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Thermal conductivity of Mg-doped $CuGeO_3$ at very low temperatures: Heat conduction by antiferromagnetic magnons

J. Takeya,[1] I. Tsukada,[1] Yoichi Ando,[1] T. Masuda,[2] and K. Uchinokura[2]
[1]*Central Research Institute of Electric Power Industry, Komae, Tokyo 201-8511, Japan*
[2]*Department of Advanced Materials Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

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Thermal conductivity κ is measured at very low temperatures down to 0.28 K for pure and Mg-doped $CuGeO_3$ single crystals. The doped samples carry a 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 κ 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 evidence that κ at very low temperatures probes the magnon transport in a disorder-induced antiferromagnetic phase of spin-gap systems.

Recently, the 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 nonmagnetic impurity essentially changes the ground state. When the disorder is introduced by the nonmagnetic impurity, antiferromagnetic (AF) ordering *immediately* appears without destroying the spin-gap feature, commonly found in a spin-Peierls (SP) compound $CuGeO_3$,[1–5] a ladder compound $SrCu_2O_3$,[6] and a newly found Haldane system $PbNi_2V_2O_8$.[7,8] Since it was believed that the spin-singlet state and antiferromagnetism were mutually exclusive, the case of $CuGeO_3$, in which both the remaining SP ordering and the AF ordering developing with impurity doping turned out to be *long-range* order,[3] is remarkable. Fukuyama *et al.* proposed a theoretical model for this anomalous phase, i.e., dimerized antiferromagnetic (D-AF) phase.[9] In their model, staggered AF moments and lattice dimerization are spatially modulated, keeping the AF and SP long-range correlations; the degree of the lattice dimerization is larger in between the impurity sites than around the impurity sites and the magnitude of the staggered moments are larger near the impurity sites.

Even though the coexistence of the two long-range orders are established in lightly doped $CuGeO_3$, it is to be elucidated how low-energy spin excitations of the SP state, which has spin gap, and those of the AF state, which is gapless in isotropic systems, compromise with each other in the D-AF phase. Recently, Saito and Fukuyama extended the theory of Ref. 9 and predicted that a ‘‘slow’’ gapless AF-magnon branch shows up in addition to the gapped SP mode when impurity is doped.[10] They predicted that the energy scale of the magnon branch is smaller than the SP gap ($\sim$24 K). Existence of this in-gap magnon branch is observed by neutron scattering for rather highly substituted samples.[11–13] (Zn concentration was 3.2% for the sample used in Ref. 11, for example). However, since recent study using high-quality Mg-doped single crystals, in which impurities distribute more homogeneously than in Zn-doped systems, has revealed disorder-induced first-order transition around the Mg concentration of $x_c = 2.4\%$,[14] only below which the long-range SP ordering is established,[15] it is essential to examine the magnetic excitations of samples with impurity concentration less than x_c. In this work, we have measured thermal conductivity κ 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 are intrinsic to the D-AF phase, indeed exist and are responsible for the excess low-temperature heat transport in the doped samples.

The $Cu_{1-x}Mg_xGeO_3$ single crystals were grown with a floating-zone method. The Mg concentration is determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).[14,15] 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.[14–16] The transition temperatures are shown in Table I for each sample. SP long-range order is observed at T_{SP}^{LRO} as a resolution limited full width at half maximum (FWHM) of the x-ray Bragg peak from lattice dimerization. The Néel temperature T_N is determined by the magnetic susceptibility.[15]

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 a microchip heater and two calibrated RuO sensors, are attached on the samples by GE varnish. Temperature differ-

TABLE I. Relevant parameters, i.e., Mg concentration x, transition temperatures T_{SP}^{LRO} and T_N, geometrical mean width $\overline{w}$, and the estimated velocity v_m^c of the in-gap magnons, of the four measured crystals.

Sample	x	T_{SP}^{LRO} [K]	T_N [K]	$\overline{w}$ [mm]	v_m^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

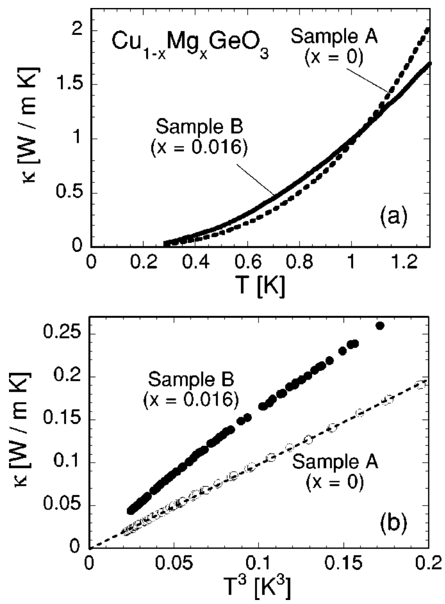

FIG. 1. (a) Thermal conductivity of $Cu_{1-x}Mg_xGeO_3$ single crystals below 1.3 K. The solid curve is for one of the $x=0.016$ samples (B) and the dashed curve is for the pure sample (A). (b) Thermal conductivity of the same sample as a function of T^3. The dashed lines show that κ is proportional to T^3 below 0.58 K for sample A.

ence 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),[17,18] 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 the thermal gradient is applied along the c axis. As shown in Table I, the geometrical mean widths $\overline{w}$ (square root of the cross section), which are proportional to the mean free path in the Casimir's limit,[17] of the pure sample (sample A) and one of the $x=0.016$ samples (sample B) are set identical for direct comparison in κ. The smooth boundaries of the crystal are 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 (Physical Properties Measurement System, 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 κ for samples A and B below 1.3 K. In Fig. 1(b), κ in the temperature range below 0.58 K ($T^3<0.2$ K^3) is plotted as a function of T^3. κ of the pure sample rapidly decreases with decreasing temperature and becomes proportional to T^3 below 0.58 K. At 1.3 K, κ of the $x=0.016$ sample is smaller than that of the pure sample, so that our previous results in a higher temperature range are reproduced.[19] It is natural that κ is suppressed in the presence of impurities, owing to the scattering by disorders. However, κ 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 κ 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 temperatures.[20] Therefore, the heat is dominantly carried by phonons there. Assuming kinetic approximation, the phonon thermal conductivity κ_{ph} is written as

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

where C_{ph} is specific heat, v_{ph} is velocity, and l_{ph} is the 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.[17,18,21] For a rectangular-shaped crystal, l_{ph} is given as

$$l_{ph}=1.12\overline{w}, \tag{2}$$

assumimg isotropic phonons.[22] We have measured the specific heat independently and examined the validity of Eqs. (1) and (2). First, v_{ph} is calculated from κ and C data by Eqs. (1) and (2), as $v_{ph}=(3\kappa)/(C1.12\overline{w})\sim1600$ m/s.[23] On the other hand, v_{ph} can be estimated only from the low-temperature C data, assuming the Debye model. Thus, the obtained value of v_{ph} is $\sim$1800 m/s, which is in good agreement with the estimation from the κ 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 κ_{ph} (any additional scattering would suppress the conductivity), we can notice that κ_{ph} of sample B cannot exceed κ of sample A in Fig. 1(b), using Eqs. (1) and (2), because $\overline{w}$ of samples 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 κ in sample B requires an additional excitation 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 κ of sample B and that of another $x=0.016$ sample with different $\overline{w}$ (sample C). The upper inset of Fig. 2 shows that the values of κ are different between samples B and C. On the other hand, as shown in the lower inset, the low-temperature $\kappa/\overline{w}$ data ($T^3<0.1$ K) of the two samples show only a 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 κ differs in proportion to $\overline{w}$ at low temperatures, it is strongly suggested that the Casimir's condition is satisfied for both samples, and that both κ_{ph} and the magnon heat transport κ_m are governed by the boundary scattering there, i.e.,

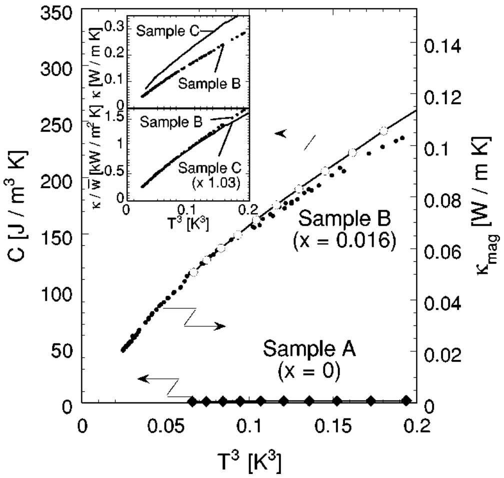

FIG. 2. Specific heat and thermal conductivity of $Cu_{1-x}Mg_xGeO_3$ with the concentration of $x=0.016$ below ~0.58 K as a function of T^3. Specific heat of the pure $CuGeO_3$ is plotted together. Inset: $\kappa/\overline{w}$ of two $x=0.016$ samples with different $\overline{w}$, i.e., samples *B* and *C*.

$$\kappa_m = \tfrac{1}{3} C_m v_m^c 1.12 \alpha_c \overline{w}, \tag{3}$$

[α_c ($\equiv \sqrt[3]{v_m^a v_m^b / v_m^{c\,2}} \sim \sqrt[3]{|J_a J_b|/J_c^2}$) is a factor due to the anisotropy of the magnon velocity[18] and v_m^i is the magnon velocity in the ith-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 ~0.58 K^3 ($T^3 < 0.2$ 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. κ_m of the $x=0.016$ sample is estimated by subtracting κ 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 ($T^3 < 0.1$ K), indicating again that Eq. (3) is satisfied in this temperature range. Assuming $J_c \sim 10 J_b \sim 100|J_a|$ and $\alpha_c \sim 0.1$,[24] v_m^c is estimated approximately to be 70 m/s from Eq. (3). The AF-magnon energy is lower than $q_c v_m^c \sim 0.12$ meV [q_c ($=\pi/4c$) is the wave number at the center of the Brillouin zone and c (=2.9 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 ($\Delta_{SP} \sim 2$ meV), we can conclude that the additional heat transport observed in the Mg-doped $CuGeO_3$ is due to the in-gap AF magnons.[25]

The magnon velocity can be estimated also for the $x=0.0216$ sample (sample *D*) in the same manner. In order to subtract κ_{ph}, it is convenient to compare $\kappa/\overline{w}$ of sample *D* to that of sample *A*, which represents the phonon contribution. $\kappa/\overline{w}$ of samples *A* and *D* is plotted against T^3 in Fig. 3(a). $\kappa/\overline{w}$ of sample *D* is larger than that of the pure sample. The difference corresponds to the magnon contribution $\kappa_m/\overline{w}$ of sample *D*. In Fig. 3(b), $\kappa_m/\overline{w}$ and independently obtained C

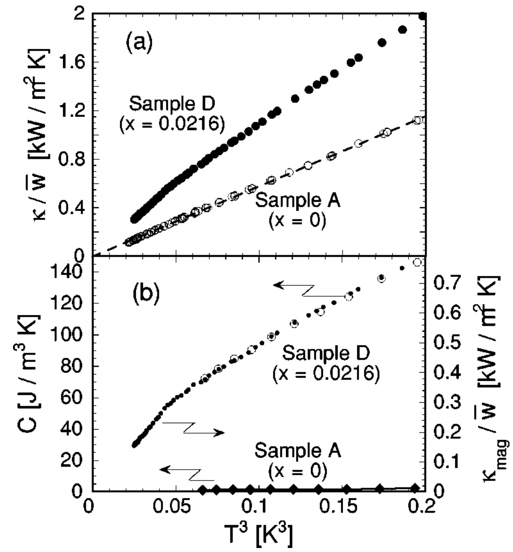

FIG. 3. (a) Thermal conductivity of $Cu_{1-x}Mg_xGeO_3$ ($x=0,0.0216$) crystals, divided by $\overline{w}$ is plotted against T^3. (b) Specific heat and thermal conductivity of $Cu_{1-x}Mg_xGeO_3$ ($x=0.0216$) below ~0.2 K as a function of T^3. Specific heat of the pure $CuGeO_3$ is plotted together.

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 $q_c v_m^c$ is ~0.23 meV, which is twice as high as that of the $x=0.016$ sample but is still much lower than the Δ_{SP}.

The velocity of AF magnon for the usual uniform Néel state is given by $2zJ_cSc$,[26] 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,[27] is taken into account, the magnon velocity of as fast as ~1000 m/s is expected (assuming $J_c = 120$ K).[24] 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 a result, a sort of spatially ''averaged'' spin, which is directly proportional to the magnon velocity, becomes much smaller than $\frac{1}{2}$. Our crude estimation from the low-temperature κ 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,[11] 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 $1.12\alpha_c\overline{w} \sim 18$ μm, according to Eq. (3), i.e., the magnons are mobile to a distance 60 000 times longer than the spin distance (c) without being scattered. Such coherent motion of the magnons is only possible with an extremely long correlation length of the corresponding magnetic order.[28] 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 the 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 coexists. While the low-temperature thermal conductivity is dominated by κ_{ph} in the pure $CuGeO_3$, magnons also carry a 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 the D-AF phase.

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