Thermal conductivity of Mg-doped CuGeO$_3$ at very low temperatures: Heat conduction by antiferromagnetic magnons

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Thermal conductivity $\kappa$ is measured at very low temperatures down to 0.28 K for pure and Mg-doped CuGeO$_3$ single crystals. The doped samples carry larger amount of heat than the pure sample at the lowest temperature. This is because antiferromagnetic magnons appear in the doped samples and are responsible for the additional heat conductivity, while $\kappa$ of the pure sample represents phonon conductivity at such low temperatures. The maximum energy of the magnon is estimated to be much lower than the spin-Peierls-gap energy. The result presents the first example that $\kappa$ at very low temperatures probes the magnon transport in disorder-induced antiferromagnetic phase of spin-gap systems.

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Recently, impurity-substitution effect on the spin-singlet ground state has been intensively studied in a variety of low-dimensional spin systems, and the results indicate that only a slight substitution of non-magnetic impurity essentially changes the ground state. When the disorder is introduced by the non-magnetic impurity, antiferromagnetic (AF) ordering immediately appears without destroying the spin-gap feature, commonly in a spin-Peierls (SP) compound CuGeO$_3$. In this work, we have measured thermal conductivity $\kappa$ at very low temperatures, using lightly Mg-doped samples. The samples are cooled down to $^3$He temperatures, in order to study the low-lying excitations. The thermal conductivity of the doped samples exceeds that of the pure sample at the lowest temperature. We will show that the in-gap magnons, which is intrinsic to D-AF phase, indeed exist and are responsible for the excess low-temperature heat transport in the doped samples.

The Cu$_{1-x}$Mg$_x$GeO$_3$ single crystals were grown with a floating-zone method. The Mg-concentration is determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). For the thermal conductivity measurement, we use pure, $x = 0.016$, and $x = 0.0216$ samples, all of which were already well characterized using dc susceptibility and synchrotron x-ray diffraction measurements. The transition temperatures are shown in Table I for each sample. SP long-range order is observed at $T_{SP}^{RO}$ as a resolution limited FWHM of the x-ray Bragg peak from lattice dimerization. The Néel temperature $T_N$ is determined by the magnetic susceptibility.

Thermal conductivity is measured down to 0.28 K with $^3$He refrigerator using “one heater, two thermometers” technique. Gold wires, which are tightly connected with

| Sample | $x$  | $T_{SP}^{RO}$ [K] | $T_N$ [K] | $w$ [mm] | $c$ [m/s] |
|--------|------|------------------|-----------|----------|---------|
| A      | 0    | 14.5             | 0.17      |          |         |
| B      | 0.016| 10.5             | 2.5       | 0.17     | 70      |
| C      | 0.016| 10.5             | 2.5       | 0.24     | 70      |
| D      | 0.0216| 8.5              | 3         | 0.10     | 140     |
FIG. 1. (a) Thermal conductivity of Cu$_{1-x}$Mg$_x$GeO$_3$ single crystals below 1.3 K. Solid curve is for one of the $x = 0.016$ samples (B) and dashed curve is for the pure sample (A). (b) Thermal conductivity of the same sample as a function of $T^3$. The dashed lines show that $\kappa$ is proportional to $T^3$ below 0.58 K for Sample A.

a microchip heater and two calibrated RuO sensors, are attached on the samples by GE-varnish. Temperature difference between the two thermometers are typically 3% of the sample temperature. Since we will discuss the thermal conductivity in the low-temperature limit (Casimir’s limit), where heat carriers are scattered dominantly by crystalline boundaries, we paid special attention both to the sample size and to the smoothness of the boundaries. Typical dimension along the c-axis is around 3 mm and thermal gradient is applied along the c-axis. As shown in Table I, the geometrical mean widths $\bar{w}$ (square root of the cross section), which is proportional to the mean free path in the Casimir’s limit, of the pure sample (Sample A) and one of the $x = 0.016$ samples (Sample B) are set identical for direct comparison in $\kappa$. The smooth boundaries of the crystal is achieved by cleaving for the b-c surfaces and by cutting with a sharp razor blade for the a-c surfaces. Also, we have measured specific heat $C$, in order to derive the mobility of the relevant heat carriers. The specific heat measurement is carried out down to 0.4 K with the commercial PPMS (Quantum Design) heat-capacity probe, using a relaxation method. The mass of the samples is typically 3 mg.

The samples used for the specific heat and the thermal conductivity measurements are cut from the same piece of the crystals.

Figure 1(a) shows temperature dependence of $\kappa$ for Samples A and B below 1.3 K. In Fig. 1(b), $\kappa$ in the temperature range below 0.58 K ($T^3 < 0.2$ K$^3$) is plotted as a function of $T^3$. $\kappa$ of the pure sample rapidly decreases with decreasing temperature and becomes proportional to $T^3$ below 0.58 K. At 1.3 K, $\kappa$ of the $x = 0.016$ sample is smaller than that of the pure sample, so that our previous results in higher temperature range are reproduced.

It is natural that $\kappa$ is suppressed in the presence of impurities owing to the scattering by disorders. However, $\kappa$ of the $x = 0.016$ sample exceeds that of the pure sample below 1 K down to the lowest temperature, which is not explained by the above simple picture.

First, let us discuss $\kappa$ of the pure sample. Magnetic excitations are negligible in the pure sample below 1.3 K, because the spin-gap energy of CuGeO$_3$ is more than one order of magnitude larger than the temperature. Therefore, the heat is dominantly carried by phonons there. Assuming kinetic approximation, the phonon thermal conductivity $\kappa_{ph}$ is written as

$$\kappa_{ph} = \frac{1}{3} C_{ph} v_{ph} l_{ph},$$

where $C_{ph}$ is specific heat, $v_{ph}$ is velocity and $l_{ph}$ is mean free path of the phonons. Since $C_{ph}$ also depends on temperature as $T^3$ at such low temperatures, $l_{ph}$ should be independent of temperature below 0.58 K. This result means that the phonon conductivity reaches the Casimir limit, where the mean free path is determined simply by the dimension of the crystal. For a rectangular-shaped crystal $l_{ph}$ is given as

$$l_{ph} = 1.12 \bar{w},$$

assuming isotropic phonons. We have measured the specific heat independently and examined the validity of Eqs. (1) and (2). First, $v_{ph}$ is calculated from $\kappa$ and $C$ data by Eqs. (1) and (2), as $v_{ph} = (3\kappa)/(C \cdot 1.12\bar{w}) \sim 1600$ m/s. On the other hand, $v_{ph}$ can be estimated only from the low-temperature $C$ data, assuming the Debye model. Thus obtained value of $v_{ph}$ is $\sim 1800$ m/s, which is in good agreement with the estimation from the $\kappa$ data. The result shows that the relation of Eqs. (1) and (2) is satisfied at the temperatures shown in Fig. 1(b) for the crystal used.

Noting that phonon conductivity governed by the boundary scattering gives the maximum value of $\kappa_{ph}$ (any additional scattering would suppress the conductivity), we can notice that $\kappa_{ph}$ of Sample B cannot exceed $\kappa$ of Sample A in Fig. 1(b), using Eqs. (1) and (2), because $\bar{w}$ of Sample A and B is identical (Table I) and little $x$ dependence is expected for $C_{ph}$ and $v_{ph}$. Therefore, the result of the excess $\kappa$ in Sample B requires an additional excitations which can carry heat at low temperatures down to 0.28 K in the Mg-doped sample. Considering the AF ordering in the impurity-doped CuGeO$_3$, it is
most likely that antiferromagnetic magnons are responsible for this excess low-temperature heat conductivity in the Mg-doped sample.

In order to examine whether the Mg-doped sample also satisfies the Casimir’s condition, under which more quantitative discussion is possible, we compare low-temperature $\kappa$ of Sample B and that of another $x = 0.016$ sample with different $\bar{w}$ (Sample C). The upper inset of Fig. 2 shows that the values of $\kappa$ are different between Samples B and C. On the other hand, as shown in the lower inset, the low-temperature $\kappa/\bar{w}$ data $(T^3 < 0.1 \text{K})$ of the two samples show only 3% difference, which is mainly due to the error in determining the distance between the gold wires connected to the thermometers. Since the result means that $\kappa$ differs in proportion to $\bar{w}$ at low temperatures, it is strongly suggested that the Casimir’s condition is satisfied for both samples and that both $\kappa_{ph}$ and the magnon heat transport $\kappa_m$ are governed by the boundary scattering there, i.e.,

$$\kappa_m = \frac{1}{3}C_m v_m^c 1.12 \alpha_c \bar{w}$$

(3)

where $\alpha_c$ $(= \sqrt{v_m^p v_m^c v_m^c / v_m^c v_m^c} \sim \sqrt{|J_p J_m|/J_m^2})$ is a factor due to the anisotropy of the magnon velocity $v_m^c$ and $v_m^c$ is the magnon velocity in the $c$-th-axis direction.

Assuming Eq. (3), we can crudely estimate $v_m^c$ with the value of $C_m$ obtained by the independent specific-heat measurement and examine whether the magnon branch is in the SP gap. The specific heat of Samples A and B is shown in Fig. 2 as a function of $T^3$ in the temperature range below $\sim 0.58 \text{K} (T^3 < 0.2 \text{K})$. Since $C$ of the pure sample (diamonds in Fig. 2), which represents $C_{ph}$ in this temperature region, is more than one order of magnitude smaller than that of the Mg-doped samples, we can neglect $C_{ph}$ and assume $C_m \sim C$ for the doped sample. $\kappa_m$ of the $x = 0.016$ sample is estimated by subtracting $\kappa$ of the pure sample and is plotted together in Fig. 2. The $\kappa_m(T)$ data show exactly the same temperature dependence as the $C(T)$ data below 0.46 K $(T^3 < 0.1 \text{K})$, indicating again that Eq. (3) is satisfied in this temperature range. Assuming $J_c \sim 10 J_b \sim 100 |J_m|$ and $\alpha_c \sim 0.1 \frac{\pi}{4c}$ $v_m^c$ is estimated approximately to be 70 m/s from Eq. (3). The AF-magnon energy is lower than $q_m v_m^c \sim 0.12 \text{meV}$ $(q_m (= \pi/4c)$ is the wave number at the center of the Brillouin zone and $c (= 2.9 \text{Å})$ is the distance between adjacent Cu atoms along the Cu-O chain]. Since this value is two orders of magnitude lower than the SP gap $(\Delta_{SP} \sim 2 \text{meV})$, we can conclude that the additional heat transport observed in the Mg-doped CuGeO$_3$ is due to the in-gap AF-magnons.

The magnon velocity can be estimated also for the $x = 0.0216$ sample (Sample D) in the same manner. In order to subtract $\kappa_{ph}$, it is convenient to compare $\kappa/\bar{w}$ of Sample D to that of Sample A, which represents the phonon contribution. $\kappa/\bar{w}$ of Samples A and D is plotted against $T^3$ in Fig. 3(a). $\kappa/\bar{w}$ of Sample D is larger than that of the pure sample. The difference corresponds to the magnon contribution $\kappa_m/\bar{w}$ of Sample D. In Fig. 3(b), $\kappa_m/\bar{w}$ and independently obtained $C$ data are plotted together. Following the same discussion as that for the $x = 0.016$ sample, $v_m^c$ is estimated approximately to be 140 m/s. The upper limit of the magnon energy

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**Figure 2.** Specific heat and thermal conductivity of Cu$_{1-x}$Mg$_x$GeO$_3$ with the concentration of $x = 0.016$ below $\sim 0.58 \text{K}$ as a function of $T^3$. Specific heat of the pure CuGeO$_3$ is plotted together. Inset: $\kappa/\bar{w}$ of two $x = 0.016$ samples with different $\bar{w}$, i.e., Samples B and C.

**Figure 3.** (a) Thermal conductivity of Cu$_{1-x}$Mg$_x$GeO$_3$ $(x = 0, 0.0216)$ crystals, divided by $\bar{w}$ is plotted against $T^3$. (b) Specific heat and thermal conductivity of Cu$_{1-x}$Mg$_x$GeO$_3$ $(x = 0.0216)$ below $\sim 0.2 \text{K}$ as a function of $T^3$. Specific heat of the pure CuGeO$_3$ is plotted together.
The velocity of AF-magnon for the usual uniform Néel state is given by \( 2zJ_c\mathcal{S} \), where \( z \) is a factor of order unity, \( J_c \) is the interaction energy and \( S \) is the spin in each magnetic site. Even when quantum fluctuations, which diminish the effective value of \( S \) to 0.2 times smaller than unity, is taken into account, the magnon velocity of as fast as \( \sim 1000 \text{ m/s} \) is expected, (assuming \( J_c = 120 \text{ K} \)). Since we obtained much smaller \( v_m^c \), it is shown that effective \( S \) is significantly suppressed owing to the SP ordering. In the model of Refs. 9 and 10, the staggered moment is strongly suppressed in between the impurity sites. As the result, a sort of spatially averaged spin, which is directly proportional to the magnon velocity, becomes much smaller than 1/2. Our crude estimation from the low-temperature \( \kappa \) gives \( v_m^c \) of the \( x = 0.0216 \) sample approximately twice as large as that of the \( x = 0.016 \) sample, indicating that \( v_m^c \) rapidly increases with \( x \). Such \( x \)-dependence is consistent with the calculation in Ref. 10. Note that \( v_m^c \) of around 1300 m/s can be estimated for the Zn-3.2%-doped sample from the neutron data of which is nearly one order of magnitude larger than the value estimated for our \( x = 0.0216 \) sample.

It should be emphasized that the mean free path of the AF-magnon in the SP gap reaches as long as 1.12\( x_r\bar{v} \sim 18 \mu m \), according to Eq. (3), i.e., the magnons are mobile to a distance 60,000 times longer than the spin-distance \( \langle c \rangle \) without being scattered. Such coherent motion of the magnons is only possible with extremely long correlation length of the corresponding magnetic order. Therefore, the mixture of SP and AF ordering in the doped CuGeO\(_3\) is certainly a true long-range order.

In summary, we have measured thermal conductivity of pure and Mg-doped CuGeO\(_3\) single crystals at very low temperatures, in order to examine the anomalous low-temperature phase in the impurity-doped CuGeO\(_3\), where SP and AF order coexist. While the low-temperature thermal conductivity is dominated by \( \kappa_{\text{ph}} \) in the pure CuGeO\(_3\), magnons also carry considerable amount of heat in the Mg-doped samples. Estimating the magnon velocity, we have shown that the AF-magnons are present in the SP gap, as predicted by Saito and Fukuyama. It is demonstrated that thermal conductivity is a powerful tool in elucidating the low-energy magnetic excitations in the disorder-induced AF phase of spin-gap systems. Our next step is to examine the excitations in the uniform AF phase in highly substituted CuGeO\(_3\), and to seek differences from that of D-ordered CuGeO

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\( q \cdot v_m^c \) is \( \sim 0.23 \text{ meV} \), which is twice as high as that of the \( x = 0.016 \) sample but is still much lower than the \( \Delta_{\text{SP}} \).

In Ref. 9, considerable magnetic susceptibility is observed below \( \sim 1 \text{ K} \), because of incoherent magnetic excitations due to residual impurities and/or defects. However, such incoherent excitations do not contribute to heat transport. Also, magnetic specific heat is negligibly small, as will be shown later (Fig. 2).

Defect scattering would give \( T \)-dependence of the mean free path. Since scattering rate \( \Gamma \) of the defect scattering decreases with temperature, it will exceed \( \Gamma \) of the boundary scattering at the low-\( T \) limit, so that the Casimir’s condition is satisfied. See Ref. 9, p. 73, for example.

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