

Heat transport of the quasi-one-dimensional alternating spin chain material $(\text{CH}_3)_2\text{NH}_2\text{CuCl}_3$

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We report a study of the low-temperature heat transport in the quasi-one-dimensional $S = 1/2$ alternating antiferromagnetic-ferromagnetic chain compound $(\text{CH}_3)_2\text{NH}_2\text{CuCl}_3$. Both the temperature and magnetic-field dependencies of thermal conductivity are very complicated, pointing to the important role of spin excitations. It is found that magnetic excitations act mainly as the phonon scatterers in a broad temperature region from 0.3 to 30 K. In magnetic fields, the thermal conductivity shows drastic changes, particularly at the field-induced transitions from the low-field Néel state to the spin-gapped state, the field-induced magnetic ordered state, and the spin polarized state. In high fields, the phonon conductivity is significantly enhanced because of the weakening of spin fluctuations.

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I. INTRODUCTION

Low-dimensional or frustrated quantum magnets were revealed to exhibit exotic ground states, magnetic excitations, and quantum phase transitions (QPTs).^{1,2} For a particular case of the spin-gapped antiferromagnets, the external magnetic field can close the gap in the spectrum, which results in a QPT between a low-field disordered paramagnetic phase and a high-field long-range-ordered one. An intriguing finding is that this ordered phase can be approximately described as a Bose-Einstein condensation (BEC) of magnons.³ Heat transport of low-dimensional quantum magnets has recently received an intensive research interest because it is very useful to probe the nature of magnetic excitations and the field-induced QPTs.⁴⁻⁸ In particular, a large spin thermal conductivity in spin chain and spin ladder systems has been theoretically predicted and experimentally confirmed in such compounds as SrCuO_2 , Sr_2CuO_3 , CaCu_2O_3 , $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, etc.⁹⁻¹² Most of these materials have simple spin structure and strong exchange coupling, which are necessary for producing high-velocity and long-range-correlated spin excitations, while the low dimensionality strongly enhances the quantum fluctuations and ensures a large population of spin excitations. However, the ground states of these materials usually have weak response to the magnetic field because the laboratory fields are too small, compared to the exchange energy. They are, in this sense, not suitable for studying the field-induced QPTs and the associated physics of magnetic excitations. Apparently, some organic magnetic materials have obvious advantages since their larger crystal unit cells and atom distances lead to much weaker exchange coupling of magnetic ions. Several materials have been studied to reveal how the heat transport behaves at the field-induced QPTs.^{8,13-15} It seems that the spin excitations are often playing a role of scattering phonons and therefore strongly suppress the thermal conductivity at the phase transitions. One alternative case is $\text{NiCl}_2\cdot 4\text{SC}(\text{NH}_2)_2$ (DTN), in which the thermal conductivity is significantly enhanced in its BEC state.^{8,16} Therefore the role of magnetic excitations in the heat transport at QPTs still needs to be carefully studied.

$(\text{CH}_3)_2\text{NH}_2\text{CuCl}_3$ (dimethylammonium copper II chloride, also known as DMACuCl_3 or MCCL) is an $S = 1/2$ alternating antiferromagnetic-ferromagnetic (AFM-FM) dimer-chain system with weak interdimer AFM coupling.¹⁷⁻²⁵ MCCL crystallizes in the monoclinic structure (space group $C2/c$) with room-temperature lattice constants $a = 17.45 \text{ \AA}$, $b = 8.63 \text{ \AA}$, $c = 11.97 \text{ \AA}$, and $\beta = 125.41^\circ$.^{18,26} The crystal structure consists of Cu-Cl-Cu bonded chains along the c axis with Cu-Cl \cdots Cl-Cu contacts along the a axis. These Cu-halide planes are separated from one another along the b axis by methyl groups, so the magnetic coupling is only expected in the ac plane. The basic features of the spin structure are illustrated in Fig. 1(a). All the spin interactions J_1 , J_3 , J_A , and J_B are AFM except that J_2 is FM. The calculations using the diagonalization method found the relations $J_B < J_A < J_1 < |J_2|$, and J_3 is nearly zero.¹⁸ The magnetic structure can be regarded as an alternating predominant AFM dimer (AF_1) and FM dimer (F_2) with the practically equal magnitude of the intradimer interactions J_1 and J_2 , respectively, which are linked by weak AFM inter-dimer interaction J_3 . It can be modeled as $-\text{F}_2\text{-AF}_3\text{-AF}_1\text{-AF}_3\text{-F}_2$.²⁴ This rather complicated magnetic structure results in interesting magnetic properties and multiple phase transitions, as shown in Fig. 1(b).^{19-21,24,25} The ground state of MCCL in the absence of the magnetic field can be viewed as a long-range-ordered chain in which alternative $S = 1$ and $S = 0$ spins are coupled by an intervening weak interaction. A spontaneous AFM order is formed below the Néel temperature $T_N = 0.9 \text{ K}$, but it is stable only in the low magnetic fields ($H < H_{c1}$, $H_{c1} = 2 \text{ T}$ at zero- T limit), and then becomes a field-induced gapped state in $H_{c1} < H < H_{c2}$ ($H_{c2} = 3.5 \text{ T}$ at zero- T limit) and finally turns into a field-induced magnetic order (FIMO) phase at $H > H_{c2}$. The rich magnetic phenomena of MCCL make it a good material to study the low- T heat transport and its relationship with the QPTs.

In this work, we study the detailed temperature and field dependencies of low- T thermal conductivity of high-quality MCCL single crystals. It is found that the magnetic excitations do not transport heat directly and there is strong scattering between magnetic excitations and phonons at zero or low

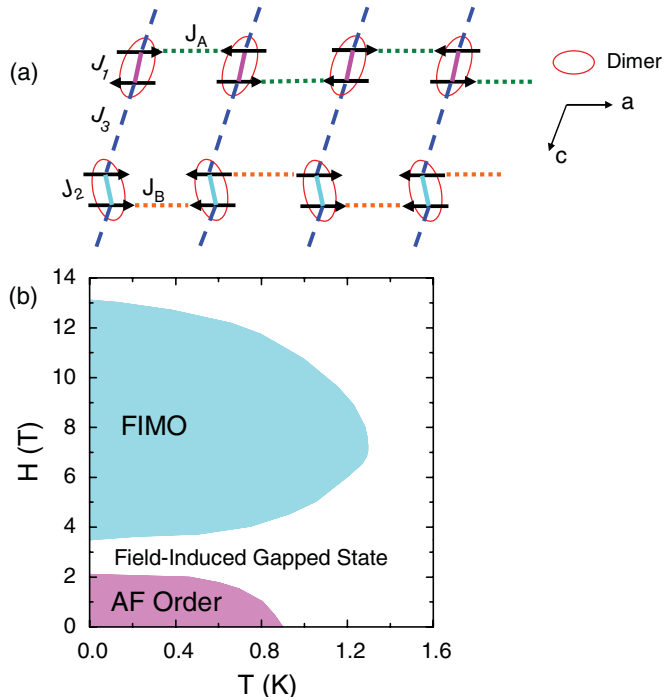


FIG. 1. (Color online) (a) A schematic plot of the spin structure of MCCL. There are two types of dimers along the a axis: (i) the AFM dimers with the intradimer interaction J_1 and the neighboring AFM interaction J_A ; (ii) the FM dimers with the intradimer interaction J_2 and the neighboring AFM interaction J_B . Spin chains (along the c axis) are contacted by alternating AFM dimers and FM dimers through AFM interaction J_3 between two types of dimers. (b) The H - T phase diagram of MCCL obtained from the former experiments.^{19–21,24,25} The magenta area and the cyan one represent the low-field spontaneous order state and the high-field induced magnetic order state, respectively, with the field-induced gapped state between them.

fields. The phonon thermal conductivity shows drastic changes across all the phase transitions mentioned above. In high-field spin-polarized state, the magnetic scattering is strongly weakened and the phonon conductivity is significantly increased in a very broad temperature region.

II. EXPERIMENT

MCCL single crystals are grown using a slow evaporation method.²⁷ Shining crystals with the typical size of $(3\text{--}6) \times (1\text{--}3) \times (1\text{--}2)$ mm³, with the bc crystallinity plane the largest naturally formed surface, are selected and polished into a parallelepiped shape for the specific-heat and thermal conductivity measurements. The specific heat is measured by the relaxation method in the temperature range 0.4–10 K using a commercial physical property measurement system (PPMS, Quantum Design). The temperature and magnetic-field dependencies of the thermal conductivity are measured using a conventional steady-state technique in a ³He refrigerator and a 14-T magnet.^{8,28,29} The heat flow is along the bc plane, in which the spin chains are included. Note that the MCCL crystals are somewhat fragile, so the trials to make well-shaped samples with other orientations are not successful.

In both specific-heat and thermal-conductivity measurements, the magnetic field is applied perpendicular to the bc plane.

III. RESULTS AND DISCUSSION

The low-temperature specific-heat data are measured for verifying the H - T phase diagram of our MCCL crystals. Figure 2 shows the data with magnetic field from 0 to 9 T. The main features of the zero-field $C(T)$ curve include a narrow and sharp peak at 0.89 K and a “shoulder” at about 5 K, as shown in Fig. 2(a). With increasing the field, the low- T peak shifts to lower temperature with the peak amplitude decreased and finally evolves to a very small peak at 0.57 K when the magnetic field is increased to 2 T. This low- T peak is clearly due to the spontaneous Néel transition, which can be suppressed by the magnetic field. With increasing magnetic field further, this low- T peak completely disappears and a new peak shows up. It can be seen from Figs. 2(b) and 2(c) that the new small peak appears at 1.06 K in 4-T field and it becomes

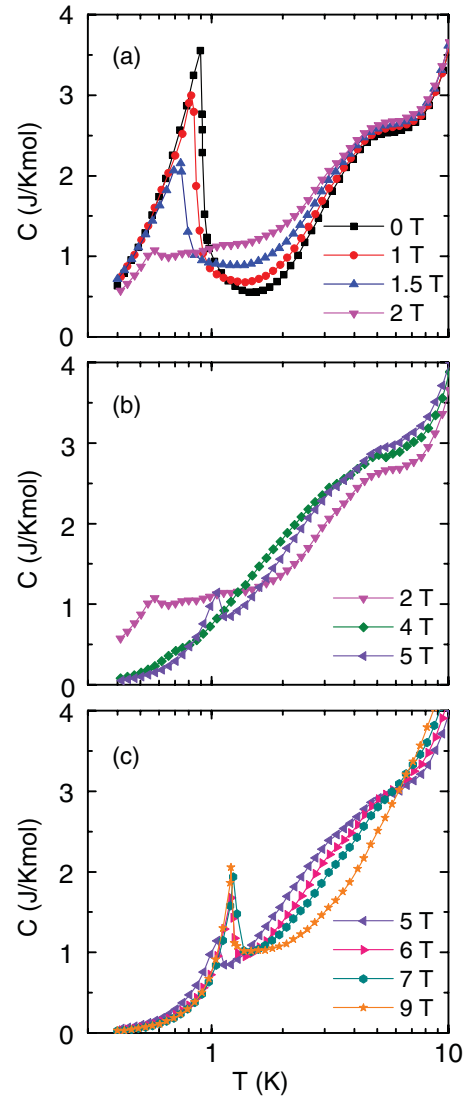


FIG. 2. (Color online) Specific heat of MCCL as a function of temperature for the magnetic field applied perpendicular to the bc plane.

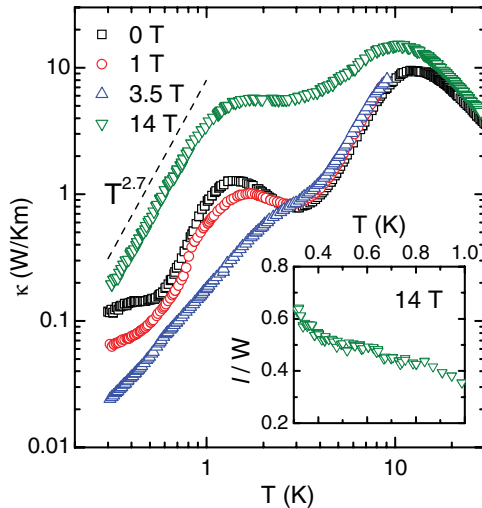


FIG. 3. (Color online) Temperature dependencies of the thermal conductivity of MCCL single crystal in the zero field and several different magnetic fields up to 14 T, which are applied perpendicular to the bc plane. The dashed line indicates a $T^{2.7}$ dependence of κ at sub-K temperatures. The inset shows the temperature dependence of the phonon mean free path l divided by the averaged sample width W in 14-T magnetic field.

bigger and sharper and shifts to a bit higher temperature with increasing magnetic field, in contrast to the field dependence of the low-field peak. More exactly, the peak temperature is highest at 7 T. Apparently, this new peak appeared in higher fields has another origin, which is known to be the transition of the FIMO phase. The phase boundaries determined from the present specific-heat data have good consistency with the former result [see Fig. 1(b)].²⁰

Figure 3 shows the temperature dependencies of κ in zero field and several magnetic fields up to 14 T. In the zero field, the temperature dependence of κ is rather complicated. The peak at ~ 12 K is likely the phonon peak as the insulators commonly have.³⁰ At lower temperatures, there appear two “diplike” features in the $\kappa(T)$ curve at ~ 3 K and ~ 0.6 K, respectively. In general, the possible reasons of these behaviors in magnetic materials could be either the strong phonon scattering by critical spin fluctuations at some magnetic phase transitions or the phonon resonant scattering by some magnetic impurities or lattice defects.^{28,30,31} The underlying mechanism can usually be judged from the magnetic-field dependence of the diplike features of $\kappa(T)$. As can be seen from Fig. 3, applying magnetic field induces drastic changes in the magnitude and the temperature dependence of κ . As far as the lower- T dip is concerned, it is found that applying magnetic fields up to 3.5 T suppresses the very-low- T κ so strongly that the dip is markedly weakened in 1 T and completely disappeared in 3.5 T. Apparently, this dip is related to the spontaneous AFM ordering, which is known to be suppressed with applying magnetic field. More exactly, in zero field, the phonon scattering by magnetic excitations or spin fluctuations is strong at high temperatures; upon lowering temperature to the spontaneous AFM state, the spin fluctuations are significantly weakened and the phonon conductivity can be increased. Thus a diplike feature is produced. However, applying magnetic

field (up to several T) can suppress the magnetic order and somehow enhance the spin fluctuations and their scattering on phonons. In passing, the temperature of the low- T dip locates at 0.6 K, a bit lower than the AFM transition temperature 0.9 K from the specific-heat data. A similar phenomenon was also observed in some other magnetic material.²⁸

The 3-K dip is also weakened in magnetic fields although its position is nearly independent on the field. From the position of this dip, it is possible to be attributed to the phonon resonant scattering by the energy gap in the spin spectrum. The neutron-scattering measurements have revealed that in the paramagnetic phase there are two magnon branches along the bc plane; one is dispersive and the other one is dispersionless with gaps of 0.95 and 1.6 meV, respectively.^{22,23,26} In this situation, phonons with 0.95 meV (~ 11 K) can be resonantly scattered by producing magnetic excitations. Since the phonon conductivity spectrum $\kappa(\omega)$ has a (broad) maximum at $\sim 3.8k_B T$,^{30,31} this magnetic scattering on phonons is therefore the strongest at ~ 3 K, which agrees well with the position of the dip. The weak dependence of dip position on the magnetic field suggests that the gap of magnetic spectra is insensitive to the field at the paramagnetic state.

In magnetic field as high as 14 T, the thermal conductivity show very drastic changes. First, the magnitude of κ is always enhanced in a broad temperature region from 0.3 to 30 K and the enhancement is rather large. Second, the 3-K dip in zero field evolves into a shoulderlike feature, suggesting that the phonon resonant scattering is still active at 14 T. Third, at sub-K temperatures $\kappa(T)$ show an approximate $T^{2.7}$ dependence, which indicates that the phonon boundary scattering is approached. It is useful to calculate the mean free path of phonons in 14 T and to judge whether the phonons are nearly free from microscopic scatterings at sub-K temperatures. The phononic thermal conductivity can be expressed by the kinetic formula $\kappa_{\text{ph}} = \frac{1}{3} C v_p l$,³⁰ where $C = \beta T^3$ is the phonon specific heat at low temperatures, v_p is the average velocity, and l is the mean free path of phonon. Here $\beta = 3.15 \times 10^{-3}$ J/K⁴ mol is obtained from the lattice specific-heat data²⁰ and $v_p = 2440$ m/s can be estimated from β .^{32,33} The obtained l from the 14-T $\kappa(T)$ data are compared with the averaged sample width $W = 2\sqrt{A/\pi} = 0.993$ mm,^{30,34} where A is the area of cross section. As shown in the inset to Fig. 3, the ratio l/W increases with lowering temperature and becomes close to 1 at 0.3 K, which means that the boundary scattering limit is nearly established at such low temperatures. In other words, the heat transport at such low temperatures is mainly contributed by the phonons, on which the microscopic scatterings are very weak. It is known from the H - T phase diagram that the 14-T field is strong enough to suppress the magnetic ordering and fully polarize the spins, so the low-energy magnons are hardly to be excited in such high field.^{28,29,32} Therefore it is naturally expected that the phonon scattering by magnons is almost smeared out in 14 T. This means that in zero and low fields, magnon excitations are mainly playing a role of phonon scatterers.

To further clarify the roles of magnetic excitations and magnetic phase transitions in the low- T heat transport of MCCL, it is useful to study the detailed magnetic-field dependence of κ . Figures 4(a) and 4(b) show the $\kappa(H)$ isotherms at temperatures below and above the zero-field $T_N = 0.9$ K,

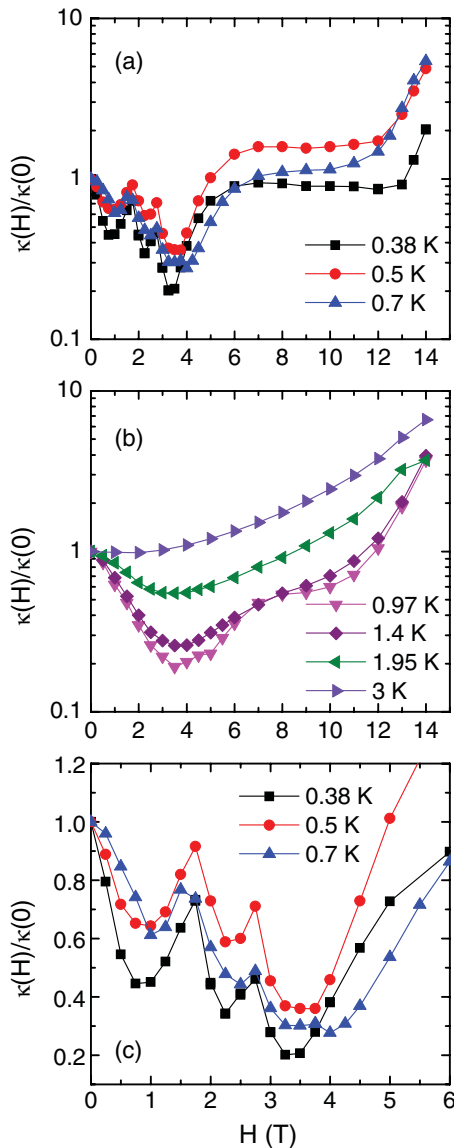


FIG. 4. (Color online) Magnetic-field dependencies of thermal conductivity of MCCL crystal at low temperatures. The magnetic fields are applied perpendicular to the bc plane. (a) $T = 0.38$ – 0.7 K. (b) $T = 0.97$ – 3 K. (c) Zoom in of the low-field plots for $T = 0.38$ – 0.7 K.

respectively. The qualitative behaviors of $\kappa(H)$ are essentially the same for temperatures below T_N . At low-field region, the κ strongly decreases with H , accompanied with three “dips” at ~ 1 , 2.25 , and 3.5 T. A “plateaulike” feature then appears at the intermediate field region, which is terminated by a quick increase of κ at high fields, with the transition fields precisely coincided with the upper phase boundary of FIMO. The strong increase of κ at the spin-polarized state can be clearly attributed to the weakening of the phonon scattering by magnons because the number of the low-energy magnons is quickly decreased.^{28,29,32} This result can be compared to the observations of $\kappa(T)$ in Fig. 3. As the $\kappa(H)$ curves show, even the 14-T field is not strong enough to completely suppress the magnetic scattering on phonons. This is the reason that the 14-T $\kappa(T)$ do not exhibit a precise T^3 dependence at

sub-K temperatures.³⁴ Nevertheless, in zero and low fields, the magnetic scattering on phonons is significant.

The low-field $\kappa(H)$ behaviors are shown more clearly in Fig. 4(c). Apparently, the dip fields at ~ 2.25 and 3.5 T correspond precisely to the lower and upper critical fields of the field-induced spin gapped state, respectively. The diplike features at these two critical fields are attributable to the phonon scattering by the strong critical spin fluctuations at the phase transitions.^{8,15} The first dip at ~ 1 T locates in the low-field AFM ordered state and is of different origin. As can be seen in Fig. 2(a), the specific-heat data below 0.7 K do not show any anomaly or obvious field dependence from 0 to 1.5 T. It is known that the spin-flop-like transition of spin structure may not be detectable by the specific-heat measurements. It is therefore very likely that the 1-T dip at very low temperatures is related to some kind of spin-flop transition, which is also reasonable considering the nearly temperature independence of the dip field.^{28,29,32,35} The spin-flop transition has been indeed observed in an earlier magnetization measurement,¹⁹ although the transition field found at ~ 0.5 T is somewhat lower than that in the heat transport data.

Another peculiar feature of the low- T $\kappa(H)$ isotherms is a “plateau” at the intermediate-field region. At 0.38 K, for example, the κ is nearly field independent from 6 to 13 T. With increasing temperature, the plateau becomes narrower and disappears above 0.97 K. This field-independence phenomenon is apparently in good agreement with the specific-heat data shown in Fig. 2(c), which are also essentially independent on field above 6 T and at very low temperatures. One clear point is that the plateau behavior shows up when the sample is in the FIMO state, which indicates that the magnon spectrum at such low- T phase does not change strongly with applying field.

Above T_N , the three low-field “dips” disappear; instead, the $\kappa(H)$ curves show a broad valleylike behavior for $T = 0.97$, 1.4 , and 1.95 K, as shown in Fig. 4(b). In these curves, the fields for the minimum κ are all located at 3.5 T, which indicates that it is not related to the lower transition field of the FIMO phase. The κ increase rather rapidly at higher fields, demonstrating that the spin fluctuations are significantly weakened. At even higher temperature of 3 K, the κ shows a monotonically increase with increasing field. Note that the high-field-induced increase of κ actually happens in a very broad temperature region, as also can be seen in Fig. 3. Since the spontaneous or field-induced magnetic orders are not relevant, the strong field dependence of κ in this temperature region is apparently related to the strong quantum fluctuations of the low-dimensional spin systems. The data indicate that the strong magnetic field tends to effectively suppress the spin fluctuations, which can strongly scatter phonons.

From above data and discussions, it is reasonably concluded that there is no clear signature that the magnetic excitations in MCCL have strong ability of transporting heat directly. This is rather different from some well-studied low-dimensional spin systems, like SrCuO_2 , Sr_2CuO_3 , CaCu_2O_3 , $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, La_2CuO_4 , etc.,^{9–12,36–38} in which the magnetic excitations show a remarkably strong heat conduction and they are hardly to be affected by the laboratory magnetic field.^{12,39} The main reason is that those inorganic materials usually have much larger exchange coupling, typically being of the order of magnitude of 100 meV. Furthermore, the spin structure of MCCL is more

complex. For example, in the spontaneous AF phase only the FM dimers ordered antiferromagnetically while the AF dimers are in the $S = 0$ ground state with strong quantum fluctuations.

It is also useful to note that the low- T $\kappa(H)$ shows a minimum at the field-induced quantum phase transition from the spin-gapped state to the FIMO state. This is rather similar to another FIMO material, $\text{Ba}_3\text{Mn}_2\text{O}_8$,⁴⁰ in which the FIMO can be discussed on the basis of the Bose-Einstein condensation of magnons.³ In contrast, another magnon BEC compound, DTN,⁸ has shown strong ability of magnetic heat transport along its spin chain direction at the phase transition from the gapped state to the field-induced AFM state.

IV. SUMMARY

The low-temperature heat transport in the quasi-one-dimensional $S = 1/2$ alternating antiferromagnetic-ferromagnetic chain compound $(\text{CH}_3)_2\text{NH}_2\text{CuCl}_3$ is found to exhibit very complicated temperature and magnetic-field dependencies. In zero field, the strong spin fluctuations of this low-dimensional system scatter phonons strongly in a broad temperature region from 0.3 to 30 K. The scattering is weakened when the spontaneous AFM ordering is formed

below T_N , while it is enhanced when the AFM order is suppressed in magnetic fields. In higher magnetic fields, at the phase transitions from the low-field Néel state to the spin-gapped state (~ 2 T) and the field-induced magnetic ordered state (~ 3.5 T), the thermal conductivity shows diplike anomalies, which suggests the strong phonon scattering by the critical fluctuations. In high fields, when the spins are being polarized, the phonon conductivity is significantly enhanced because of the weakening of spin fluctuations. Due to the complex low- T phase diagram and the multiple field-induced QPTs, it is now difficult to perform the quantitative analysis on either the temperature or the magnetic-field dependencies of κ . Further knowledge about the magnetic spectra of this material is necessary for deeper understanding of the heat transport properties.

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