Magnetic Field Enhancement of Heat Transport in the 2D Heisenberg Antiferromagnet $K_2V_3O_8$

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The thermal conductivity and heat capacity of single crystals of the spin 1/2 quasi-2D Heisenberg antiferromagnet $K_2V_3O_8$ have been measured from 1.9 to 300 K in magnetic fields from 0 to 8 T. The zero field thermal conductivity data are consistent with resonant scattering of phonons by magnons near the zone boundary. Application of a magnetic field greater than 1 T, however, produces a new magnetic ground state with substantial heat transport by long wavelength magnons.

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The physics of low-dimensional quantum antiferromagnets has attracted much attention in recent years among both theoretical and experimental physicists. In many quasi-one-dimensional systems rigorous theoretical predictions can be made [1–4], while in the two-dimensional cuprate systems there remains the tantalizing proximity of antiferromagnetism and superconductivity [5]. In the insulating magnetic systems there has been much interest of late [6–10] in using thermal conductivity measurements to probe excitations in a fashion analogous to the use of electrical conductance measurements to probe excitations in metallic systems. In this Letter we report thermal conductivity and heat capacity studies of the insulating $S = 1/2$, 2D square lattice antiferromagnet $K_2V_3O_8$, which reveals a remarkable variation of the thermal conductivity with both temperature and magnetic field. The present results suggest a general method for analyzing heat transport in other quasi-2D antiferromagnetic compounds such as La_2CuO_4 or MnF_2.

$K_2V_3O_8$ crystallizes in a tetragonal unit cell with space group $P4bm$ and $a = 0.887$ nm and $c = 0.5215$ nm [11]. The magnetic $S = 1/2$ V^{+4} atoms form a simple 2D square lattice. Previous magnetic measurements indicated that the data were best described by a 2D Heisenberg model with coupling constant $J = 12.6$ K [12]. Lumsden *et al.* [13] used a combination of neutron scattering and magnetic susceptibility data from single crystals to show that $K_2V_3O_8$ orders magnetically at about 4 K and exhibits weak ferromagnetism and field induced spin reorientations. These authors were able to understand the unusual magnetic field and temperature response of the system by incorporating both the symmetric and antisymmetric components of the Dzyalosinskii-Moriya (DM) interaction in addition to a Heisenberg Hamiltonian. This analysis indicates that $J_c/J \approx 10^{-3}$, where J_c is a measure of the coupling between neighboring V^{+4} spins along the c axis. The inclusion of DM interactions results in a small and anisotropic gap, Δ, in the spin wave excitations (magnons) of $K_2V_3O_8$ of the order of 1 K. The gap has been recently verified in measurements of the magnon spectrum of $K_2V_3O_8$ using inelastic neutron scattering [14]. In most respects the magnon excitations in the a-a plane are what is expected for a quasi-2D Heisenberg antiferromagnetic; the energy of the excitations is linear in k for most wave numbers and flattens to zero slope near the zone boundary ($k = \pi/2a$) at an energy near 27 K (about $2J$). The linear portion of the magnon spectrum gives a magnon velocity of about 3×10^4 cm/s, a value more than 10 times smaller than the estimated average sound velocity in $K_2V_3O_8$. Very little dispersion was found for magnons along the c direction.

Single crystals of $K_2V_3O_8$ (typical dimensions $0.5 \times 0.5 \times 0.05$ cm^3) were grown via a flux technique as described previously [13]. The crystals were mounted for thermal conductivity measurements in a physical property measurement system (PPMS) from Quantum Design. Four wire thermal conductivity measurements were made using the thermal transport option from Quantum Design that has been thoroughly tested in our laboratory for several months using a variety of thermal conductivity standards. Heat capacity measurements were also made using the PPMS system.

Figure 1 shows the measured thermal conductivity of $K_2V_3O_8$ along the a axis for temperatures from 1.9 to 300 K in magnetic fields up to 8 T. For these data the magnetic field was applied in the a-a plane but perpendicular

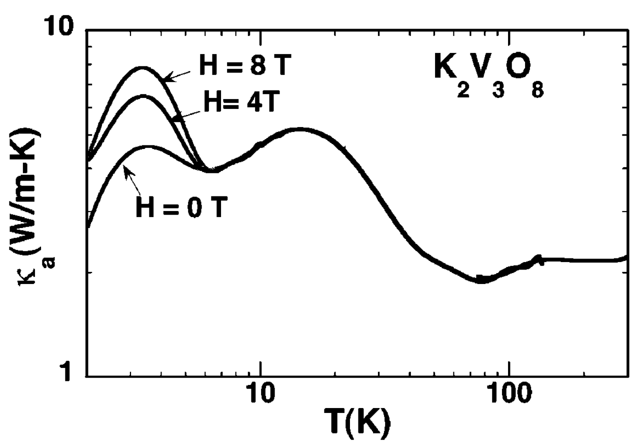

FIG. 1. Thermal conductivity of a $K_2V_3O_8$ crystal measured with the heat current along the a axis and a magnetic field also in the a-a plane but perpendicular to the direction of heat flow.

to the direction of heat flow. There are several unusual features to the data. From 150 to 300 K the thermal conductivity is weakly temperature dependent rather than decreasing as T^{-1} which is typical of dielectric crystals. The flat temperature dependence appears to be partially due to the increase of the heat capacity in this temperature region that compensates for any decrease in the phonon (or magnon) mean free path. At about 110 K there is a noticeable drop in the thermal conductivity which is associated with a local structural distortion of the apical oxygen of the V^{+4} square pyramids [15]. A reduction in the local symmetry is similar to the introduction of additional point defects into the crystal. More point defects will lower the thermal conductivity, as is observed in the temperature range from 110 to 70 K. This distortion was recently characterized using infrared spectroscopy, heat capacity, and dielectric constant measurements [15]. Magnetic susceptibility measurements in this temperature range, however, showed no evidence of an anomaly, and low temperature structural data from powder neutron diffraction experiments indicated no obvious change in the crystal structure space group due to the distortion [16]. The most interesting aspects of the thermal conductivity data, however, occur at temperatures below 70 K.

In an insulating magnetic system heat is carried primarily by acoustic phonons and magnons ($\kappa_{\text{total}} = \kappa_{\text{phonon}} + \kappa_{\text{magnon}}$). Additionally, magnons can scatter phonons or phonons can scatter magnons. One of the major problems in using a heat current to probe the magnetic excitations of a material is determining what part of the heat current is carried by each quasiparticle. The simplest expression that describes the thermal conductivity of a solid is similar for both magnons and phonons and is given by $\kappa = 1/3 C_v v d$, where C_v is the heat capacity per unit volume of the phonons (magnons), v is the average sound (magnon) velocity, and d is the average mean free path for the acoustic phonons (magnons). An estimate of the temperature variation of d was determined using the measured thermal conductivity and heat capacity data ($H = 0$ data) and the appropriate sound (5×10^5 cm/s) or magnon velocity (3×10^4 cm/s). Phonon mean free paths can be extremely large in crystals at low temperature and in some cases are limited by the macroscopic dimensions of the crystal. Is there any constraint on the magnon mean free path? With a gap, Δ, in the magnon spectrum, the dispersion is linear in k only for large wave vectors, with a corresponding nonzero magnon velocity v_{magnon}. For small k the magnon velocity is nearly zero ($d\omega/dk \approx 0$). A natural crossover is given by $\Delta = v_{\text{magnon}} k_c \hbar$. Modes with $k \ll k_c$ do not contribute to heat transport, while for $k \gg k_c$ modes carry heat in the usual way. This suggests [17] that $d_c = h v_{\text{magnon}}/\Delta$ is a natural distance playing the role of an effective cutoff length that can be used empirically as an upper limit for the magnon mean free path in the simplest model for κ. Applying this to $K_2V_3O_8$, with a gap of 1 K and $v_{\text{magnon}} = 3 \times 10^4$ cm/s, this implies an upper limit for d_c of 14 nm. For temperatures less than 30 K this value is at least an order of magnitude too small to account for the measured thermal conductivity values even assuming that all of the heat capacity below 30 K is of magnetic origin. Hence in zero magnetic field it is likely that virtually all of the heat conduction is phononic in origin even when $k_B T \gg \Delta$. This conclusion is also consistent with a minimum in κ_a at 6.5 K that occurs near a maximum in C_m/T, where C_m is the magnetic portion of the heat capacity (Fig. 2). A low temperature minimum in κ is typically observed in materials where the phonons are resonantly scattered by a localized defect that has only appreciable cross section within a narrow energy range [18]. The zero field thermal conductivity data can be modeled using the formalism developed by Calloway [19] and Klemens [20] along with expressions for various phonon scattering processes [18,21],

$$\kappa_{\text{lattice}} = 1/3 \int_0^{\omega_D} v^2 \tau(\omega, T) \frac{dC}{d\omega} d\omega\,, \tag{1}$$

$$\tau^{-1}(\omega, T) = \sum_i \tau_i^{-1}(\omega, T)\,, \tag{2}$$

where ω_D is the Debye frequency, v is the velocity of sound, τ_i is the relaxation time for the ith phonon scattering mechanism, T is the temperature, and $dC/d\omega$ is the specific heat per angular frequency within the Debye model. Standard expressions from the literature [18,21] are used for boundary scattering: v/D, point defect scattering: $C\omega^4$, both normal and umklapp scattering: $B\omega^2 T e^{-b/T}$, and resonant scattering: $AT^3\omega^2/(\omega^2 - \omega_0^2)^2$, where D is the smallest dimension of the crystal (0.05 cm), and C, B, b, A, and ω_0 are adjustable parameters. A reasonable description of the thermal conductivity data is generated using a Debye temperature of 700 K, a value consistent

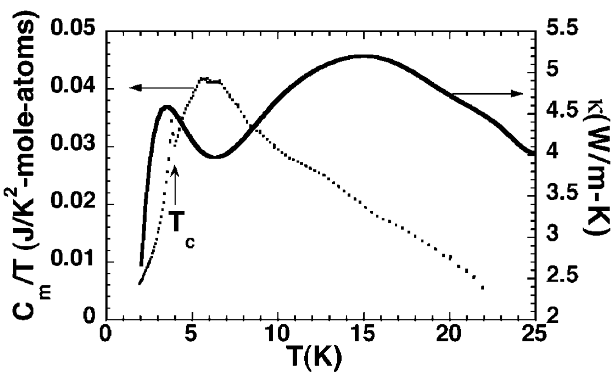

FIG. 2. Estimated magnetic contribution to the heat capacity divided by T [$C_m(T)/T$] and measured thermal conductivity versus temperature. The magnetic heat capacity was estimated by subtracting a Debye lattice contribution from the total heat capacity. For temperatures below 10 K over 80% of the total heat capacity is of magnetic origin for any reasonable value for the Debye temperature (200–800 K). The small heat capacity anomaly associated with the onset of 3D magnetic order is noted in the figure.

with the heat capacity data, and the values for C, B, b, A, and $T_{\rm res} = \hbar\omega_0/k_B$ shown in Fig. 3. The value of $T_{\rm res}$ obtained from the model (23 K) is not sensitive to variations in the other parameters and is not sensitive to the exact functional form used to describe the resonant scattering. It is generally found that a low temperature minimum in κ at a temperature $T_{\rm res}$ corresponds to resonant scattering at an energy 3 to 4 times $k_B T_{\rm res}$ [18]. The only energy scale in the problem that corresponds to 23 ± 5 K is the top of the magnon band, which corresponds to magnons near the zone boundary. At the zone boundary, the magnons have a large density of states and the excitations roughly correspond to localized spin flips with zero velocity ($d\omega_{\rm magnons}/dk = 0$). This is exactly the type of excitation that could give rise to resonant scattering and hence we suggest that resonant scattering by magnons near the zone boundary is responsible for the minimum in κ at 6.5 K.

The application of a magnetic field results in a large increase in the thermal conductivity for temperatures below 6 K (see Fig. 1). We considered the magnetic field dependence of the resonant scattering rate as a possible explanation for this effect as was successfully done for $SrCu_2(BO_3)_2$ [6]. This assumption produced either a small decrease or no change in κ with increasing magnetic field and hence was ruled out as the origin of the magnetic field dependence of κ. Isothermal measurements of κ in a magnetic field are presented in Fig. 4 for two orientations of the field with respect to the direction of heat flow. Below a critical magnetic field the thermal conductivity does not change within the precision of our measurements: $H = 0.55$ T for a magnetic field applied along the a axis and $H = 0.95$ T for a magnetic field applied along the c axis. These fields are close to the spin reorientation values found at 2 K using magnetization and neutron scattering data [13] (0.65 T for $H \parallel a$ and 0.85 T for $H \parallel c$). At both fields the V^{4+} spins rotate from along the c axis into the a-a plane always remaining perpendicular to the applied magnetic field. To understand these data we recall a very general result from the theory of antiferromagnetic magnons in the long wavelength limit [22]. In a magnetic field the magnon spectrum is split into two branches with magnon energies (or frequencies) $\hbar\omega_k = \sqrt{(v_m\hbar k)^2 + \Delta^2} \pm g\mu H$. When $g\mu H/k_B$ exceeds a value of the order of 1 K, there will no longer be a gap in the magnon spectra at $k = 0$ for the lower magnon branch. With no gap, the correlation length for the magnons in this branch can become much larger than the 14 nm value suggested above and the magnon velocity becomes finite at $k = 0$ ($d\omega/dk \neq 0$). A significantly larger mean free path and finite velocity for magnons in this branch should enable these magnons to carry measurable amounts of heat. This simple picture cannot be quantitatively correct since for $H \geq H_c$ a new magnetic ground state is formed. The experimental data, however, suggest that the thermal and field dependence of the occupation of this new ground state, $n_m(H,T)$ should be defined as 0 for $H \leq H_c$ and given by Eq. (3) for $H \geq H_c$.

$$n_m(T,H) = \frac{e^{-(\Delta - g\mu H)/k_B T}}{1 + e^{-(\Delta - g\mu H)/k_B T} + e^{-(\Delta + g\mu H)/k_B T}} - n(T,H_c)\,. \quad (3)$$

At $T = 3.7$ K, and for magnetic fields greater than the critical value, $(\Delta/g\mu)$, $n_m(T,H)$ is linear in field for small fields $[n_m(T,H) \approx g\mu(H - H_c)/k_B T]$ and slowly saturates at higher fields. The thermal conductivity data shown

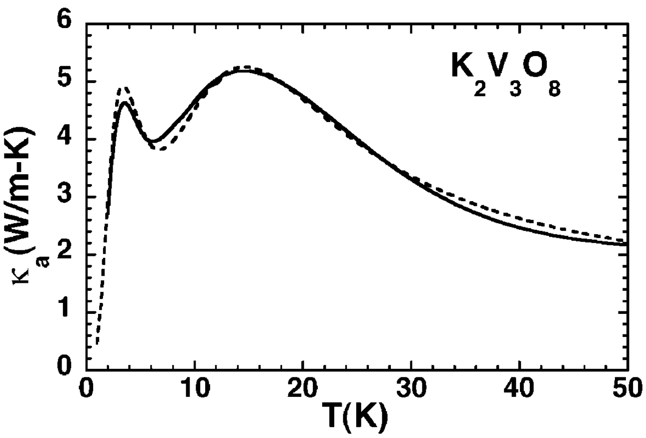

FIG. 3. Thermal conductivity data (solid line) compared to model calculation (dashed line) described in text with the following choice of parameters: $T_{\rm res} = 23$ K, $b = 60$ K, $C = 1.75 \times 10^{-43}$ s^3, $B = 3 \times 10^{-17}$ s/K, and $A = 5 \times 10^8$ s^{-3} K^{-3}. The values for b, C, and B are typical for dielectric crystals.

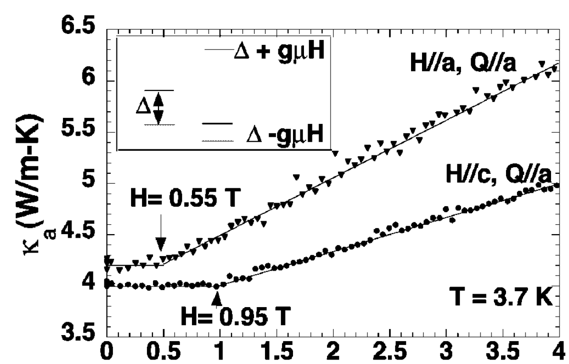

FIG. 4. In-plane thermal conductivity vs magnetic field at $T = 3.7$ K for fields parallel to the a or c axis (the two data sets have been offset for clarity). The thermal conductivity does not change with magnetic field for fields less than the critical values noted in the figure. These fields are close to the spin reorientation values found at 2 K using magnetization and neutron scattering data [13] (0.65 T for $H \parallel a$ and 0.85 T for $H \parallel c$). At both fields the V^{+4} spins rotate from along the c axis into the a-a plane always remaining perpendicular to the applied magnetic field. The inset schematically shows the effect of a magnetic field on the two magnon branches near $k = 0$. At the critical field there is no gap at $k = 0$ in the lower branch of the magnon spectra.

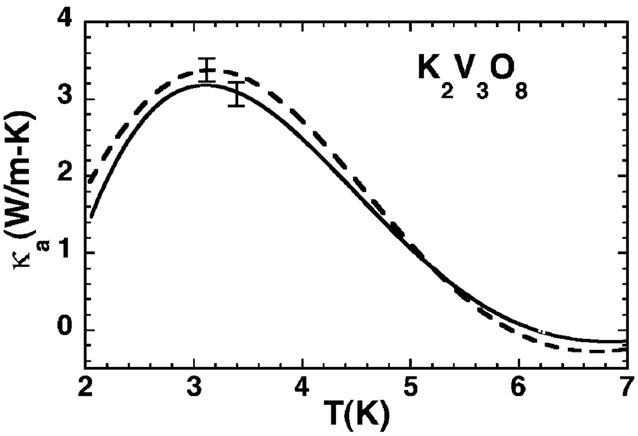

FIG. 5. Thermal conductivity of a $K_2V_3O_8$ crystal at 8 T minus the thermal conductivity at 0 T (solid line) versus temperature. Thermal conductivity at 4 T minus thermal conductivity at 0 T versus temperature (dashed line) scaled using Eq. (3). There are no adjustable parameters.

in Fig. 4, which should be proportional to $n_m(T, H)$, is qualitatively described by this functional form (including data taken at higher fields that is not shown in Fig. 4). The slopes of the data shown in Fig. 4 differ by about a factor of 2 depending on the direction of the field with respect to the a-a plane. If the field is applied in the a-a plane the increase of the thermal conductivity with field is, within experimental error, the same whether the field is parallel or perpendicular to the direction of the heat current. Only when the field is applied along the c axis does the thermal conductivity increase more slowly with field. When the field is applied along the c axis the spins tilt slightly out of the a-a plane, and this tilting increases with increasing field. The slower increase of the magnon thermal conductivity with $H \parallel c$ may be related to this tilting. We are not aware of any theoretical treatment dealing with the effect of spin orientation on magnon heat transport, but for $K_2V_3O_8$ this appears to be a significant effect. Finally, we note that the temperature dependence predicted by Eq. (3) accounts for the magnon thermal conduction in a field since our experimental data taken in various magnetic fields scale with $n_m(T, H)$, within experimental error, as shown in Fig. 5. This scaling indicates that the various magnon scattering mechanisms do not change significantly for $H > H_c$ and that the only change with field is the number of magnons in the new ground state.

In summary, the thermal conductivity data from $K_2V_3O_8$ indicate resonant scattering of phonons by magnons near the zone boundary and heat transport by long wavelength magnons. The magnon heat transport occurs only after a small anisotropic gap is closed at $k = 0$ by the application of a magnetic field. The unusual magnetic and thermal properties of $K_2V_3O_8$ suggest a general method for analyzing the thermal conductivity of other quasi-2D antiferromagnetic compounds such as La_2CuO_4 or MnF_2. The essential observation is that if there is a gap, Δ in the magnon spectra at $k = 0$, it is likely that for magnetic fields less than $\Delta/g\mu$ phonons will carry most of the heat (even when $k_BT \gg \Delta$). The application of a magnetic field greater than $\Delta/g\mu$ will result in the closure of the gap and the formation of a new magnetic ground state with magnons that can carry heat. It is important to realize that the magnon gap in compounds such as $K_2V_3O_8$, La_2CuO_4, or MnF_2 is due to the anisotropy in J rather than the magnitude of J. For example, in La_2CuO_4 J is about 2200 K, but the gap in the magnon spectra is only about 12.5 K. The results reported in this Letter thus suggest a variety of new experiments and a need for a better theoretical understanding of heat transport quasi-2D Heisenberg antiferromagnets.

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