Low-temperature thermal conductivity of antiferromagnetic $S = 1/2$ chain material CuCl$_2$·2((CH$_3$)$_2$SO)

W. P. Ke$^1$, J. Shi$^2$, F. B. Zhang$^1$, Z. Y. Zhao$^1$, C. Fan$^1$, X. Zhao$^1$$^,$$^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

$^2$Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People’s Republic of China

$^3$School of Physical Sciences, University of Science and Technology of China, Hefei, Anhui 230026, People’s Republic of China

We study the heat transport of $S = 1/2$ chain compound CuCl$_2$·2((CH$_3$)$_2$SO) along the $b$ axis (vertical to the chain direction) at very low temperatures. The zero-field thermal conductivity ($\kappa$) shows a distinct kink at about 0.9 K, which is related to the long-range antiferromagnetic (AF) transition. With applying magnetic field along the $c$ axis, $\kappa(H)$ curves also show distinct changes at the phase boundaries between the AF and the high-field disordered states. These results indicate a strong spin-phonon interaction and the magnetic excitations play a role in the $b$-axis heat transport as phonon scatterers.

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Low-dimensional quantum magnets were revealed to exhibit exotic ground states, magnetic excitations, and quantum phase transitions (QPTs). The heat transport in these materials has attracted much attention due to the role of magnetic excitations. In quasi-one-dimensional systems, particularly for the $S = 1/2$ chains or spin ladders, a large contribution of magnetic excitations to transporting heat along the spin chains was theoretically predicted and experimentally confirmed. Along other directions, however, the magnetic excitations are weakly dispersive and they cannot carry heat but scatter phonons. In some examples, such spin-phonon interactions are so strong that the thermal conductivity ($\kappa$) show remarkable feature of resonant phonon scattering and can be changed by magnetic field very strongly.

CuCl$_2$·2((CH$_3$)$_2$SO) (abbreviated as CDC) is an $S = 1/2$ spin chain material. It crystallizes in an orthorhombic structure, with the space group $Pnma$ and the room-temperature lattice constants $a = 8.054$, $b = 11.546$, and $c = 11.367$ Å. The Cu-Cl-Cu bonds form spin chains along the $a$ axis with strong superexchange interactions between Cu$^{2+}$ spins mediated by Cl$^-$ ions. The magnetic structure was determined as an AF chain system with the intrachain interactions $J = 1.43$ meV. Inelastic neutron scattering revealed that the spectra of magnetic excitations include both the soliton and the bound-spinon states in the presence of staggered fields. The specific heat heat results showed a long-range AF transition at $T_N = 0.93$ K, which changes with applying magnetic fields. When the field is along the $b$ axis, the AF state is enhanced and the transition temperature increases with increasing field. With magnetic fields along the $a$ or the $c$ axis, the transition moves to lower temperatures with increasing field and disappears at about 6 and 3.9 T for $H \parallel a$ and $c$, respectively, which corresponds to a second-order QPT from the magnetically ordered state to a disorder state. In addition, a spin-flop transition occurs at about 0.3 T ($H \parallel c$), due to the competitions among the spin anisotropy, the interchain interactions, and the staggered fields. CDC was recently found to exhibit magnetically induced multifermicity and therefore the spin-phonon coupling in this material would be an interesting physical issue.

Here we report a study on the thermal conductivity ($\kappa$) of CuCl$_2$·2((CH$_3$)$_2$SO) single crystal at very low temperatures down to 0.3 K and in magnetic fields up to 14 T. It is found that, for the heat current vertical to the spin-chain direction, the magnetic excitations play a role of scattering phonons. Applying magnetic field along the $c$ axis can suppress the magnetic excitations and lead to a large increase of $\kappa$ at high fields.

The CDC single crystals with nearly a parallelepiped shape were grown using a solution method. The largest naturally formed surface is the $ab$ plane and the longest edge is along the $b$ axis (the spin chains are along the $a$ axis). The thermal conductivities were measured along the $b$ axis by using a conventional steady-state technique. The specific heat was measured by the relaxation method in the temperature range from 0.4 to 30 K using a commercial physical property measurement system (PPMS, Quantum Design). The magnetic susceptibility and magnetization were measured using a SQUID-VSM (Quantum Design). One difficulty in this work is that the CDC crystals are so fragile that they are easily broken upon cooling. It is almost impossible to carry out the low-$T \kappa$ measurements on a CDC crystal without introducing any damage. In fact, every time after a thermal cycle, the crystals were broken into several pieces or some obvious cracks appeared. In this work, the thermal conductivity data were collected on a sample with some cooling-produced cracks. Therefore, it should noted that the magnitude of $\kappa$ is likely smaller.

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$^a$Electronic mail: xiazhao@ustc.edu.cn
$^b$Electronic mail: xfsun@ustc.edu.cn
than the intrinsic value. However, the qualitative behaviors of $\kappa$, particularly the field dependencies, are able to demonstrate the role of magnetic excitations in the heat transport properties.

Figure 1(a) shows the low-$T$ magnetic susceptibility and magnetization of a CDC single crystal with $H \parallel c$. A broad peak of $\chi(T)$ at about 10 K demonstrates the low-dimensional characteristic of the spin systems. The magnetization shows a good linear behavior at temperatures down to 2 K. These results are essentially consistent with the earlier results.\textsuperscript{13,14}

Figure 1(b) shows the low-$T$ specific heat data of a CDC single crystal with $H \parallel c$. In zero field, the curve displays an obvious deviation from the $T^3$ law (the simple crystal lattice specific heat) below 12.5 K, which is caused by the enhancement of the magnetic correlations. At lower temperatures, a sharp peak shows up at 0.92 K, which is known to be a long-range AF transition. Applying magnetic field along the $c$ axis can suppress the AF order with the transitions peak shifting to lower temperatures. Note that the data show exponential $T$-dependence at very low temperatures, indicating a gapped magnetic excitation. These phenomena are consistent well with the earlier results.\textsuperscript{13} An interesting phenomenon is that in high field (6 T), while the AF transition peak disappears and the low-$T$ specific heat is strongly suppressed, the specific heat at high temperatures is somewhat enhanced. As a result, the $C(T)$ curve shows a pronounced hump at low temperatures. Apparently, the spin fluctuations are still very strong in high magnetic fields.

Figure 2(a) shows the temperature dependencies of $\kappa$ with $H \parallel c$ and heat current $J \parallel b$. At zero field, $\kappa(T)$ displays a kink-like feature at $T < 1$ K, which is apparently related to the AF transition shown by the specific heat data. In principle, this feature can be caused by either a magnon heat transport below $T_N$ or a strong phonon scattering by magnetic excitations at the critical region of phase transition. In the present work, the $\kappa$ was measured along the $b$ axis, in which the spin interactions are weak. Therefore, the magnetic excitations can influence the heat transport only by scattering phonons; that is, the feature of the zero-field $\kappa(T)$ at $T < 1$ K is likely related to a phonon scattering by the critical fluctuations. Upon applying magnetic field to 3 T, the kink-like feature becomes weaker and shifts to lower temperature, which corresponds to the suppression of the AF transition. In a high magnetic field of 14 T, this feature disappears while another kink-like feature shows up at about 2.5 K, which is likely due to the phonon-resonance scattering induced by an energy gap of the spin spectrum. This field-induced gap is related to the presence of a staggered $g$-tensor and Dzyaloshinskii-Moriya interactions.\textsuperscript{14} Using either the boson model or the sin-Gordon model, the gap was estimated to be about 0.8 meV at 14 T field along the $c$ axis.\textsuperscript{11} In a scenario of resonant phonon scattering by magnetic excitations associated with a spin gap, the strongest scattering occurs when the thermal energy $k_BT$
and the gap size $\Delta$ has a relationship of $\Delta = 3.8k_B T$. Thus, the phonon resonant scattering is expected to locate at about 2.4 K, which matches well with the experimental data shown in Fig. 2(a) (an arrow indicates the kink of 14 T data at $\sim 2.7$ K).

In passing, it is worthy of pointing out that the thermal conductivity along the spin-chain direction (the $a$ axis) is expected to display the magnon heat transport, because of the significant magnon dispersion along the chain. However, the measurement along the $a$ axis was not yet successful for CDC crystals, because one needs to cut the crystal along the direction vertical to the naturally formed longest dimension and would very easily damage this fragile material.

Figure 2(b) shows the detailed field dependencies of $\kappa$ with $H \parallel c$ and $J \parallel b$. At lowest temperature (0.38 K), the $\kappa(H)$ isotherms show a weak decrease at low fields and a small but sharp increase at $\sim 3.25$ T; above 4 T, the $\kappa$ is nearly independent of field. At higher temperatures (0.55 – 1.04 K), the $\kappa(H)$ show similar behavior but with some small differences. First, the enhancement of $\kappa$ in high fields is more significant. Second, the increase of $\kappa$ at $\sim 3.25$ T becomes not so sharp and moves to lower fields. The high-field plateau is formed at much higher field or not formed up to 14 T. For even higher temperature of 2.1 K, the field dependence becomes weaker again and shows a smooth increase function. At 5.5 K, the field dependence changes sign; that is, the $\kappa$ is suppressed with applying field although it seems to be recovering at very high fields. In general, the low-field suppression of $\kappa$ is caused by the magnetic excitations scattering phonons, while the high-field increase of $\kappa$ is due to the suppression of magnetic excitations. Note that the sharp increases of the low-$T$ $\kappa(H)$ curves have a good correspondence to the transition from the low-field AF state to the high-field paramagnetic state, which has already been determined in some earlier works by using other measurements as shown in Fig. 3.

It is common to many magnetic materials that the magnetic excitations can interact with phonons and sometimes introduce very strong magnetic-field dependence of thermal conductivity. In particular, all the multiferroic materials, of which the heat transport properties have been studied are known to exhibit strong interactions between magnetic excitations and phonons. Our data show that the field dependence of $\kappa$ in CDC is comparable to many other materials, which indicates a rather strong spin-phonon coupling in this organic material.

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