Thermal Conductivity of the Spin Peierls Compound CuGeO$_3$

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(Received CuGeO-6.tex)

The recent discovery of the inorganic Spin-Peierls (SP) compound CuGeO$_3$ has revived interests in this phenomenon. Spin-Peierls transition occurs in quasi-one-dimensional magnetic systems when the energy gained by splitting the degeneracy of the original magnetic ground state exceeds the lattice deformation energy. The SP ground state is therefore a nonmagnetic singlet. The SP transition occurs in magnetic fields above a critical field $H_{c}$.

The lowest excited triplet states. The appearance of the state with a magnetic energy gap between the singlet and the triplet states demonstrates its own unusual peak in $\kappa$ at $\sim$5.5 K. This low-temperature peak is strongly suppressed with magnetic fields in excess of 12.5 T.

PACS numbers: 66.70.+f, 75.30.Kz, 75.50.Ee

The thermal conductivity $\kappa$ of the Spin-Peierls (SP) compound CuGeO$_3$ was measured in magnetic fields up to 16 T. Above the SP transition, the heat transport due to spin excitations causes a peak at $\sim$22 K, while below the transition the spin excitations rapidly diminish and the heat transport is dominated by phonons; however, the main scattering process of the phonons is with spin excitations, which demonstrates itself in an unusual peak in $\kappa$ at $\sim$5.5 K. This low-temperature peak is strongly suppressed with magnetic fields in excess of 12.5 T.

While the phase diagram of CuGeO$_3$ is now well established, no transport measurements have been reported to date on this system. Such measurements are important for the determination of the basic scattering mechanisms in this system, both above and below the SP transition and in the high-field I phase. Since the SP transition is basically a magnetoelastic transition, heat transport which is expected to take place by phonons and spin excitations is ideal to probe these quasiparticles.

In this Letter we report thermal conductivity measurements of high quality CuGeO$_3$ single crystals along the chain direction in magnetic fields up to 16 T. One of our main results is an observation of the spin-excitation continuum above the SP transition causing a broad maximum at $\sim$22 K in the thermal conductivity $\kappa(T)$. This spinon heat transport disappears rapidly below $T_{SP}$, causing a kink in $\kappa(T)$, and phonons become the dominant heat carrier. The most intriguing observation is that the phonon thermal conductivity below $T_{SP}$ shows an unusual peak at $\sim$5.5 K. This peak is strongly suppressed with magnetic field above $H_{c}\approx$12.5 T where the SP order disappears. In the I phase above $H_{c}$ the thermal conductivity increases, which supports the idea of a new spectrum of magnetic excitations that are mobile and can carry heat through the crystal.

The thermal conductivity results are supplemented with specific heat and magnetic susceptibility measurements all done on the same samples. The specific heat data are useful for deriving the thermal diffusivity (and thus the information on scattering times) from $\kappa$; in the analysis of the low-temperature specific heat data, we suggest a new fit that is consistent with the simple theoretical idea of an almost mean-field SP transition and try to resolve some controversy over the analysis of the specific heat data.

Single crystal fibers of CuGeO$_3$ were grown using the laser-heated pedestal growth technique, a miniaturized float zone process. Powders of pure CuGeO$_3$ are cold-pressed and sintered into a pellet, from which we cut several source rods of about 2.6 mm in diameter. Previously grown single crystal fibers are used as seeds. Our samples were grown using a 20 mm/h pull rate (seed) and about 5 mm/h feed rate (source rod) in a flowing O$_2$.
atmosphere. The as-grown crystals are ∼4 cm long and 1 - 2 mm in diameter.

Thermal conductivity measurements were performed using a “two thermometer, one heater” method. Samples of size 7 × 2 × 0.2 mm³ were cut from the as-grown crystal, where the long dimension is along the chains (c-axis). The base of the sample was anchored to a copper block held at the desired temperature. A strain-gauge heater was used to heat the sample. A matched pair of microchip Cernox thermometers were carefully calibrated and then mounted on the sample. The maximum temperature difference between the sample and the block was 0.2 K. Typical temperature gradient used between the two thermometers was ∼0.5 K above 20 K and 0.2 K below 20 K. Radiation shield was used and was kept at the average temperature of the sample. Specific heats were measured in the temperature range 1.7 - 20 K using the relaxation method. The addenda heat capacity was measured independently, with no sample attached, in separate runs. The particulars of our apparatus, which allows us an extremely high sensitivity measurements, are described in greater detail elsewhere [1]. Magnetic susceptibility measurements were performed using a Quantum-Design SQUID magnetometer in the field range of 0 - 7 T.

Figure 1 shows the thermal conductivity of a CuGeO₃ single crystal in the temperature range 1.5 - 40 K. We also plotted in Fig.1 the specific heat data measured on the same crystal in the temperature range 1.8 - 16 K. Note that the transition is clearly seen in the specific heat and its sharpness is similar to the best crystals reported to date. Before we turn to the discussion on the thermal conductivity, it is useful to analyze the specific heat data and see its correspondence to previously published results. Ignoring the transition region, we fit the data above the SP transition (T_{SP}=14.08 K) to the form: 
\[c/T = \gamma + \beta T^2\]
while at low temperatures we use the form: 
\[c/T = \delta(\Delta/k_B T)^n e^{-\Delta/k_B T} + \beta T^2\]
Note that we introduced the ratio \((\Delta/k_B T)^n\) as a prefactor to the exponential decay of the spin contribution at low temperatures. While all previous publications [8][15] used n=1, such a fit is erroneous and will hold only at very low temperatures, typically below 1% of the transition temperature. At higher temperatures an exact expression for c/T of the spin system is needed for a meaningful fit. In fact, we believe that the discrepancies in the literature [8][13] between the value of \(\beta\) above and below \(T_{SP}\) stems from the use of incorrect fitting formula for the low temperature portion. Since the actual transition is 3-dimensional in nature, the most reasonable model to use is that of BCS which gives \(n=5/2\) [15]. While the fit above the transition is straightforward, at low temperatures using the full formula with the gap function is problematic, for the fitting program will encounter a singular matrix. Since the effect of the SP transition on the Debye temperature is expected to be negligible, a physical approach is to use the value obtained for \(\beta\) above \(T_{SP}\) for the low temperature fit.

Following the above discussion, we first fit the tempera-

ature range above the transition (14.5 - 20 K), which gives \(\gamma = 105.5\text{ mJ/mole-K}^2\) and \(\beta = 0.2164\text{ mJ/mole-K}^4\). We then fit the low temperature portion (1.8 - 5 K) using the same \(\beta\) to obtain the gap. Using \(n=5/2\) results in \(\delta = 377.86\text{ mJ/mole-K}^2\) and \(\Delta = 25.7\text{ K}\). This gives the ratio \(2\Delta/k_BT_c\) of 3.65, indicating a slightly stronger coupling than the BCS weak coupling limit of 3.52. It is useful to check the consistency of the parameter \(\delta\) by converting it to the units of number of states per Cu atom, \(m\). This is easily done by multiplying \(\delta\) by \(J\) (\(J\) as extracted from the literature lies in the range 80 to 150 K. Here we choose an averaged value of \(J ≃ 115\text{ K}\) and by the volume of a unit cell \((a × b × c=1.2×10^{-22}\text{ cm}^3)\). For the BCS formula with \(n=5/2\) we get \(m=2.07\) (note the \(\sqrt{2}\pi\) factor in the prefactor of BCS formula [8]). This analysis suggests that the density of magnetic excitations is exactly 2 states per Cu-atom at low temperatures. Thus, the use of the exact expression of \(c/T\) for the fit at \(T < T_{SP}\) leads to a totally consistent analysis with a reasonable value of \(\Delta\).

We turn now to the thermal conductivity \(\kappa\) in zero field shown in Fig.1. As the temperature is lowered from 40 K, \(\kappa(T)\) increases and peaks at ∼22 K below which it starts to drop rapidly. At the SP transition, \(\kappa(T)\) shows a kink towards a faster drop. However, instead of continuously dropping (presumably exponentially), \(\kappa(T)\) shows a minimum and a subsequent increase to a new maximum at ∼5.5 K followed by a sharp decrease as the temperature is lowered further. As a first approach to understand the thermal conductivity we use a simple kinetic approximation. Assuming two types of heat carriers, phonons and spin excitations, the thermal conductivity can be written as: 
\[\kappa = \kappa_s + \kappa_p = c_s D_s + c_p D_p\]
Here the subscript \(s\) denotes the magnetic (spinon) component and \(p\) the phonon contribution. \(c\) is the specific heat and \(D\) the diffusivity of the relevant excitations. While the magnetic contribution to the specific heat could be fitted with a \(\gamma T\) term near \(T_{SP}\), the full description of the magnetic specific heat is more complicated and in fact is a matter of current controversy [11][14]. For the pure one-dimensional system with only NN interaction, the specific heat will rise from low temperatures to a broad maximum at \(\sim J/2\). This maximum shifts towards lower temperatures as the NN interaction increases from zero. In fact, current models that fit the magnetic susceptibility and Raman scattering data suggest \(\alpha\) to be in the range 0.24 - 0.36 [10][11][12][29]. For example, Castilla et al. [11] argued that for CuGeO₃ the competing exchange between NN and NNN interactions is moderately large but smaller than \(\alpha_c\). Other authors report [11][14] that a larger value of \(\alpha\) (∼0.35) gives good fits to the experimental data.

Since the magnetic contribution to the thermal conductivity will be proportional to the magnetic specific heat, it is reasonable to assume that the peak at ∼22 K is just a reflection of this magnetic density of states. The fact that this peak appears at a lower temperature than the
susceptibility (typically ∼55 K) we also measured the susceptibility on the same sample confirming the peak at the same temperature) is a consequence of the temperature dependence of the diffusivity $D_s \sim T^{-q}$ with $q > 1$. Assuming that $\kappa_s$ is negligible by ∼100 K and approximating $\kappa_p$ to be constant except at very low temperatures, we can subtract in the temperature range 15 to 50 K a constant phonon background of $\kappa_p \approx 0.4$ W/cmK.

The remaining contribution approximates $\kappa_s$, which has a peak at ∼22 K. Shifting this peak to ∼50 K in $c_s$ requires a power $q$ of 4 or 5 in the formula of the diffusivity. In fact, a simple scaling approach to estimate the spinon diffusivity above $T_{SP}$ yields $D_s \sim (J/h)a^2(k_B T/J)^{-q}$, where $a$ is the distance between adjacent spins. Dividing the estimated $\kappa_s$ by this expression for the diffusivity yields an approximate contribution of the magnetic excitations to the specific heat. Using $q=4$, this magnetic specific heat shows a broad maximum at ∼50 K. Near $T_{SP}$ the obtained curve is linear in $T$ with a coefficient $\gamma^* \approx 31$ mJ/mole-K² (with $J$≈115 K), within a factor of 3 of the $\gamma$ estimated from the specific heat data near $T_{SP}$. Since we omitted constants and numbers of order unity, it is indeed very encouraging that the two estimates are only a factor of 3 different from each other. Moreover, we subtracted a constant $\kappa_p$ to obtain $\kappa_s$, a very simplified approximation. Thus, being able to obtain a reasonable value for the linear coefficient of the spinon specific heat give us confidence that indeed the maximum of the thermal conductivity at ∼22 K is of the same origin as the maximum in the susceptibility. In addition, the fact that this maximum is shifted so much to lower temperatures suggests that the mean free path of the magnetic excitations increases very rapidly as the temperature is lowered.

The SP transition is manifested in $\kappa$ by a sharp downward change in slope. This drop is clearly related to the emergence of a spin gap and thus has the same origin as the one observed in the susceptibility [1] or the strong decrease of $1/T_1$ below $T_{SP}$ as seen in NMR measurements [2]. It is however difficult to determine the exact functional form of the decrease because of the subsequent increase in $\kappa$ and the unusual peak at ∼5.5 K. Nevertheless, if we confine ourselves to $T < 5$ K, the data can be analyzed; assuming that $\kappa_s$ diminishes below $T_{SP}$, we can assume $\kappa$ is only due to phonons for $T \ll T_{SP}$. Using our heat capacity result, we can divide $\kappa$ by the lattice specific heat, $c_p = \beta T^3$. The resulting diffusivity in units of cm²/sec is displayed in the inset to Fig.1, plotted against $T^{-1}$. Remember that we expect the plotted $D$ to represent $D_p$ only below ∼5 K ($T^{-1} >0.2$ K⁻¹). In this temperature range it is clear that $D \sim T^{-1}$, a temperature dependence commonly attributed to a phonon scattering rate due to planar defects such as the strain field of dislocations [2]. In fact, transmission electron microscope investigation of our crystal found planar defects whose average distance is about 10 µm [2].

Based on the low-temperatures result discussed above, we can assume a model in which $\kappa$ is dominated by phonons below ∼12 K and exhibiting a competition between two scattering mechanisms that cause the peak at ∼5.5 K. If we assume phonons are scattered both by defects and by spin excitations, we can write $D_p = [AT + B(\Delta/T)^r e^{-\Delta/T}]^{-1}$, where $A$ and $B$ are constants and $r$ is a power smaller than $n$ (as introduced above). Here, $A$ can be determined from the low-temperature behavior (inset of Fig.1). Dividing $\kappa$ by $c_p = \beta T^3$ again and assuming $1 < r < 2$ ($r$ has to be in that range to accommodate the spin-excitations density of states as found earlier and to give a maximum to the formula), we estimate $B \sim 10^{-3}$ sec/cm². It is easy to calculate now the phonon mean free path due to phonon-spinon interaction, $\ell_{p-s}$. Using the estimates for $B$ and $r$ and a sound velocity of ∼$5 \times 10^5$ cm/sec, we find $\ell_{p-s}(T = T_{SP}) \approx 10$ µm; this value is compatible with the phonon mean free path for planar-defect scattering, $\ell_{p-d}$, estimated from the inset of Fig.1 ($\ell_{p-d} \sim 20$ µm at 5 K), which agrees with the actual planar-defect distance of ∼10 µm.

Figure 2 shows $\kappa(T)$ in the field range 0 - 16 T. One striking feature here is the strong suppression of the 5.5-K peak with magnetic field; $\kappa$ changes by more than a factor of 3 at 5.5 K, a big magneto-thermal effect. This strong effect of the field on the peak is another confirmation that its origin is related to the magnetic excitations in the SP phase. Note that the position of the peak does not shift much as a function of temperature for magnetic fields below 12 T, similar to the gap that does not change much. The peak becomes a shoulder at 14 T and a new low temperature dependence of the scattering times. Again, examining $\kappa(T)$ in 14 and 16 T, we find that the diffusivity is proportional to $1/T$ below $T \sim 4$ K. Since $\kappa$ at low temperatures is greatly suppressed and the diffusivity has still the $1/T$ dependence, we may conclude that phonons are strongly scattered by solitons in the I phase. Also, the smallness of $\kappa$ in the I phase compared to the SP phase suggest that solitons do not carry much heat. Note that the solitons are simultaneously magnetic
and structural excitations: they carry spin 1/2 and are domain walls in the dimerized lattice.

Finally, we briefly discuss the increase in $\kappa$ in the I phase from 14 to 16 T. The $T^3$ dependence of the magnetic specific heat in the I phase was explained by Bhattacharjee et al. [24] as the specific heat of the gapless phason modes. The increase of this phason with increasing field can be the cause of the increase in $\kappa$, although the magnetic field dependence of the phason has not been calculated. Another possibility is that the solitons themselves carry heat and the soliton contribution is proportional to the soliton population. However, since there is no theory for either soliton transport or phonon-soliton scattering, we cannot check the consistency of the soliton scenario.

To summarize, our thermal conductivity measurement of CuGeO$_3$ revealed four characteristic features: (a) a broad peak centered at $\sim 22$ K above the SP transition, (b) downward kink at $T_{SP}$ as temperature is lowered, (c) unusual peak centered at $\sim 5.5$ K below $T_{SP}$, (d) strong suppression of the 5.5-K peak with high magnetic fields. These observations are consistently understood by considering both phonon and spinon heat transports, which are analyzed in combination with specific heat data. In particular, the unusual 5.5-K peak is a consequence of phonons scattered both by defects and by spin excitations.

AK wishes to thank CRIEPI for the opportunity to spend time in their laboratory in Komae where much of the work was done. SGD thanks the support of the Alexander von Humboldt Foundation. Work at Stanford University was supported by AFOSR. Samples were prepared at the Center for Materials Research, Stanford University.

FIG. 1. Thermal conductivity and specific heat of CuGeO$_3$ single crystal in $H=0$. Inset: Low temperatures diffusivity extracted by dividing $\kappa$ by the fitted lattice specific heat.

FIG. 2. A set of $\kappa(T)$ in magnetic fields up to 16 T. Inset: $\kappa$ as a function of magnetic field at 4.2 K. Note the hysteresis at the SP to I transition at $\sim 12.5$ T.

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Fig. 2