usual insulators. 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 $\sim 22$ K, having a good correspondence to 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. This phenomenon was also found in some multiferroic materials exhibiting strong spin-phonon coupling, such as HoMnO$_3$. Although this explanation does not bring obvious contra-
FIG. 4: (Color online) (a) Temperature dependences of thermal conductivity of LiCu$_2$O$_2$ 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.

not feasible for us now to get the magnetic heat transport along the spin chains in these LiCu$_2$O$_2$ crystals. An effective way to detwin the LiCu$_2$O$_2$ 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. The exchange coupling in LiCu$_2$O$_2$ is known to be more than one order of magnitude smaller 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.

On the other hand, the low-$T$ peak is gradually suppressed by the magnetic field, similar to those in many antiferromagnetically ordered materials. 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 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 a clear evidence that below the long-range-order transition temperature the magnons act as heat carriers in LiCu$_2$O$_2$. 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$_2$O$_2$ since there is a 1.4 meV gap in the magnetic excitation spectrum, found by the electron spin resonance experiments. It can be seen that the heat transport properties of LiCu$_2$O$_2$ are rather conventional 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. However, the $\kappa(H)$ curves do not show any anomaly across these transitions, in contrast to some observations in other compounds. 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. Therefore, it is not clear whether the magnon spectrum is gapless at the spin re-orientation transition in this spirally ordered antiferromagnet.

IV. SUMMARY

The Zn-doping and magnetic-field dependences of thermal conductivity of LiCu$_2$O$_2$ 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$_2$O$_2$ behaves similarly as that in the three-dimensional antiferromagnets. The absence of the characteristic transverse magnon response in LiCu$_2$O$_2$ may be related to the complexity of spin systems as well as the structure and spin frustration.

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