Low-Temperature Heat Transport in the Low-Dimensional Quantum Magnet $NiCl_2$-$4SC(NH_2)_2$

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We report a study of the low-temperature thermal conductivity of $NiCl_2$-$4SC(NH_2)_2$, which is a spin-1 chain system exhibiting the magnon Bose-Einstein condensation (BEC) in a magnetic field. It is found that the low-T thermal conductivity along the spin-chain direction shows strong anomalies at the lower and upper critical fields of the magnon BEC state. In this state, magnons act mainly as phonon scatterers at relatively high temperature, but change their role to heat carriers upon temperature approaching zero. The result demonstrates a large thermal conductivity in the magnon BEC state and points to a direct analog between the magnon BEC and the conventional one.

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Bose-Einstein condensation (BEC) denotes the formation of a collective quantum ground state of identical particles obeying Bose statistics. This fascinating state of matter is well established for liquid ^{4}He and ultracold alkali atoms. It turns out that a form of BEC can also be observed in quantum magnets [1–5], in which the density of magnons (bosons) can be tuned by an external magnetic field (playing the role of chemical potential). Recently, this so-called magnon BEC state has been experimentally realized in a growing number of dimerized spin-1/2 systems, such as the three-dimensional system $TlCuCl_3$ [6,7], the quasi-two-dimensional system $BaCuSi_2O_6$ [8,9], and the spin-ladder compounds $(CH_3)_2CHNH_3CuCl_3$ and $(C_5H_{12}N)_2CuBr_4$ [10,11], etc. A common characteristic of these quantum magnets is the spin-gapped ground state at zero field. The external magnetic field can close the spin gap and lead to a long-range antiferromagnetic (AF) order when the Zeeman energy overcomes the gap between the singlet ground state and the excited triplet states. It is notable that some alternative theories have also been proposed to explain the field-induced AF ordered state in quantum magnets, challenging the validity of the magnon BEC scenario for these systems [12,13]. To firmly establish the BEC of magnons and to develop a deeper understanding of this novel state of matter, it would be desirable to look for obvious analogs in the basic physical properties between the magnon BEC and the conventional one. One of the outstanding properties of the superfluid ^{4}He is the extremely large thermal conductivity (κ) [14,15], which is well understood using the two-fluid model. It is natural to ask whether the thermal conductivity (by magnons) in the magnon BEC state behaves similarly to that in the superfluid ^{4}He. The first experimental exploration done by Kudo *et al.* [16] did reveal an enhancement of thermal conductivity at the magnon BEC transition of $TlCuCl_3$. However, without carefully studying the anisotropic heat transport, it is not clear whether the enhancement is caused by the weakening of phonon scattering or the appearance of magnetic heat carriers.

The organic compound $NiCl_2$-$4SC(NH_2)_2$ [dichloro-tetrakis thiourea-nickel (II), abbreviated as DTN] is the only quantum spin-1 system, rather than spin-1/2 dimers, to exhibit the BEC of spin degrees of freedom [17–22]. It has a tetragonal crystal structure (space group I4) [23], which satisfies the axial spin symmetry requirement for a BEC. The Ni spins are strongly coupled along the tetragonal c axis (Fig. 1), making DTN a system of weakly interacting spin-1 chains with single-ion anisotropy larger than the intrachain exchange coupling. The anisotropy, intrachain, and interchain exchange parameters of Ni spins were determined to be $D = 8.9$ K, $J_c = 2.2$ K, and $J_{a,b} = 0.18$ K [17–20], respectively. It was found that the Ni spin triplet is split into a $S_z = 0$ ground state and $S_z = \pm 1$

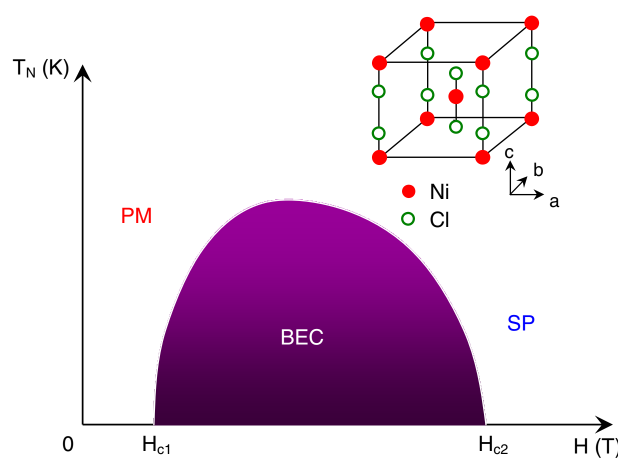

FIG. 1 (color online). Temperature-field phase diagram of DTN ($H \parallel c$) obtained from magnetization, specific heat, and magnetocaloric effect measurements [17–20]. PM and SP represent the low-field quantum paramagnetic state and high-field spin-polarized state, respectively. Magnon BEC is a magnetic-field-induced AF ordered state, with the lower and upper critical fields H_{c1}(~2 T) and H_{c2}(~12 T). The maximum of field-dependent critical temperature is about 1.2 K, where H_{c1} and H_{c2} merge. Inset: Unit cell of tetragonal structure showing Ni and Cl atoms. The other atoms are omitted for clarity.

excited states with an anisotropy gap of D, which precludes any magnetic order at zero field. When a magnetic field is applied along the c axis, the Zeeman effect lowers the $S_z = 1$ level until it becomes degenerate with $S_z = 0$ ground state at H_{c1}, which is essentially the same as that occurs in the spin-1/2 dimerized systems. Between H_{c1} and H_{c2} and below the maximum $T_c(H) \sim 1.2$ K (Fig. 1), the magnetic field induces an AF order or a magnon BEC. For magnetic field perpendicular to the c axis, however, the $S_z = 0$ ground state mixes with a linear combination of the $S_z = \pm 1$ excited states and there is no level crossing with increasing field and therefore no magnetic order [17]. DTN was found to be an ideal system for studying the magnon BEC in the sense that its lower and upper critical fields are not high, about $H_{c1} \sim 2$ T and $H_{c2} \sim 12$ T, which are easily achievable by the common laboratory magnets. In this Letter, we show that the low temperature and high-magnetic-field thermal conductivity of DTN single crystals indeed demonstrates a large thermal conductivity in the magnon BEC state.

High-quality $NiCl_2$-$4SC(NH_2)_2$ single crystals are grown from aqueous solution of thiourea and nickel chloride [23]. The typical size of single crystals is (0.5–2) × (0.5–2) × (3–4) mm^3. X-ray diffraction indicates that the parallelepiped crystals are grown along the c axis (the maximum dimension) while the four side surfaces are the (110) crystallographic plane. So it is easy to prepare samples for the thermal conductivity measurements either along (κ_c) or perpendicular to (κ_{ab}) the direction of spin chains. The thermal conductivity is measured using a conventional steady-state technique and two different processes: (i) using a "one heater, two thermometers" technique in a ^{3}He refrigerator and a 14 T magnet for taking data at temperature regime of 0.3–8 K; (ii) using a chromel-constantan thermocouple in a ^{4}He cryostat for taking zero-field data above 4 K [24]. It is worth emphasizing that a careful precalibration of resistor sensors is indispensable for the precise thermal conductivity measurements in high magnetic fields and at low temperatures.

Figure 2 shows the temperature dependences of κ_c and κ_{ab} in zero field and several magnetic fields up to 14 T. As in usual insulating crystals [25], there is a clear phonon peak at 8–9 K in both κ_c and κ_{ab}, for which the peak magnitude is 8.5 and 24 W/K m, respectively. It can be seen that the heat conductivity of this organic crystal is rather large compared to common organic materials; actually, the phonon peak in DTN is comparable or even larger than that in many inorganic crystals, such as transition-metal oxides. One remarkable behavior of $\kappa(T)$ in zero field is a "shoulderlike" feature at $\sim$2 K; in addition, the "shoulder" moves to lower temperature upon increasing the magnetic field. This kind of temperature dependence in $\kappa(T)$ usually indicates a resonant phonon scattering [25] by some lattice defects, magnetic impurities, or magnon excitations, etc. Apparently, the sensitivity of the shoulder to the applied field suggests the magnetic origin of this resonant scattering. Another

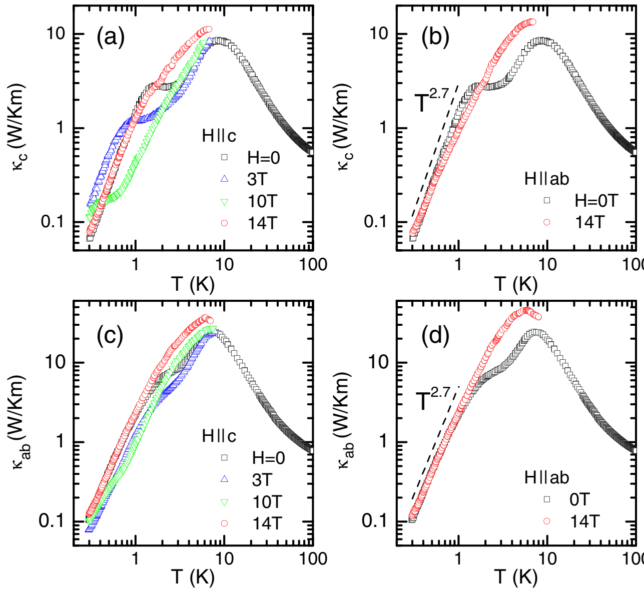

FIG. 2 (color online). Temperature dependences of thermal conductivities of DTN single crystals for κ_c and κ_{ab} in both the zero field and several different magnetic fields up to 14 T, which applied along the c axis or the ab plane. The dashed lines in panels (b) and (d) indicate that the zero-field thermal conductivities at sub-Kelvin temperatures show a $T^{2.7}$ temperature dependence.

important feature of $\kappa(T)$ is that at sub-Kelvin temperature regime, the thermal conductivity shows a $T^{2.7}$ dependence, which is close to the T^3 law of the standard temperature dependence of the phonon thermal conductivity in the boundary scattering limit [25]. One possible reason of the slight deviations from T^3 law is due to the phonon specular reflections at the sample surface [26,27].

Detailed magnetic-field dependence of the low-temperature thermal conductivity is a key to understanding the mechanism of heat transport in the low-dimensional spin systems [28]. Figure 3 shows the $\kappa(H)$ isotherms for both κ_c and κ_{ab}; in each case the magnetic field is applied both along the c axis and along the ab plane. Although the $\kappa(H)$ behaviors in general are rather complicated in these four measurement configurations, one can easily notice the most striking result shown in Fig. 3(a), that is, at very low temperatures $\kappa_c(H)$ display two peaklike anomalies across $\sim$2.5 and 12 T ($\parallel c$), which are very close to the reported critical fields H_{c1} and H_{c2} [17–19], and the anomalies are getting enhanced upon temperature approaching zero. Furthermore, $\kappa_{ab}(H)$ also show steep changes across these two characteristic fields for $H \parallel c$. The interesting point is that both $\kappa_c(H)$ and $\kappa_{ab}(H)$ do not show any drastic change at $\sim$2.5 and 12 T for $H \perp c$. Since DTN does not exhibit any field-induced magnetic ordering or magnon BEC state when the magnetic field is perpendicular to the c axis [17], these data clearly indicate that the strong peaklike anomalies in Fig. 3(a) are related to the quantum phase transitions at H_{c1} and H_{c2}.

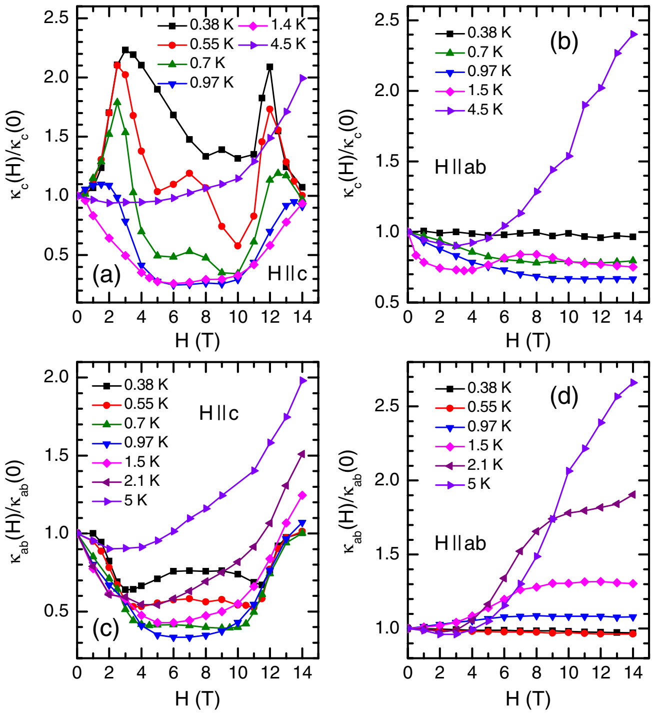

FIG. 3 (color online). Magnetic-field dependences of thermal conductivities of DTN single crystals at low temperatures.

It is interesting to compare $\kappa_c(H)$ and $\kappa_{ab}(H)$ behaviors in the c-axis field, in which the magnon BEC can occur. Above 1.4 K, κ_c and κ_{ab} have essentially similar magnetic-field dependences, as shown in Figs. 3(a) and 3(c), while the difference between them shows up and becomes larger upon lowering temperature. For clarity, Fig. 4 shows a direct comparison of $\kappa_c(H)$ and $\kappa_{ab}(H)$ at sub-Kelvin temperatures. At 0.97 K, both $\kappa_c(H)$ and $\kappa_{ab}(H)$ show a "U"-shaped curve: a steep decrease across 2.5 T, a strong suppression but weak field dependence in the intermediate field regime, and a steep recovery of conductivity across 12 T. There is also a small difference between these two curves, that is, a small and broad peak below 2 T shows up in $\kappa_c(H)$ isotherm. With lowering temperature, the behavior of $\kappa_{ab}(H)$ does not change much, except that the suppression of the thermal conductivity in the intermediate field regime is gradually getting weaker and two shallow "dips" appear at $\sim$3 and 11.5 T. In the meantime, the behavior of $\kappa_c(H)$ changes much more drastically. First, the large peaklike anomalies at $\sim$2.5 and 12 T show up below 0.7 K and become more significant upon $T \rightarrow 0$ K. Second, the suppression of thermal conductivity in the intermediate field regime is getting weaker rather rapidly with lowering temperature and finally evolves to an enhancement (compared to the zero-field conductivity) at 0.38 K, which strongly suggests that there are two competing impacts on thermal conductivity induced by the magnetic field. Apparently, the main difference between κ_c and κ_{ab} can only come from anisotropic magnetic contributions to heat transport, acting as either heat carriers or phonon scatterers. Because of the strong anisotropy of the magnon dispersion [17], it is a natural conclusion that the strong suppression of $\kappa_{ab}(H)$ at $H_{c1} < H < H_{c2}$ is mainly due to the phonon scattering by magnons; on the other hand, although the magnon scattering can also weaken the phonon thermal conductivity along the c axis, the magnons (with stronger dispersion in this direction) can act as heat carriers and make an additional contribution to the heat transport. Furthermore, between the two competing roles of magnons in affecting κ_c, i.e., scattering phonons or carrying heat, the latter one is apparently dominant at low temperatures. Note that because of the two competing effects of magnons on the heat transport, the ability of magnons to carry heat must be much larger than what the raw $\kappa_c(H)$ data ($H \parallel c$) demonstrate. To our knowledge, there has been no such clear evidence showing a large thermal conductivity in the magnon BEC state.

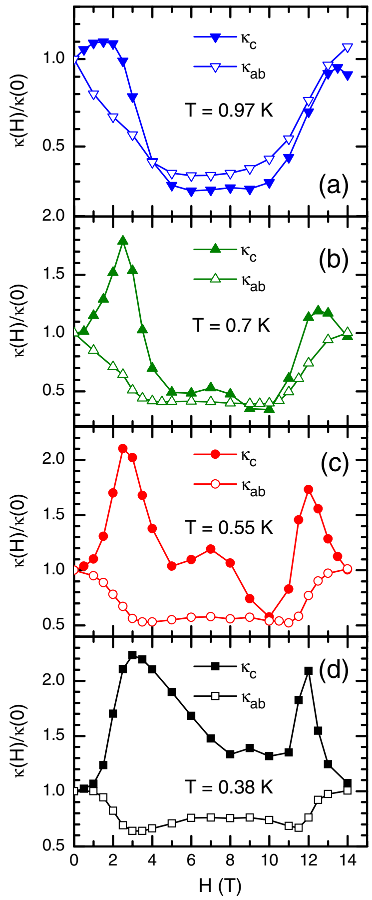

FIG. 4 (color online). Comparison of $\kappa_c(H)$ and $\kappa_{ab}(H)$ isotherms for $H \parallel c$ at sub-Kelvin temperatures. (a) $T = 0.97$ K; (b) $T = 0.7$ K; (c) $T = 0.55$ K; (d) $T = 0.38$ K.

Besides the above clear information demonstrated by the anisotropic heat transport behaviors, one may notice that the details of the $\kappa(H)$ data are actually rather complicated and some considerable further investigations are needed. In principal, the competing roles of magnons acting as phonon scatterers and as heat carriers may lead to complicated field dependence of κ ($H \parallel c$), including the peaklike anomalies of $\kappa_c(H)$ at H_{c1} and H_{c2} and the local maximum between two peaks. Besides, the peaklike anomalies can be closely related to the maximized magnon population at H_{c1} and H_{c2}, since the dispersion becomes quadratic at the critical fields while it is linear for $H_{c1} < H < H_{c2}$ [29]; another contribution to the nonmonotonic field dependence of $\kappa_c(H)$ between H_{c1} and H_{c2} may be coming from some upper magnon branches having rather small gap at the intermediate field [22]. On the other hand, the $\kappa_c(H)$ and $\kappa_{ab}(H)$ for $H \perp c$ are also rather complicated. In general, the field dependences of κ at very low temperature are rather weak, consistent with the fact that for $H \perp c$ there is no field-induced transition and the magnetic excitations are always gapped [17,20]. The most drastic field dependence is the strong increase of κ_{ab} and κ_c at 4–5 K, which is actually very similar to the behaviors in $H \parallel c$. This is probably because in such a high temperature region, where the temperature scale is comparable to the spin anisotropy gap, there is strong phonon scattering caused by magnetic excitations [remember the resonant scattering feature of $\kappa(T)$ in zero field shown in Fig. 2], which can be weakened when the applied field increases the energy of magnetic excitations [18,19].

It is intriguing to point out that the experimental phenomenon cannot be simply explained as the strong magnetic heat transport found in some low-dimensional spin systems [30]. Actually, it was originally predicted that the spin transport is diffusive and finite in the spin-1 chain material since it is not an integrable system [31], while the experimental results were quite controversial, both low and high magnon thermal conductivities have been observed in different compounds [32–34]. It is notable that in the magnon BEC state, the spin system is no longer one dimensional; instead, it is a three-dimensional ordered state [17–19]. Because of the crossover of the dimensionality and the character of magnetic quasiparticles at the BEC transition [35], it is natural to expect a different mechanism of magnon heat transport from that of the low-dimensional systems when the field-induced long-range magnetic order is established.

To summarize the main finding of this work, the magnon heat transport is found to be large in the magnon BEC state of DTN single crystals, pointing to a direct analogy between the magnon BEC and the conventional one. Since the BEC condensate does not carry entropy, the large low-T magnon heat transport can only be related to the uncondensed part of magnons. An elaborate theory, probably based on the two-fluid model established for superfluid ^{4}He [15], is called for quantitatively describing the heat transport in this novel state of quantum magnet.

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