Thermal Conductivity due to Spins in the Two-Dimensional Spin System Ba$_2$Cu$_3$O$_4$Cl$_2$

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We have measured the temperature dependences of the thermal conductivity of Ba$_2$Cu$_{3-x}M_x$O$_4$Cl$_2$ ($M = $ Pd, Ni, Co; $x = 0, 0.03$) single crystals including two-dimensional (2D) Cu$_3$O$_4$ planes consisting of a strong 2D spin network of Cu$^{2+}$ spins and a weak 2D spin network of Cu$^{2+}$ spins. It has been found that the thermal conductivity due to spins, $\kappa_{\text{spin}}$, exists in the thermal conductivity parallel to the Cu$_3$O$_4$ plane owing to the strong 2D spin network of Cu$^{2+}$ spins and exhibits a broad peak around room temperature. The maximum value of $\kappa_{\text{spin}}$ is ~7 W/Km and comparable with that in Nd$_2$CuO$_4$ with almost the same 2D spin network of Cu$^{2+}$ spins. The $\kappa_{\text{spin}}$ has been found to be suppressed by 1% impurities on account the decrease in the mean free path of magnetic excitations, suggesting that $\kappa_{\text{spin}}$ is expected to be enhanced in 2D quantum spin systems such as Ba$_2$Cu$_3$O$_4$Cl$_2$ by reducing the amount of impurities in a single crystal. Moreover, it has concluded that the frustration between Cu$^{2+}$ and Cu$^{2+}$ spins little affects the existence of $\kappa_{\text{spin}}$. 
1. Introduction

In several low-dimensional quantum spin systems, the thermal conductivity due to magnetic excitations, namely, due to spins, $\kappa_{\text{spin}}$, has been observed conspicuously. As for one-dimensional (1D) quantum spin systems, $\kappa_{\text{spin}}$ has been observed in antiferromagnetic (AF) spin systems of Sr$_2$CuO$_4$,\(^{1-4}\) SrCuO$_2$,\(^{5-7}\) Sr$_{14}$Cu$_{24}$O$_{41}$,\(^{8-13}\) Sr$_2$V$_3$O$_9$,\(^{14}\) and ACoX$_3$ (A = Cs, Rb; X = Cl, Br)\(^{15}\) with the spin quantum number $S = 1/2$ and of Y$_2$BaNiO$_5$\(^{16,17}\) and AgVP$_2$S$_6$\(^{18}\) with $S = 1$. $\kappa_{\text{spin}}$ is especially large in Sr$_2$CuO$_3$, SrCuO$_2$, and Sr$_{14}$Cu$_{24}$O$_{41}$, which is understood to be owing to the large velocity of magnetic excitations, $v_{\text{spin}}$, due to the large AF superexchange interaction between the nearest neighbor Cu$^{2+}$ spins.\(^{19}\) In two-dimensional (2D) quantum spin systems, $\kappa_{\text{spin}}$ has also been observed in AF spin systems of La$_2$CuO$_4$,\(^{20-23}\) Nd$_2$CuO$_4$,\(^{24}\) and Sr$_2$CuO$_2$Cl$_2$\(^{25}\) with $S = 1/2$ and of La$_2$NiO$_4$ with $S = 1$.\(^{22}\) $\kappa_{\text{spin}}$ is especially large in La$_2$CuO$_4$, Nd$_2$CuO$_4$, and Sr$_2$CuO$_2$Cl$_2$, which is understood to be due to the AF superexchange interaction as large as $\sim$1500 K between the nearest neighbor Cu$^{2+}$ spins in the 2D spin network of Cu$^{2+}$ spins in the 2D CuO$_2$ plane. It is characteristic of these 2D quantum spin systems that $\kappa_{\text{spin}}$ exhibits the maximum around room temperature, which is suitable for the application of the large $\kappa_{\text{spin}}$.

The compound Ba$_2$Cu$_3$O$_4$Cl$_2$ is regarded as a 2D quantum spin system. The crystal structure is layered and composed of an alternate stack of the 2D Cu$_3$O$_4$ plane and the Ba$_2$Cl$_2$ blocking layer along the $c$-axis, as shown in Fig. 1(a). There are two Cu sites, namely, Cu$_A$ and Cu$_B$ sites in the Cu$_3$O$_4$ plane, where Cu$_A^{2+}$ ions with $S = 1/2$ form the abovementioned 2D CuO$_2$ plane and Cu$_B^{2+}$ ions with $S = 1/2$ are alternately located at the center of the square composed of four Cu$_A^{2+}$ ions, as shown in Fig. 1(b). The Raman scattering experiment has revealed that the exchange interaction between the nearest neighbor Cu$_A^{2+}$ spins, $J_A$, in the 2D spin network of Cu$_A^{2+}$ spins is AF and $\sim$1500 K, while that between the nearest neighbor Cu$_B^{2+}$ spins, $J_B$, in the 2D spin network of Cu$_B^{2+}$ spins is AF and $\sim$120 K.\(^{26}\) The inelastic neutron scattering experiment has revealed that the exchange interaction between the adjacent Cu$_A^{2+}$ and Cu$_B^{2+}$ spins, $J_{AB}$, is ferromagnetic and about -140 K.\(^{27}\) Therefore, frustration exists between Cu$_A^{2+}$ and Cu$_B^{2+}$ spins. From the temperature dependence of the magnetization, it has been found that two magnetic phase transitions occur at $T_{N1} \sim 30$ K and at $T_{N2} \sim 330$ K.\(^{28-31}\) The elastic neutron scattering experiment has revealed that $T_{N1}$ and $T_{N2}$ are AF transition temperatures of Cu$_B^{2+}$ and Cu$_A^{2+}$ spins, respectively.\(^{31}\)

Since Ba$_2$Cu$_3$O$_4$Cl$_2$ includes the 2D CuO$_2$ plane as well as La$_2$CuO$_4$, Nd$_2$CuO$_4$, and Sr$_2$CuO$_2$Cl$_2$, large $\kappa_{\text{spin}}$ is expected to be observed. However, the frustration between Cu$_A^{2+}$
and CuB\textsuperscript{2+} spins in the Cu\textsubscript{3}O\textsubscript{4} plane may interrupt the appearance of large $\kappa$\textsubscript{spin}. In this paper, we have grown large-sized single crystals of $\text{Ba}_2\text{Cu}_{3-x}\text{M}_x\text{O}_4\text{Cl}_2$ ($M = \text{Pd, Ni, Co}; x = 0, 0.03$) including no and 1% impurities of nonmagnetic Pd\textsuperscript{2+} ($S = 0$) and magnetic Ni\textsuperscript{2+} ($S = 1$) and Co\textsuperscript{2+} ($S = 3/2$) and measured the thermal conductivity, to investigate whether $\kappa$\textsubscript{spin} exists in $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$. Moreover, the origin of the maximum of $\kappa$\textsubscript{spin} around room temperature in the 2D quantum spin systems consisting of the 2D CuO\textsubscript{2} plane has been discussed.

2. Experimental

Single crystals of $\text{Ba}_2\text{Cu}_{3-x}\text{M}_x\text{O}_4\text{Cl}_2$ ($M = \text{Pd, Ni, Co}; x = 0, 0.03$) were grown by the floating-zone method without the use of solvent, referring to the literature by Yamada et al.\textsuperscript{32)} The growth was performed under flowing O\textsubscript{2} of 4 atm at the rate of 10 mm/h. The grown crystals were confirmed by the powder x-ray diffraction to be of the single phase of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ without any impurity phases. The diffraction spots of the x-ray back-Laue photography were very sharp, indicating the good quality of the obtained single crystals. The chemical composition was confirmed by the inductively coupled plasma mass spectrometry (ICP-MS) to coincide with the nominal composition, as listed in Table I. For the characterization of the obtained single crystals, the magnetic susceptibility was also measured using a SQUID magnetometer (Quantum Design, MPMS).

Thermal conductivity measurements were carried out by the conventional four-terminal steady-state method. On the thermal conductivity data obtained by this method, the effect of the thermal radiation is marked at high temperatures above ~150 K. Therefore, the thermal conductivity due to the thermal radiation, $\kappa$\textsubscript{radiation}, has to be subtracted from the observed thermal conductivity. The temperature dependence of $\kappa$\textsubscript{radiation} was estimated as follows. First, the thermal conductivity was measured at room temperature by the laser-flash method giving a rather correct value with little influence of the thermal radiation.\textsuperscript{33)} Next, the value of $\kappa$\textsubscript{radiation} at room temperature was estimated as the difference between the values obtained by these two methods. Finally, the temperature dependence of $\kappa$\textsubscript{radiation} was estimated using the equation, $\kappa$\textsubscript{radiation} = 4$\sigma$A$sT^3$\textsuperscript{34)}, where $\sigma$ is the Stefan-Boltzmann constant, $\varepsilon$ the reflectivity, $A$s the surface area, and the $T$ temperature of a sample. The value of $\varepsilon A_s$ was calculated from the value of $\kappa$\textsubscript{radiation} at room temperature. All the thermal conductivity data shown in this paper were obtained after the subtraction of $\kappa$\textsubscript{radiation}. The value of $\kappa$\textsubscript{radiation} at room temperature was 30 – 50 % of that of the thermal conductivity measured by the four-terminal steady-state method.
For the estimate of the Debye temperature, the specific heat was measured by the thermal relaxation method using a physical property measurement system (Quantum Design, PPMS).

3. Results and discussion

Figure 2 shows the temperature dependences of the magnetization in a magnetic field of 0.5 T applied in the \textit{ab}-plane, namely, in the Cu$_3$O$_4$ plane of Ba$_2$Cu$_{3-x}$M$_x$O$_4$Cl$_2$ ($M = \text{Pd, Ni, Co}; x = 0, 0.03$) on zero-field cooling and field cooling. For $x = 0$, it is found that, with decreasing temperature, the magnetization increases a little at high temperatures below 400 K, drastically jumps up at $T_{N2} = 330$ K, gradually increases, exhibits a broad peak around 80 K, and decreases. Then, the magnetization shows a hysteresis at low temperatures below $T_{N1} = 32$ K. This temperature dependence of the magnetization for $x = 0$ is almost the same as that in the former report by Noro \textit{et al.}\textsuperscript{29} For $x = 0.03$ of $M = \text{Pd and Ni}$, $T_{N2}$ is clearly found to decrease compared with those of $x = 0$, while $T_{N1}$ increases for $x = 0.03$ of $M = \text{Co}$. These changes in $T_{N2}$ by Pd, Ni, and Co impurities indicate that these impurities are substituted for Cu, though the microscopic origin of the increase or decrease in $T_{N2}$ is not clear in detail.

Figure 3(a) shows the temperature dependences of the thermal conductivity along the [110] direction, namely, along the Cu$_A$-O-Cu$_A$ direction in the Cu$_3$O$_4$ plane, $\kappa_{[110]}$, and along the [001] direction perpendicular to the Cu$_3$O$_4$ plane, $\kappa_{[001]}$, of Ba$_2$Cu$_3$O$_4$Cl$_2$. It is found that there is a large anisotropy between $\kappa_{[110]}$ and $\kappa_{[001]}$. That is, $\kappa_{[001]}$ exhibits a peak at $\sim 30$ K and monotonously decreases with increasing temperature. On the other hand, $\kappa_{[110]}$ exhibits a peak at $\sim 25$ K and decreases with increasing temperature, but the decrease becomes gentle at high temperatures above $\sim 80$ K and $\kappa_{[110]}$ shows a broad peak around room temperature. Since the [110] direction is parallel to the Cu$_3$O$_4$ plane including 2D CuO$_2$ plane and this kind of behavior of the thermal conductivity has been observed in La$_2$CuO$_4$ also,\textsuperscript{20} the peaks at low temperatures of $\sim 30$ K and $\sim 25$ K in $\kappa_{[001]}$ and $\kappa_{[110]}$, respectively, are inferred to be caused by the contribution of the thermal conductivity due to phonons, $\kappa_{\text{phonon}}$, while the broad peak around room temperature only in $\kappa_{[110]}$ is inferred to be due to $\kappa_{\text{spin}}$.

To estimate $\kappa_{\text{spin}}$, at first the estimate of $\kappa_{\text{phonon}}$ is necessary, for the observed thermal conductivity is regarded as the sum of $\kappa_{\text{phonon}}$ and $\kappa_{\text{spin}}$. In Ba$_2$Cu$_3$O$_4$Cl$_2$, it is unsuitable to estimate $\kappa_{\text{spin}}$ simply as the difference between $\kappa_{[110]}$ and a constant multiple of $\kappa_{[001]}$, assuming that $\kappa_{[001]}$ is due to only $\kappa_{\text{phonon}}$. This is because $\kappa_{\text{phonon}}$ is very anisotropic,
considering the large differences between $\kappa_{[110]}$ and $\kappa_{[001]}$ of the magnitude and broadening of the low-temperature peak due to $\kappa_{\text{phonon}}$. Therefore, the contributions of $\kappa_{\text{phonon}}$ to both $\kappa_{[110]}$ and $\kappa_{[001]}$ have to be estimated using a suitable theoretical model. The $\kappa_{\text{phonon}}$ is simply given by the following equation based on the Debye model,$^{35}$

$$\kappa_{\text{phonon}} = \frac{k_B}{2\pi v_{\text{phonon}}(\frac{k_B}{h})} \frac{k_B}{h} T^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} \tau(x, T) dx,$$  

(1)

where $x = \hbar \omega / k_B T$, $\omega$ is the phonon angular frequency, $\hbar$ the Planck constant, $k_B$ the Boltzmann constant, $\Theta_D$ the Debye temperature, $v_{\text{phonon}}$ the phonon velocity, and $\tau(x, T)$ the relaxation time of the phonon scattering. The $v_{\text{phonon}}$ is described as

$$v_{\text{phonon}} = \Theta_D \left( \frac{k_B}{\hbar} \right) \left( \frac{6\pi^2 n}{6} \right)^{-1/3},$$  

(2)

where $n$ is the number density of atoms. The phonon scattering rate $\tau^{-1}(x, T)$ is given by the sum of scattering rates due to several scattering processes as follows,

$$\tau^{-1}(x, T) = \tau^{-1}(\omega, T) = \frac{v_{\text{phonon}}}{L_b} + A \omega^4 + D \omega + B \omega^2 T \exp \left( -\frac{\Theta_D}{bT} \right),$$  

(3)

where the first term represents the phonon scattering by boundaries; the second, the phonon scattering by point defects; the third, the phonon scattering by lattice distortions; the fourth, the phonon-phonon scattering in the umklapp process. $L_b$ is the distance between two temperature terminals and $A$, $D$, $B$, and $b$ are fitting parameters. Using Eqs. (1) – (3) and putting $\Theta_D$ at 470 K from the specific heat measurements, $\kappa_{\text{phonon}}$ was estimated as drawn by dashed lines in Fig. 3(a). It is found that $\kappa_{[001]}$ is well fitted in the whole temperature region, indicating that $\kappa_{[001]}$ is due to only $\kappa_{\text{phonon}}$. This is reasonable, because $\kappa_{\text{spin}}$ is not expected to be observed in $\kappa_{[001]}$ on account of the very weak magnetic correlation along the [001] direction. In the case of the estimate of $\kappa_{\text{phonon}}$ in $\kappa_{[110]}$, only the data of $\kappa_{[110]}$ at low temperatures below the peak temperature of ~25 K were used for the fit with Eqs. (1) – (3), assuming that there was little $\kappa_{\text{spin}}$ at the low temperatures. This assumption is reasonable, because $\kappa_{\text{spin}}$ is expected to decrease in proportion to $T^2$ with decreasing temperature at low temperatures due to the $T^2$ dependence of the specific heat in a 2D AF spin system.$^{36}$ In this case, $\kappa_{\text{phonon}}$ is a little overestimated, while $\kappa_{\text{spin}}$ is a little underestimated. However, the estimate of large $\kappa_{\text{spin}}$ around room temperature is little influenced. Values of the parameters used for the best fit are listed in Table II. It is found that values of $A$ and $D$ in $\kappa_{[001]}$ are much larger than those in $\kappa_{[110]}$, indicating the large phonon scattering rate by point defects and lattice distortions probably in the [001] direction. This is reasonable, because the atomic bonding in the [001] direction is much weaker than in the [110] direction, as suggested by the
strong cleavability in the (001) plane. The value of $B$ in $\kappa_{[001]}$ is larger than that in $\kappa_{[110]}$, indicating the large phonon-phonon scattering rate in the umklapp process in the [001] direction. This is also reasonable, taking into account the fact that the size of the first Brillouin zone in the [001] direction is smaller than that in the [110] direction owing to the $c$-axis length being larger than the $a$- and $b$-axis lengths. In addition, these values of the parameters listed in Table II are comparable with those obtained in several low-dimensional quantum spin systems,\(^2\),\(^4\),\(^5\),\(^14\),\(^15\) except for $D$ values. The large $D$ values in Ba\(_2\)Cu\(_3\)O\(_4\)Cl\(_2\) are inferred to be due to the strong cleavability. Accordingly, the estimate of $\kappa_{\text{phonon}}$ in $\kappa_{[110]}$ seems to be appropriate.

Thereupon, looking at $\kappa_{[110]}$ shown in Fig. 3(a), it is clearly found that another large contribution to the thermal conductivity except for $\kappa_{\text{phonon}}$ exists at high temperatures above ~80 K, so that the large contribution is regarded as being due to $\kappa_{\text{spin}}$.

To confirm the large contribution of $\kappa_{\text{spin}}$ at high temperatures above ~80 K, the temperature dependences of the thermal conductivity along the [110] direction have been measured for Ba\(_2\)Cu\(_3\)-\(x\)M\(_x\)O\(_4\)Cl\(_2\) ($M = \text{Pd, Ni, Co}; x = 0.03$) including 1% impurities of Pd, Ni, and Co, as shown in Figs. 3(b), 3(c), and 3(d), respectively. It is found that both the peak at ~25 K and the broad peak around room temperature are suppressed by the 1% impurities, though the peak at ~25 K in the crystal with 1% Co is not suppressed so much.

To estimate $\kappa_{\text{spin}}$ in Ba\(_2\)Cu\(_3\)-\(x\)M\(_x\)O\(_4\)Cl\(_2\) ($M = \text{Pd, Ni, Co}; x = 0.03$), $\kappa_{\text{phonon}}$ was also estimated using Eqs. (1) – (3) as in the above case of $x = 0$. The best fit result of $\kappa_{\text{phonon}}$ is shown by dashed lines in Figs. 3(b), 3(c), and 3(d), and values of the used parameters are listed in Table II. It is found that the value of $B$ relating to the phonon-phonon scattering is not so dependent on the kind of impurity, which is reasonable. On the other hand, values of $A$ and $D$ are dependent on the kind of impurity. Since they are also dependent on the crystalline quality, the difference of the $A$ and $D$ values among 1% impurity-substituted crystals is not discussed clearly. However, it is clearly found that another contribution to the thermal conductivity except for $\kappa_{\text{phonon}}$, namely, $\kappa_{\text{spin}}$ still exists at high temperatures above ~80 K in Ba\(_2\)Cu\(_3\)-\(x\)M\(_x\)O\(_4\)Cl\(_2\) ($M = \text{Pd, Ni, Co}; x = 0.03$).

Figure 4 displays the temperature dependences of $\kappa_{\text{spin}}$ obtained by subtracting $\kappa_{\text{phonon}}$ from the observed $\kappa_{[110]}$ for Ba\(_2\)Cu\(_3\)-\(x\)M\(_x\)O\(_4\)Cl\(_2\) ($M = \text{Pd, Ni, Co}; x = 0, 0.03$). It is found that $\kappa_{\text{spin}}$ of $x = 0$ clearly exhibits a peak at ~310 K and that this peak is suppressed by the 1% impurities and most suppressed by Pd. Since $S$ values of Pd\(^{2+}\), Ni\(^{2+}\), and Co\(^{2+}\) are 0, 1, and 3/2, respectively, and different from $S = 1/2$ of Cu\(^{2+}\), this is interpreted as being due to the strong scattering of magnetic excitations by ions with different $S$ values. It appears that
especially nonmagnetic Pd$^{2+}$ ions with $S = 0$ strongly scatter magnetic excitations, leading to the strongest suppression of $\kappa_{\text{spin}}$. Such impurity effects on $\kappa_{\text{spin}}$ have been also observed in La$_2$CuO$_4$. Therefore, the present results strongly support the existence of $\kappa_{\text{spin}}$ in Ba$_2$Cu$_3$O$_4$Cl$_2$ and the maximum value of $\kappa_{\text{spin}}$ is $\approx 7$ W/Km. This is comparable with that in Nd$_2$CuO$_4$. Since the value of $J_A$ is comparable with the AF superexchange interaction between the nearest neighbor Cu$^{2+}$ spins in the CuO$_2$ plane of Nd$_2$CuO$_4$, it is understood that the 2D spin network consisting of Cu$_A^{2+}$ spins in the Cu$_3$O$_4$ plane contribute to $\kappa_{\text{spin}}$. Accordingly, it follows that the frustration between Cu$_A^{2+}$ and Cu$_B^{2+}$ spins little affects the existence of $\kappa_{\text{spin}}$.

Here, we estimate the mean free path of magnetic excitations, $l_{\text{spin}}$. In general, $\kappa_{\text{spin}}$ is given by the following equation,

$$\kappa_{\text{spin}} = \sum_k C_k v_k l_k = \frac{1}{(2\pi)^d} \int C_k v_k l_k dk,$$  \hspace{1cm} (4)

where $C_k$, $v_k$, and $l_k$ are the specific heat, velocity, and mean free path of the magnetic excitation with the wave number $k$, respectively. $d$ is the dimension of a spin network. Assuming that both $v_k$ and $l_k$ are independent of $k$ and $T << J/k_B$ ($J$: the exchange interaction between the nearest neighbor spins), eq. (4) is transformed as

$$\kappa_{\text{spin}} = \frac{k_B^2 l_{\text{spin}}^2}{2 \pi c h^2 v_{\text{spin}}} T^2 \int_0^{x_{\text{max}}} \frac{x^3 e^x}{(e^x - 1)^2} dx,$$  \hspace{1cm} (5)

where $c$ is the $c$-axis length, $x = \hbar v_{\text{spin}} / k_B T$, $x_{\text{max}} = 2\sqrt{\pi} \hbar v_{\text{spin}} / a k_B T$, and $a$ is the $a$-axis length. Both $l_{\text{spin}}$ and $v_{\text{spin}}$ are assumed to be independent of temperature and $v_{\text{spin}}$ is given by the following equation,$^{25}$

$$v_{\text{spin}} = \sqrt{8SZ_c} a / \hbar,$$  \hspace{1cm} (6)

where $Z_c$ is 1.18 and called the Oguchi correction.$^{38}$ $\kappa_{\text{spin}}$ is roughly fitted using Eqs. (5) and (6), as shown by dashed lines in Fig. 4. Values of $l_{\text{spin}}$ used for the best fit, which are regarded as the upper values due to the scattering of magnetic excitations by impurities at low temperatures of $T << J/k_B$, are listed in Table III. It is found that the value of $l_{\text{spin}}$ of $x = 0$ decreases by the 1% impurities and markedly decreases by Pd. The marked decrease in $l_{\text{spin}}$ by Pd is understood to be due to the division of the spin network by nonmagnetic Pd$^{2+}$ ions. On the other hand, the decrease in $l_{\text{spin}}$ by Ni and Co is not so marked, because magnetic Ni$^{2+}$ and Co$^{2+}$ ions do not divide the spin network completely. The decrease in $l_{\text{spin}}$ by the 1% impurities indicates that $l_{\text{spin}}$ already reaches the upper limit at $\approx 310$ K. That is, the scattering of magnetic excitations by impurities is dominant at low temperatures below $\approx 310$ K. As in the case of 1D quantum spin systems such as Sr$_2$CuO$_3$ and SrCuO$_2$, especially ...
accordingly, it is possible to enhance $\kappa_{\text{spin}}$ in 2D quantum spin systems such as Ba$_2$Cu$_3$O$_4$Cl$_2$ by reducing the amount of impurities in a single crystal.

Finally, it may be worthwhile pointing out the possibility of the existence of $\kappa_{\text{spin}}$ due to the spin network of Cu$^{2+}$ spins. Taking into account the fact that $\kappa_{\text{spin}}$ due to the 2D spin network of Cu$_A^{2+}$ spins (with $J_A \sim 1500$ K and $T_{N2} \sim 330$ K) exhibits a peak at $\sim 310$ K, it is possible that $\kappa_{\text{spin}}$ due to the 2D spin network of Cu$_B^{2+}$ spins (with $J_B \sim 120$ K and $T_{N1} \sim 30$ K) exists and exhibits a peak at a low temperature below $T_{N1}$. As shown in Fig. 4, in fact, $\kappa_{\text{spin}}$ increases with decreasing temperature at low temperatures below $\sim 25$ K. This is caused by the misfit of $\kappa_{[110]}$ with $\kappa_{\text{phonon}}$ based on the Debye model at low temperatures below $\sim 25$ K. Therefore, it is possible that $\kappa_{\text{spin}}$ due to the 2D spin network of Cu$_B^{2+}$ spins exists at low temperatures, though it is very hard to separate $\kappa_{\text{spin}}$ from $\kappa_{\text{phonon}}$.

4. Summary

We have grown large-sized single crystals of Ba$_2$Cu$_{3-x}$M$_x$O$_4$Cl$_2$ ($M =$ Pd, Ni, Co; $x = 0, 0.03$) and measured the thermal conductivity. For $x = 0$, $\kappa_{[001]}$ perpendicular to the Cu$_3$O$_4$ plane has been found to exhibit a peak at $\sim 30$ K and monotonously decreases with increasing temperature, while $\kappa_{[110]}$ parallel to the Cu$_3$O$_4$ plane has been found to exhibit a peak at $\sim 25$ K and a broad peak around room temperature. It has been concluded that the peaks at low temperatures of $\sim 30$ K and $\sim 25$ K in $\kappa_{[001]}$ and $\kappa_{[110]}$, respectively, are caused by the contribution of $\kappa_{\text{phonon}}$, because the peaks and the whole temperature dependence of $\kappa_{[001]}$ were well fitted with $\kappa_{\text{phonon}}$ based on the Debye model. On the other hand, the broad peak around room temperature in $\kappa_{[110]}$ has been concluded to be due to $\kappa_{\text{spin}}$, because $\kappa_{[110]}$ is parallel to the Cu$_3$O$_4$ plane including the 2D spin network of Cu$_A^{2+}$ spins with $J_A$ as large as $\sim 1500$ K and because the maximum value of $\kappa_{\text{spin}}$ of $\sim 7$ W/Km estimated is comparable with that in Nd$_2$CuO$_4$ with almost the same 2D spin network of Cu$^{2+}$ spins. It has also supported the existence of $\kappa_{\text{spin}}$ that the $\kappa_{\text{spin}}$ was suppressed by 1% impurities of magnetic Ni$^{2+}$ and Co$^{2+}$ with $S$ values different from that of Cu$^{2+}$ and most suppressed by 1% impurities of nonmagnetic Pd$^{2+}$. Accordingly, it has concluded that the frustration between Cu$_A^{2+}$ and Cu$_B^{2+}$ spins little affects the existence of $\kappa_{\text{spin}}$. Moreover, it has been found that the suppression of $\kappa_{\text{spin}}$ by 1% impurities is due to the decrease in $l_{\text{spin}}$. Therefore, it is expected to enhance $\kappa_{\text{spin}}$ in 2D quantum spin systems such as Ba$_2$Cu$_3$O$_4$Cl$_2$ by reducing the amount of impurities in a single crystal.
In addition, it has been found that $\kappa_{\text{spin}}$ due to the 2D spin network of Cu$_B$$^{2+}$ spins with $J_B$ as small as $\approx 120$ K may exist and exhibit a peak at a low temperature below $T_{N1}$.

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Table I. Chemical compositions obtained by the inductively coupled plasma mass spectrometry (ICP-MS) for Ba$_2$Cu$_{3-x}$M$_x$O$_4$Cl$_2$ ($M =$ Pd, Ni, Co; $x =$ 0, 0.03).

| Sample      | Ba   | Cu   | $M$  |
|-------------|------|------|------|
| $x =$ 0     | 1.990| 3.000|      |
| $x =$ 0.03  | 2.081| 2.973| 0.027|
| $x =$ 0.03  | 1.925| 2.971| 0.029|
| $x =$ 0.03  | 1.969| 2.972| 0.028|
Table II. Parameters used for the best fit of the temperature dependence of the thermal conductivity $\kappa_{[001]}$ and $\kappa_{[110]}$ in Ba$_2$Cu$_{3-x}M_x$O$_4$Cl$_2$ ($M = \text{Pd, Ni, Co}; \; x = 0, 0.03$) with Eqs. (1) – (3).

| Sample   | Direction | $L_0$ ($10^{-3}$ m) | $A$ ($10^{-42}$ s$^3$) | $D$ ($10^{-3}$) | $B$ ($10^{-17}$ s/K) | $b$ |
|----------|-----------|---------------------|------------------------|-----------------|-----------------------|-----|
| $x = 0$  | [001]     | 0.700               | 1.90                   | 1.20            | 1.83                  | 7.2 |
|          | [110]     | 1.06                | 0.140                  | 0.127           | 0.620                 | 6.9 |
| $x(\text{Pd}) = 0.03$ | [110]     | 0.750               | 0.770                  | 0.190           | 0.450                 | 7.3 |
| $x(\text{Ni}) = 0.03$ | [110]     | 0.588               | 0.570                  | 0.120           | 0.620                 | 6.9 |
| $x(\text{Co}) = 0.03$ | [110]     | 0.888               | 0.140                  | 0.127           | 0.580                 | 5.9 |

Table III. Mean free path $l_{\text{spin}}$ used for the best fit of $\kappa_{\text{spin}}$ in Ba$_2$Cu$_{3-x}M_x$O$_4$Cl$_2$ ($M = \text{Pd, Ni, Co}; \; x = 0, 0.03$) with Eqs. (5) and (6).

| Sample     | $l_{\text{spin}}$ (Å) |
|------------|------------------------|
| $x = 0$    | 425 ± 25               |
| $x(\text{Pd}) = 0.03$ | 70 ± 15               |
| $x(\text{Ni}) = 0.03$ | 220 ± 20               |
| $x(\text{Co}) = 0.03$ | 140 ± 20               |
Fig. 1. (color online) (a) Crystal structure of \( \text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2 \). The dashed lines indicate the unit cell. (b) Schematic picture of the \( \text{Cu}_3\text{O}_4 \) plane with two Cu sites, namely, \( \text{Cu}_A \) sites (red spheres) and \( \text{Cu}_B \) sites (yellow spheres).
Fig. 2. (color online) Temperature dependences of the magnetization in a magnetic field of 0.5 T applied in the $ab$-plane of $\text{Ba}_2\text{Cu}_{3-x}M_x\text{O}_4\text{Cl}_2$ ($M = \text{Pd}, \text{Ni}, \text{Co}; x = 0, 0.03$) on zero-field cooling (open circles) and on field cooling (closed circles).
Fig. 3. (color online) Temperature dependences of the thermal conductivity along the [110] direction, namely, along the Cuₐ-O-Cuₐ direction in the Cu₃O₄ plane, κ[110], of Ba₂Cu₃₋ₓMₓO₄Cl₂ with (a) x = 0, (b) M = Pd and x = 0.03, (c) M = Ni and x = 0.03, and (d) M = Co, x = 0.03. For x = 0 in (a), the temperature dependence of the thermal conductivity along the [001] direction perpendicular to the Cu₃O₄ plane, κ[001], is also displayed. Error bars are due to errors in the thermal conductivity measurements performed by the laser-flash method at room temperature for the estimate of κrad. Dashed lines are κphonon estimated using eqs. (1) – (3) based on the Debye model.
Fig. 4. (color online) Temperature dependences of $\kappa_{\text{spin}}$ obtained by subtracting $\kappa_{\text{phonon}}$ from the observed $\kappa_{[110]}$ for Ba$_2$Cu$_{3-x}$M$_x$O$_4$Cl$_2$ ($M = \text{Pd, Ni, Co}; x = 0, 0.03$). Error bars are due to errors in the thermal conductivity measurements performed by the laser-flash method at room temperature for the estimate of $\kappa_{\text{radiation}}$. Dashed lines are the best fit results using Eqs. (5) and (6).