Magnon-mediated thermal conductivity in the dimerized spin-gap compound $BaCu_2V_2O_8$

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We have measured the thermal conductivity (κ) of the quasi-one-dimensional spin-gap compound $BaCu_2V_2O_8$ with heat flow parallel and perpendicular to the chain axis. Distinctive differences in the magnitude and temperature dependence between these directions have been observed. A weak but non-negligible contribution to κ along the chain has been identified, attributed to the magnon heat transport. An analysis using a simple kinetic approach has been employed to rationalize this contribution. We also estimated the temperature dependent mean-free path for the magnon scattering. The result implies that the magnon-phonon scattering is a major process for the magnon-assisted κ at intermediate temperatures.

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While there have been a significant body of work concentrating on the magnetic nature of low dimensional quantum spin systems, the studies of heat transport in these materials are not ubiquitous.[1] Among the limited number of reports,[2–9] the main focus for the transport property is to explore the additional contribution from the spins to the total thermal conductivity, providing complementary information on the magnetic excitations. In general, such the spin-mediated thermal conductivity (κ_m) is rather small as compared to the lattice thermal conductivity (κ_L) driven by the phonons. This renders certain difficulties on the determination of κ_m in most of the spin chain systems. However, exceptions have been found in the spin ladder compounds $(Sr,Ca,La)_{14}Cu_{24}O_{41}$, where κ_m exhibits a huge anomalous high peak along the ladder direction with a magnitude as large as about 100 W/m K.[2,3] Such a feature has been attributed to the conservation of heat current, leading to ballistic energy propagation in the thermal transport.

In this Brief Report, we report on the measurement of the thermal conductivity of the spin-gap compound $BaCu_2V_2O_8$ at temperatures between 8 and 350 K. $BaCu_2V_2O_8$ crystallizes in a tetragonal structure with the space group $I\text{-}42d$.[10] Within this structure, the Cu^{2+} ions have bridged by oxygen ions, forming the CuO_4 square plaquettes along the crystallographic c direction. The one-dimensional (1D) characteristic in the c direction is responsible for the formation of a spin gap in this material. In earlier studies, the spin gap has been interpreted by means of the alternating chain model, based on the analyses of magnetic susceptibility and heat-capacity data.[11] Within the alternating chain scenario, one interaction $J_1=260$ K is along the Cu-O-V-O-Cu path in the c axis and another $J_2=52$ K is along the Cu-O-Cu path which is almost perpendicular to the chain direction. The rather small ratio of $J_2/J_1 \simeq 0.2$ has been argued to be the origin of the observed spin gap. On the other hand, according to the crystal structure of $BaCu_2V_2O_8$, the spin chain is allowed to be described as an arrangement of the spin dimers. Each dimer consists of two CuO_4 square plaquettes and the weak interdimer interactions are considered to be responsible for the observed large spin gap. Such a picture has been proposed to be more realistic for the understanding of spin-gap nature in $BaCu_2V_2O_8$, according to the nuclear magnetic resonance (NMR) results.[12] A very recent theoretical study using first-principles calculations to obtain the effective Cu-Cu hopping integrals indicated a predominant exchange interaction between the next-nearest-neighbor (NNN) Cu ions,[13] supporting the validity of the nearly isolated dimer model for the origin of the spin gap in $BaCu_2V_2O_8$.

The raw material was synthesized by a standard solid-state reaction technique using high-purity reagents of Ba_2CO_3 (4N), CuO (4N), and V_2O_5 (4N) in the molar ratio 1:2:1. Single crystal $BaCu_2V_2O_8$ was grown by a spontaneous nucleation method, described elsewhere.[14] The orientations of the crystal surfaces were confirmed using x-ray Laue back-scattering analysis. Typical size of the single crystal is about $2\times2\times6$ mm^3 with the long dimension parallel to the c axis. Thermal conductivity measurements were carried out in a closed-cycle refrigerator, using a direct heat-pulse technique.[15] The sample was cut to a rectangular parallelepiped shape with one end of the sample glued (with thermal epoxy) to a copper block that served as a heat sink, while a calibrated chip resistor as a heat source glued to the other end. The heat current was applied to the directions parallel and perpendicular to the c axis. The temperature difference was detected by using an E-type differential thermocouple with junctions thermally attached to two well-separated positions along the sample. The temperature difference was controlled to be less than 1 K to minimize the heat loss through radiation, and the sample space is maintained in a good vacuum (approximately 10^{-4} torr) during measurements. All experiments were performed during warming with a rate slower than 20 K/h. The uncertainty of our thermal-conductivity measurements is less than 10%, mainly arising from the error on the determination of the geometrical factor of the specimen.

Temperature dependence of the thermal conductivity parallel and perpendicular to the c axis, denoted as $\kappa_{\parallel}(T)$ and $\kappa_{\perp}(T)$, were displaced in Fig. 1. For each orientation, κ

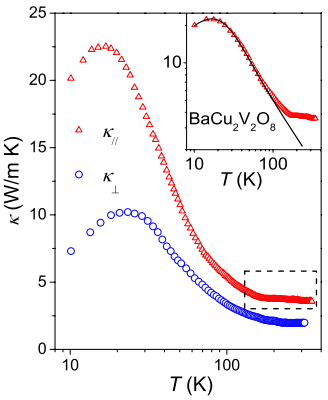

FIG. 1. (Color online) Temperature dependence of thermal conductivity of $BaCu_2V_2O_8$ along and perpendicular to the chain direction. The dashed box denotes a region in which the magnon-mediated thermal conductivity becomes significant. The solid curve shown in the inset is a fit to the calculated phonon thermal conductivity.

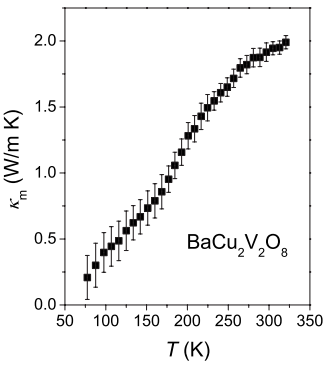

FIG. 2. Magnon thermal conductivity as a function of temperature for $BaCu_2V_2O_8$.

shows a maximum between 20 and 30 K which is a typical feature for the reduction of thermal scattering at lower temperatures. The maximum takes place at the temperature where the phonon mean-free path is approximately equal to the crystal site distance. After passing through the maximum, $\kappa_\perp(T)$ drops with increasing temperature, tending to vary with $1/T$ while $\kappa_\parallel(T)$ exhibits a distinct shoulderlike feature at higher temperatures, as highlighted by the dashed box. It denotes a region in which the spin-mediated thermal conductivity becomes significant, and a further discussion concerning this part will be given in later sections. Similar observations have been reported for the spin chain materials and also have been attributed to additional heat conduction channel mediated by the spins.[4–7,9] However, such a feature was not observed in $\kappa_\perp(T)$ due to weak interactions in the perpendicular direction. Since the singlet-triplet (magnon) excitation of dimerized states is the elementary excitation in $BaCu_2V_2O_8$, we hereafter associate this additional contribution of κ with the magnon thermal conductivity κ_m.

Due to the fact that $BaCu_2V_2O_8$ is an insulator, the observed κ mainly arises from the lattice thermal conductivity. Here κ_L was modeled using the Debye approximation[16,17]

$$\kappa_L = \frac{k_B}{2\pi^2 v}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x-1)^2}\tau_P dx, \tag{1}$$

where $x=\hbar\omega/k_BT$ is dimensionless, ω is the phone frequency, $\hbar$ is the reduced Planck constant, k_B is the Boltzmann constant, θ_D is the Debye temperature, v is the average phonon velocity, and $1/\tau_P$ is the phonon-scattering relaxation rate. Here $1/\tau_P$ is the combination of three scattering mechanisms and can be expressed as

$$1/\tau_P = \frac{v}{L} + A\omega^4 + B\omega^2 T e^{-\theta_D/3T}, \tag{2}$$

where the grain size L and the coefficients A and B are fitting parameters. The terms in Eq. (2) represent the scattering rates for the grain-boundary, point-defect, and phonon-phonon Umklapp scattering, respectively. In general, the grain-boundary scattering is a dominant mechanism for the low-temperature κ_L, while the Umklapp procedure is important at high temperatures. The point-defect scattering, on the other hand, has a strong influence on the appearance of the shape and position of the phonon peak occurring in the intermediate temperature regime. Taking $\theta_D=390$ K given from the specific-heat measurement,[11] the experimental data for $\kappa_\parallel(T)$ can be fitted very well as $T<70$ K. The fitting curve is drawn as a solid line in the inset of Fig. 1.

The magnon thermal conductivity here was obtained by subtracting κ_L from the total κ. In Fig. 2 we plotted the deduced κ_m with estimated error bars. Below about 90 K, κ_m is not well resolved because of the undistinguished difference between κ and κ_L due to experimental uncertainty. We thus only discuss the result of κ_m above this temperature. The T-dependent $\kappa_m(T)$ reflects an increase of thermally excited magnons responsible for the heat transport, following an activated behavior. At high temperatures, κ_m tends to saturate with a maximum value of approximately 2 W/K m, which is about 40 times smaller than that found in $Sr_{14}Cu_{24}O_{41}$.[2,3,8] The small value of κ_m in $BaCu_2V_2O_8$ could be attributed to the short magnon mean-free path l_m, as we will discuss this part below. To calculate l_m, we employed a simple kinetic expression in a first-order approximation using the resulting κ_m. Assuming a momentum-independent mean-free path and triplet excitation within the dimer, one can express κ_m as

$$\kappa_m = \frac{3N_s l_m}{\pi\hbar}\left(\frac{k_B}{T}\right)^2 \int_{\Delta_{\text{dimer}}}^{T_{\max}} \frac{e^{t/T}}{(e^{t/T}+3)^2} t^2 dt, \tag{3}$$

where $t=\varepsilon/k_B$, with ε representing the excitation energy. Here N_s is the number of dimer per unit area and $T_{\max}$ is the maximum band energy in units of k_B. Taking $\Delta_{\text{dimer}}=450$ K from NMR Knight shifts[12] and $T_{\max}\simeq 10\Delta_{\text{dimer}}$ in $BaCu_2V_2O_8$, the temperature dependence of l_m can be obtained, as illustrated in Fig. 3. Note that the assumption of $T_{\max}\simeq 4500$ K does not significantly affect the data fitting for temperatures $T \ll T_{\max}$.

Because we could not ambiguously determine the values of κ_m for $T<70$ K, a further information about the low-temperature l_m in $BaCu_2V_2O_8$ will not be discussed here. On the other hand, we found a strong temperature dependence of l_m between 70 and 150 K, as indicated by a rapid drop in l_m

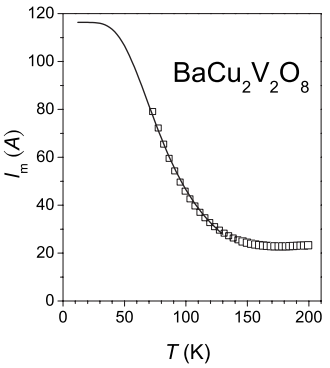

FIG. 3. Temperature dependence of magnon mean-free path for $BaCu_2V_2O_8$. The solid line is a fit to Eq. (4).

with increasing temperature. Above 150 K, l_m tends to be a constant with a value of about 20 Å. Assuming that the different scattering mechanisms act independently to the mean-free path, the entire temperature variation of l_m can be reasonably reproduced using the following formula:

$$\frac{1}{l_m} = \frac{1}{l_o} + A_m T e^{-T_m/T}. \tag{4}$$

From such a fitting, shown as a solid curve in Fig. 3, the fitting parameters $l_o = 1.16 \times 10^{-8}$ m, $A_m = 1.05 \times 10^7$ m^{-1} K^{-1}, and $T_m = 210$ K were obtained. Here l_o is the mean distance between magnetic defects in a spin chain which is temperature independent. From the Curie-tail of the magnetic susceptibility, the concentration of the paramagnetic defects arising from isolated Cu^{2+} ions was estimated to be 4.2% per mole.[18] This corresponds to the average defect distance of 90 Å, quite close to the obtained value of $l_o \approx 110$ Å and such agreement suggests the validity of our present analyses. The second term in Eq. (4) represents the magnon-phonon scattering process with A_m characterized as the strength of the corresponding interaction and T_m the minimum energy needed for the magnon-phonon umklapp process. It is noted that the obtained T_m is much smaller than $\Delta_{\text{dimer}} = 450$ K but is close to $\theta_D/2 = 195$ K. Such a result indicates that the magnon-magnon scattering is less likely and the magnon-phonon scattering would be a dominant process for the observed κ_m in this temperature range.

In summary, we have measured the thermal conductivity of the dimerized spin-gap system $BaCu_2V_2O_8$. We found a weak but discernible contribution to κ along the chain, attributed to the heat transport assisted by the magnons. A simple kinetic approach has been employed to rationalize this contribution. In addition, the temperature dependent mean-free path for the magnon scattering was evaluated and the results indicate the importance of magnon-phonon scattering for the observed κ_m at intermediate temperatures.

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