Magnetic State of the Geometrically Frustrated Quasi-One-Dimensional Spin System $\text{Cu}_3\text{Mo}_2\text{O}_9$ Studied by Thermal Conductivity

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We have measured the thermal conductivity of the geometrically frustrated quasi-one-dimensional spin system $\text{Cu}_3\text{Mo}_2\text{O}_9$ in magnetic fields. A contribution of the thermal conductivity due to spins has been observed in the thermal conductivity along the spin chains. The thermal conductivity due to phonons, $\kappa_{\text{phonon}}$, has been found to decrease by the application of a magnetic field, which has been explained as being due to the reduction in the spin gap originating from the spin-singlet dimers. Moreover, it has been found that $\kappa_{\text{phonon}}$ increases with increasing field in high fields above $\sim 7$ T at low temperatures. This suggests the existence of a novel field-induced spin state and is discussed in terms of the possible spin-chirality ordering in a frustrated Mott insulator.

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1. Introduction

The thermal conductivity in low-dimensional quantum spin systems has attracted great interest, because a large amount of thermal conductivity due to spins, namely, magnetic excitations, $\kappa_{\text{spin}}$, has been observed along the direction where the antiferromagnetic (AF) exchange interaction is strong. In the AF spin-chain systems $\text{Sr}_2\text{CuO}_3$\textsuperscript{1–3} and $\text{SrCuO}_2$\textsuperscript{1,4} and the two-leg spin-ladder system $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$\textsuperscript{5–9} for example, the thermal conductivity due to spinons and magnons, which are magnetic excitations in these systems, has been observed, respectively. In addition, the thermal conductivity has attracted considerable interest, because it is closely related to the magnetic state. That is, the thermal conductivity exhibits a marked change according to the change in the magnetic state, owing to the marked change in the scattering of heat carriers by magnetic excitations. In the spin-Peierls system $\text{CuGeO}_3$\textsuperscript{10,11} and the two-dimensional spin-dimer system $\text{SrCu}_2(\text{BO}_3)_2$\textsuperscript{12,13} the thermal conductivity due to phonons, $\kappa_{\text{phonon}}$, has been found to be enhanced at low temperatures below the temperature comparable to the spin-gap energy owing to the reduction in the phonon-spin scattering rate and to be suppressed by the application of a magnetic field because of the reduction in the spin gap.\textsuperscript{12,13} Furthermore, a marked enhancement of the thermal conductivity has been observed at low temperatures below the AF transition temperature, $T_N$, in several AF spin systems.\textsuperscript{14–20} In the frustrated spin system $\text{Dy}_2\text{Ti}_2\text{O}_7$, recently, the thermal conductivity has been found to be affected by the change in the state of magnetic monopoles, which are magnetic excitations in this system.\textsuperscript{21,22} Accordingly, the thermal conductivity is recognized as a very useful probe to detect a change in the magnetic state and a phase transition.

The compound $\text{Cu}_3\text{Mo}_2\text{O}_9$ is a quasi-one-dimensional spin system with the quantum spin number $S = 1/2$ of $\text{Cu}^{2+}$ ions. As shown in Fig. 1(a), distorted tetrahedral spin-chains composed of spin chains of Cu1 and spin dimers of Cu2 and Cu3 run along the $b$-axis. The spin chains are arranged in the $ac$-plane as shown in Fig. 1(b). $\text{Cu}^{2+}$ spins interact with one another by AF superexchange interactions, whose magnitude has been estimated from the inelastic neutron-scattering experiment as follows.\textsuperscript{23,24} Both the interaction between Cu1 and Cu2, $J_1$, and that between Cu1 and Cu3, $J_2$, are $\sim 19$ K. The intradimer interaction between Cu2 and Cu3, $J_3$, which is equal to the spin-gap energy, $\Delta$, of the spin dimers, is $\sim 67$ K. The intrachain interaction between Cu1’s, $J_4$, is $\sim 46$ K. The interchain interaction is as negligibly weak as $\sim 2.2$ K.

The magnetization and specific heat measurements have revealed that $\text{Cu}_3\text{Mo}_2\text{O}_9$ undergoes an AF transition accompanied by weak ferromagnetism (WF) due to the Dzyaloshinsky-
Moriya interaction at 8 K. In the AF ordered state, the dispersion branch of magnetic excitations of the spin dimers remains together with that of the AF order and the direction of Cu1 spins is almost parallel to the $b$-axis but is slightly canted from the $b$-axis. Although canted components of the magnetic moments are in disorder in zero field, they are ordered by the application of a magnetic field of 0.1 T along the $a$-axis and of 0.8 T along the $c$-axis. In the AF ordered state, furthermore, it has been found from dielectric constant and magnetization measurements that Cu$_3$Mo$_2$O$_9$ shows magnetic and ferroelectric orders simultaneously without any magnetic superlattice formation, which has been understood as being due to the possible charge redistribution in a frustrated Mott insulator. The direction of

![Crystal structure diagram](image)

**Fig. 1.** (Color online) (a) Crystal structure of Cu$_3$Mo$_2$O$_9$. Distorted tetrahedral spin-chains run along the $b$-axis. (b) Crystal structure viewed from the $b$-axis. Dashed lines indicate the unit cell containing two distorted tetrahedral spin-chains.
the spontaneous electric polarization changes from the c-axis to the a-axis by the application of a magnetic field of $\sim 8$ T along the c-axis,\textsuperscript{26} which has been also observed in the electron-spin-resonance spectrum of the powder sample.\textsuperscript{29} At present, the phase diagram of Cu$_3$Mo$_2$O$_9$ in magnetic fields at low temperatures is as shown in Fig. 2.\textsuperscript{26,30,31} Nevertheless, the magnetic state of Cu$_3$Mo$_2$O$_9$ has not yet been clarified completely. Accordingly, we have measured the thermal conductivity of single-crystal Cu$_3$Mo$_2$O$_9$ in magnetic fields, in order to investigate the magnetic state of Cu$_3$Mo$_2$O$_9$ as well as the existence of $\kappa_{\text{spin}}$.

2. Experimental

Single crystals of Cu$_3$Mo$_2$O$_9$ were grown by the continuous solid-state crystallization method.\textsuperscript{32} Thermal conductivity measurements were carried out by the conventional steady-state method. One side of a rectangular single-crystal, whose typical dimensions were about $5 \times 1 \times 1$ mm$^3$, was anchored on a heat sink of copper with indium solder. A chip-resistance of 1 k$\Omega$ (Alpha Electronics MP1K000) was attached as a heater to the opposite side of the single crystal with GE7031 vanish. The temperature difference across the crystal (0.03–0.4 K) was measured with two Cernox thermometers (Lake Shore Cryotronics CX-1050-SD). The accuracy of the absolute value of the thermal conductivity was $\pm 10\%$ mainly due to the uncertainty of the sample geometry. Magnetic fields up to 14 T were applied parallel to the principal crystallographic axes.

![Graphical representation of phase diagram](image)

Fig. 2. (Color online) Phase diagram of Cu$_3$Mo$_2$O$_9$ in magnetic fields along the principal crystallographic axes at low temperatures.\textsuperscript{26,30,31} AFM, PM, FE, and PE indicate the antiferromagnetic, paramagnetic, ferroelectric, and paraelectric phases, respectively. $P_s$ indicates the spontaneous electric polarization. Triangles, squares, and circles were determined from the dielectric constant measurements along the a- and c-axes and specific heat measurements, respectively. Open and solid symbols were obtained from the data of magnetic-field and temperature dependences, respectively.
3. Results and Discussion

Figure 3 shows the temperature dependence of the thermal conductivity along the $a$-, $b$-, and $c$-axes, $\kappa_a$, $\kappa_b$, and $\kappa_c$, of Cu$_3$Mo$_2$O$_9$, respectively. It is found that $\kappa_a$ and $\kappa_c$ perpendicular to the spin chains are similar to each other and monotonically decrease with decreasing temperature down to $T_N = 8$ K. Although $\kappa_b$ parallel to the spin chains also decreases with decreasing temperature down to $\sim 20$ K, on the other hand, $\kappa_b$ increases with decreasing temperature from $\sim 20$ K down to $T_N$. Both $\kappa_a$, $\kappa_b$, and $\kappa_c$ increase suddenly just below $T_N$ with decreasing temperature and exhibit a peak at approximately 5 K. In nonmagnetic insulators, $\kappa_{\text{phonon}}$ typically increases with decreasing temperature from room temperature and shows a peak at a low temperature around 10 K. In spin-gap systems, moreover, thermal conductivity typically increases with decreasing temperature at low temperatures below the temperature comparable to the spin-gap energy. Taking into account the observation of the dispersion branch of magnetic excitations of the spin dimers,\textsuperscript{23,24} therefore, the monotonic decrease with decreasing temperature at high temperatures implies that the mean free path of phonons, $l_{\text{phonon}}$, is strongly suppressed probably by magnetic fluctuations due to the spin frustration.

![Figure 3](image-url)

**Fig. 3.** (Color online) Temperature dependence of the thermal conductivity along the $a$-, $b$-, and $c$-axes, $\kappa_a$, $\kappa_b$, and $\kappa_c$, for Cu$_3$Mo$_2$O$_9$ single crystals in zero field, respectively. The inset shows the temperature dependences of $\kappa_a$, $\kappa_b$ and $\kappa_c$ in a wide temperature-range up to 150 K. The arrow indicates the antiferromagnetic transition temperature, $T_N$. 
Fig. 4. (Color online) Temperature dependence of the thermal conductivity along the $a$- and $b$-axes, $\kappa_a$ and $\kappa_b$, respectively, for Cu$_3$Mo$_2$O$_9$ single crystals in magnetic fields parallel to the (a) $a$-, (b) $b$-, and (c) $c$-axes.

The sudden increases in $\kappa_a$, $\kappa_b$, and $\kappa_c$ just below $T_N$ are inferred to be due to the increase in $l_{\text{phonon}}$ owing to the marked reduction in the phonon-spin scattering rate caused by the development of the AF long-range order, as observed in several antiferromagnets.\textsuperscript{14–20}

It is found that the magnitude of $\kappa_b$ is larger than those of $\kappa_a$ and $\kappa_c$. Furthermore, only $\kappa_b$ increases with decreasing temperature at temperatures between $\sim 20$ K and $T_N$, which can hardly be explained as being due to the anisotropy of $\kappa_{\text{phonon}}$. Therefore, these anisotropic behaviors of the thermal conductivity are reasonably attributed to the contribution of $\kappa_{\text{spin}}$ to $\kappa_b$, because magnetic excitations can carry heat along the $b$-axis where the magnetic correlation is developed at low temperatures below $J_4$. Such anisotropic contribution of $\kappa_{\text{spin}}$ has been observed in several low-dimensional spin systems.\textsuperscript{1–9, 19, 33–38}

Figure 4 shows the temperature dependences of $\kappa_a$ and $\kappa_b$ of Cu$_3$Mo$_2$O$_9$ in magnetic fields along the $a$-, $b$-, and $c$-axes, $H_{||a}$, $H_{||b}$, and $H_{||c}$, respectively. It is found that both $\kappa_a$ and $\kappa_b$ decrease with increasing field at low temperatures below $\sim 40$ K. The decrease in $\kappa_a$ by the application of a magnetic field indicates the decrease in $l_{\text{phonon}}$ due to the increase in the phonon-spin scattering rate, namely, the enhancement of the scattering of phonons by magnetic excitations, because the contribution of $\kappa_{\text{phonon}}$ is dominant in $\kappa_a$ perpendicular to the spin chains and the contribution of $\kappa_{\text{spin}}$ is negligible. It is known in spin-gap systems that $\kappa_{\text{phonon}}$ is enhanced below the temperature comparable to the spin-gap energy, owing to the
marked decrease in the number of magnetic excitations. Moreover, the enhancement of $\kappa_{\text{phonon}}$ is suppressed by the application of a magnetic field,\textsuperscript{10,12,13} owing to the increase in the number of magnetic excitations because of the reduction in the spin gap. In the magnetic dispersion of Cu$_3$Mo$_2$O$_9$, there is a flat branch of magnetic excitations of the spin dimers.\textsuperscript{23,24} Such a flat magnetic branch is expected to scatter phonons strongly, because the momentum conservation law is easily satisfied in the phonon-spin scattering process. Surely, $\kappa_{\text{phonon}}$ is suppressed owing to the disorder of the AF correlation induced by the application of the magnetic field in AF spin-chain systems. However, since the magnetic dispersion branch in AF spin-chain systems is dispersive, it is not easy to satisfy both the momentum and energy conservation laws in the phonon-spin scattering process. Therefore, magnetic excitations of the spin dimers are expected to scatter phonons stronger than those of the AF spin chains. Furthermore, considering that the temperature below which the suppression by the application of a magnetic field is observed is comparable to $\Delta = 67$ K\textsuperscript{23,24}, the suppression of not only $\kappa_a$ but also $\kappa_b$ by the application of a magnetic field is interpreted as being caused by the enhancement of the phonon-spin scattering due to the reduction in the spin gap. However, neither enhancement of $\kappa_a$, $\kappa_b$, nor $\kappa_c$ is observed in zero field below $\sim 40$ K comparable to $\Delta$. This may indicate that phonons are strongly scattered by magnetic fluctuations due to the spin frustration even at low temperatures below $\Delta$. Furthermore, the decrease in $\kappa_b$ by the application of a magnetic field is more marked than that in $\kappa_a$. This indicates that not only $\kappa_{\text{phonon}}$ but also $\kappa_{\text{spin}}$ decreases by the application of a magnetic field, because there exists the contribution of $\kappa_{\text{spin}}$ to $\kappa_b$ parallel to the spin chains in zero field as described above. It is reasonable that $\kappa_{\text{spin}}$ is affected by magnetic fields up to 14 T, because $J_4 \sim 46$ K is not much larger than the energy of a magnetic field of 14 T. Namely, magnetic excitations carrying heat are scattered by the disorder of the antiferromagnetic correlation along the $b$-axis induced by the application of a magnetic field. In fact, it has been reported that $\kappa_{\text{spin}}$ in the quasi-one-dimensional spin system Sr$_2$V$_3$O$_9$ with the intrachain interaction of 82 K is suppressed by the application of a magnetic field of 14 T.\textsuperscript{36,37} As for the behavior of the thermal conductivity in magnetic fields at low temperatures below $T_N$, it is slightly complicated.

Figures 5(a)–5(d) show the magnetic-field dependences of $\kappa_a(H)/\kappa_a(0)$, and $\kappa_b(H)/\kappa_b(0)$ of Cu$_3$Mo$_2$O$_9$, normalized by the value in zero field, in $H_{||a}$, $H_{||b}$ and $H_{||c}$ at 3 and 10 K. First, we compare $\kappa_a(H)/\kappa_a(0)$ and $\kappa_b(H)/\kappa_b(0)$. It is found that both $\kappa_a(H)/\kappa_a(0)$ and $\kappa_b(H)/\kappa_b(0)$ show a complicated but similar behavior in general terms, but $\kappa_b(H)/\kappa_b(0)$ tends to decrease with increasing field more than $\kappa_a(H)/\kappa_a(0)$. Here, $\kappa_b$ parallel to the spin chains is described as the sum of $\kappa_{\text{phonon}}$ and $\kappa_{\text{spin}}$, while $\kappa_a$ perpendicular to the spin chains is given by only $\kappa_{\text{phonon}}$. 
Therefore, it is inferred that the complicated field-dependence of the thermal conductivity is due to $\kappa_{\text{phonon}}$, while $\kappa_{\text{spin}}$ monotonically decreases with increasing field, as shown in Fig. 5(e).

Next, we discuss the magnetic-field dependence of $\kappa_a(H)/\kappa_a(0)$ in order to investigate the

\begin{figure}[h]
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\includegraphics[width=\textwidth]{fig5}
\caption{(Color online) (a)–(d) Magnetic-field dependence of the thermal conductivity along the $a$- and $b$-axes normalized by the value in zero field, $\kappa_a(H)/\kappa_a(0)$ and $\kappa_b(H)/\kappa_b(0)$, respectively, for Cu$_3$Mo$_2$O$_9$ single crystals in magnetic fields parallel to the $a$-, $b$-, and $c$-axes at 3 and 10 K. (e)–(h) Schematic diagrams of the magnetic-field dependence of the thermal conductivity due to magnetic excitations, $\kappa_{\text{spin}}$, and phonons, $\kappa_{\text{phonon}}$. (e) $\kappa_{\text{spin}}$ suppressed by the reduction in the spin gap. (f) $\kappa_{\text{phonon}}$ enhanced by the appearance of the long-range order of the canted components in the weak ferromagnetic state. (g) $\kappa_{\text{phonon}}$ suppressed by the reduction in the spin gap. (h) $\kappa_{\text{phonon}}$ enhanced in high magnetic fields.}
\end{figure}
magnetic and dielectric states, because the behavior of \( \kappa_a(H)/\kappa_a(0) \) originating from only \( \kappa_{\text{phonon}} \) is expected to reflect these states through the scattering of phonons more simply than that of \( \kappa_b(H)/\kappa_b(0) \). It is found that the field dependence of \( \kappa_a(H)/\kappa_a(0) \) at 3 K is very different depending on the applied-field-direction, as shown in Fig. 5(a). In low magnetic fields, \( \kappa_a(H)/\kappa_a(0) \) increases up to \( \sim 2 \) T with increasing fields of \( H_{||a} \) and \( H_{||c} \), while it decreases up to \( \sim 5 \) T with increasing field of \( H_{||b} \). Since the long-range order of canted components of the magnetic moments in WF appears above \( H_{||a} \sim 0.1 \) T and \( H_{||c} \sim 0.8 \) T but it does not in \( H_{||b} \), the increase in \( \kappa_a(H)/\kappa_a(0) \) with increasing fields of \( H_{||a} \) and \( H_{||c} \) is explained as being caused by the appearance of the long-range order of the canted components in WF leading to the suppression of the phonon-spin scattering. Therefore, there is an enhanced component of \( \kappa_{\text{phonon}} \) in both \( H_{||a} \) and \( H_{||c} \), as shown in Fig. 5(f). The decrease in \( \kappa_a(H)/\kappa_a(0) \) in \( H_{||b} \) is explained as being caused by the increase in the phonon-spin scattering rate due to the reduction in the spin gap by the application of a magnetic field. Furthermore, it is found that \( \kappa_a(H)/\kappa_a(0) \) starts to decrease above \( \sim 2 \) T with increasing fields of \( H_{||a} \) and \( H_{||c} \), which is interpreted as being caused by both the saturation of the enhancement of \( \kappa_a(H)/\kappa_a(0) \) by the appearance of the long-range order of the canted components in WF, as shown in Fig. 5(f), and the decrease in \( \kappa_a(H)/\kappa_a(0) \) due to the reduction in the spin gap, as shown in Fig. 5(g).

In high magnetic fields, \( \kappa_a(H)/\kappa_a(0) \) tends to increase above \( \sim 7 \) T with increasing fields of \( H_{||a} \), \( H_{||b} \), and \( H_{||c} \), as shown in Fig. 5(a). In particular, it is remarkable that there is a kink in \( \kappa_a(H)/\kappa_a(0) \) at \( H_{||c} \sim 7.5 \) T, where the phase transition occurs, that is, the direction of the spontaneous electric polarization changes from the \( c \)-axis to the \( a \)-axis with increasing field, as shown in Fig. 2. A similar kink is also observed in \( \kappa_b(H)/\kappa_b(0) \) at \( H_{||c} \sim 7.5 \) T. In \( H_{||a} \) and \( H_{||b} \), on the other hand, no anomaly suggesting any phase transitions has been observed at around 7 T in the specific heat and magnetization measurements. However, since the differential magnetization has shown a kink at \( H_{||b} = 6 \) T at 2 K, the enhancement of \( \kappa_a(H)/\kappa_a(0) \) above \( \sim 7 \) T may be caused by an unknown field-induced order and/or a change in the magnetic state. Accordingly, there is an enhanced component of \( \kappa_{\text{phonon}} \) in \( H_{||a} \), \( H_{||b} \), and \( H_{||c} \), as shown in Fig. 5(h). The enhancement of \( \kappa_a(H)/\kappa_a(0) \) above \( \sim 7 \) T is also observed at 10 K above \( T_N \), as shown in Fig. 5(c).

Here, it is noted that the enhancement of \( \kappa_a(H)/\kappa_a(0) \) above \( \sim 7 \) T means the increase of \( l_{\text{phonon}} \), because both the specific heat and velocity of phonons are usually almost independent of magnetic field. In other words, it means that the scattering rate of phonons decreases with increasing field, corresponding to the decrease in magnetic excitations and/or the development of a magnetic order. According to the calculation of the magnetic dispersion in
magnetic fields by Matsumoto et al., no anomaly such as any change in the ground state has been suggested at ~ 7 T.

Here, in order to explain the enhancement of $\kappa_{\text{phonon}}$ above ~ 7 T, we introduce the theory proposed by Bulaevskii and Batista and Khomskii concerning spontaneous currents and charge redistribution in a Mott insulator regarded as a geometrically frustrated spin system. Since the ferroelectricity in Cu$_3$Mo$_2$O$_9$ has been understood on the basis of the charge redistribution, the spontaneous currents may be useful to explain the enhancement of $\kappa_{\text{phonon}}$. In a geometrically frustrated Mott insulator, the exchange interaction between three spins forming a triangle causes a spontaneous current running along the triangle. This spontaneous current only appears in a non-coplanar spin-state and is proportional to the scalar spin-chirality given by $S_1 \cdot (S_2 \times S_3)$, where $S_i$ ($i = 1, 2, 3$) is a spin angular momentum on the site $i$. In the case that the spins of Cu2 and Cu3 form a spin-singlet dimer, distorted tetrahedral spin-chains can be regarded as simple spin-chains composed of only Cu1 spins and there is no chirality in the spin chain, as shown in Fig. 6(a). In the case that spin-singlet dimers are broken by the application of a magnetic field, on the other hand, finite values of spin chirality appear in the triangles, because spins revive on the Cu2 and Cu3 sites, as shown in Fig. 6(b). Therefore, it is possible that the enhancement of $\kappa_{\text{phonon}}$ above ~ 7 T is caused by the ordering of spin chiralities, because the ordering is able to be brought about by the magnetic interaction even in the absence of any magnetically ordered state.

Finally, the magnetic-field dependence of $\kappa_a(H)/\kappa_a(0)$ at low temperatures below ~ 40 K
is summarized as follows, on the basis of the scenario adopting the spin-chirality ordering. In zero field, a few excitations of spin-singlet dimers in the spin-gap state due to thermal fluctuations scatter phonons, as shown in Fig. 7(a). Since the number of magnetic excitations increases with increasing field below ~ 7 T by the reduction in the spin gap, \( l_{\text{phonon}} \) is shortened because of the increase in the phonon scattering rate, as shown in Fig. 7(b). In high magnetic fields above ~ 7 T, the order of magnetic excitations, namely, the order of spin chiralities, is developed, as shown in Fig. 7(c), so that \( \kappa_{\text{phonon}} \) increases owing to the decrease in the phonon scattering rate. The reason why the enhancement of \( \kappa_a(H)/\kappa_a(0) \) is different depending on the applied-field-direction is as follows. Spontaneous currents along the triangles composed of three spins induce orbital moments, which are coupled with the magnetic field. Therefore, the magnitude of the scalar spin-chirality might be related to the magnetic field penetrating the triangles. Accordingly, since the areas of the triangles viewed from the \( b \)-axis are homogeneous, the chirality order may be homogeneous in \( H_{||b} \), leading to
the large enhancement of $\kappa_{\text{phonon}}$. On the other hand, since the areas of the triangles viewed from the $a$- and $c$-axes are inhomogeneous, the chirality order may be inhomogeneous in $H_{\parallel a}$ and $H_{\parallel c}$, leading to the small enhancement of $\kappa_{\text{phonon}}$. To confirm this scenario adopting the spin-chirality order, further experimental and theoretical investigations are necessary.

4. Summary

In order to investigate the magnetic state and the existence of $\kappa_{\text{spin}}$, we have measured $\kappa_a$, $\kappa_b$, and $\kappa_c$ of Cu$_3$Mo$_2$O$_9$ single crystals in magnetic fields up to 14 T. In zero field, it has been found that $\kappa_a$, $\kappa_b$, and $\kappa_c$ are suppressed at high temperatures probably by magnetic fluctuations due to the spin frustration, while they are enhanced just below $T_N$ as in the case of several antiferromagnets. By the application of a magnetic field, $\kappa_a$, $\kappa_b$, and $\kappa_c$ have been found to be suppressed at low temperatures below $\sim 40$ K and this has been explained as being due to the reduction in the spin gap originating from the spin-singlet dimers of Cu2 and Cu3. Since it has been found that the magnitude of $\kappa_b$ parallel to the spin chains is larger than those of $\kappa_a$ and $\kappa_c$ and that the decrease in $\kappa_b$ by the application of a magnetic field is more marked than that in $\kappa_a$, it is concluded that there exists a contribution of $\kappa_{\text{spin}}$ to $\kappa_b$. Furthermore, it has been found that the magnetic-field dependences of $\kappa_a$ and $\kappa_b$ at 3 and 10 K are complicated and different depending on the applied-field-direction. In low magnetic fields below $\sim 7$ T, both $\kappa_a$ and $\kappa_b$ have been found to decrease with increasing field due to the reduction in the spin gap. Moreover, $\kappa_a$ at 3 K has been found to markedly change in $H_{\parallel c}$ and $H_{\parallel e}$ in correspondence to the appearance of the long-range order of the canted components in WF. In high magnetic fields above $\sim 7$ T, on the other hand, both $\kappa_a$ and $\kappa_b$ at 3 K have been found to tend to increase with increasing field. In $H_{\parallel c}$, a kink has been observed at $\sim 7.5$ T in both $\kappa_a$ and $\kappa_b$, owing to the field-induced phase transition. In $H_{\parallel b}$, it has been found that the increase in $\kappa_a$ above $\sim 7$ T is most marked and is observed even at 10 K above $T_N$ in spite of the absence of any phase transition, suggesting the existence of a novel field-induced spin state. A possible state is the ordered one of the spin chirality in a frustrated Mott insulator.

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