Low-temperature spin excitations in frustrated ZnCr$_2$O$_4$ probed by high-field thermal conductivity

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The magnetoelastic excitations of spin frustrated ZnCr$_2$O$_4$ are studied by the magnetic field dependence of the thermal conductivity k down to 50 mK. Above the first-order magnetostructural transition at $T_{N,S} \approx 12.5$ K, spin fluctuations are strongly coupled to acoustic phonons, leading to a glasslike dependence of $k(T)$, up to Θ_{CW}. In the symmetry broken phase below $T_{N,S}$, k shows a dominant magnetic contribution even at the lowest temperatures probed in this work. Application of a magnetic field above 2.5 T destabilizes the spin-bond structure, leading to a sudden increase and a nonconventional temperature dependence of the thermal conductivity. The possibility of the coexistence of gapped and gapless excitations in this magnetic phase is discussed.

I. INTRODUCTION

The large low-temperature magnetic entropy in spin ice Ho$_2$Ti$_2$O$_7$,[1] or the magnetic charges (monopoles) found in this material,[2] have the same fundamental origin as the absence of magnetic order and the gapless excitations in organic EtMe$_3$Sb[Pd(dmit)$_2$]$_2$:[3] namely geometrically frustrated spin interactions. In an ideal, unperturbed situation, a collection of antiferromagnetic (AF) exchange-coupled spins in a lattice with a triangular motif do not order: the low-energy excitations of such a state are characteristic of a correlated paramagnet or a spin-liquid. For $S = 1/2$ in this configuration, a superposition of valence-bond singlets can support a quantum spin-liquid state.[4] Charge doping in such a liquid was proposed to support spin-singlet molecules that are able to move and carry charge in a superconducting state, providing one of the early attempts to explain high-T_C superconductivity.[5,6] The search for a model system in which to study the resonating valence bond liquid and the unconventional excitations of quantum spin liquids (magnetic monopoles, spinons, etc.) boosted the experimental research in geometrically frustrated materials.[7]

Spinels of general formula A^{2+}Cr$_2^{3+}$O$_4$, Zn^{2+}, Mg^{2+}, . . . being a nonmagnetic ion, are *a priori* one of the simplest systems in which to study the low-energy magnetic excitations of a three-dimensional (3D) Heisenberg magnet in an environment of strong geometrical frustration. The flexibility of the spinel structure provides a unique way to tune the nearest neighbor exchange coupling J and the frustration parameter $f = \Theta_{CW}/T_N$ through chemical doping at the tetrahedral A^{2+} site. Moreover, the spin anisotropy and the orbital degrees of freedom that could reduce frustration are not expected to be relevant in the Cr^{3+}:t_{2g}^3 configuration. Also, charge fluctuations are not an issue; their Mott charge gap is much larger than typical frustrated organic systems. The drawback is their sensitivity to small perturbations that break

the lattice and/or magnetic symmetry, selecting one over the many possible spin configurations.[8,9] For example, ZnCr$_2$O$_4$ undergoes a Jahn-Teller structural distortion and develops a noncollinear coplanar magnetic order below $T_{N,S} = 12.5\,(5)$ K. Below $T_{N,S}$, the low-energy intensity of the spin-excitation spectrum suggests the possible existence of hexamer and heptamer bond-spin structures.[10–12] These spin-molecules play the role of the elementary excitations of the frustrated spin system.

Here, we report $k(T,H)$ for single crystalline ZnCr$_2$O$_4$, down to 50 mK and up to 14 T. In the ordered phase, the magnetic contribution is dominant even at the lowest temperature probed, showing the persistence of spin fluctuations. Above $H \approx 2.5$ T, the thermal conductivity increases sharply, in a new magnetic ground state induced by H.

II. EXPERIMENT

Single-phase, polycrystalline, and single crystals of ACr$_2$O$_4$ ($A =$ Mg and Zn) spinels were synthesized by solid-state reaction and grown by chemical transport, respectively.[13] Thermal conductivities below 1 K were measured using a one-heater, two-thermometers technique with RuO$_2$ sensors in a dilution refrigerator.[14]

III. DISCUSSION

The temperature dependence of k is shown in Fig. 1 for the whole series of samples: ACr$_2$O$_4$ ($A =$ Cd^{2+}, Zn^{2+}, Mg^{2+}) and nonmagnetic ZnAl$_2$O$_4$. The temperature dependence of k is qualitatively similar in polycrystalline and single crystals; only the absolute value of the latter is considerably larger due to the reduction in grain-boundary scattering. On the other hand $k(T)$ for CdCr$_2$O$_4$ ($f \approx 9$) and nonmagnetic ZnAl$_2$O$_4$ follows the expected trend in a dense polycrystalline material:[15] there
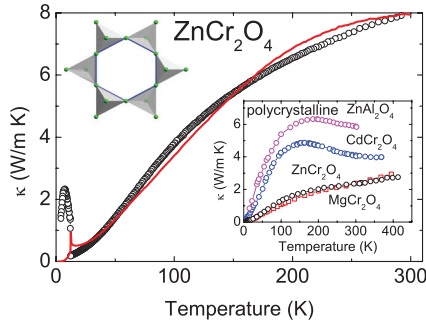
FIG. 1. (Color online) Temperature dependence of the thermal conductivity in single-crystal $ZnCr_2O_4$. The solid line in the main panel corresponds to the estimation of $k(T) = (1/3)C_v v\Lambda$. Data for polycrystalline ACr_2O_4 (A = Cd^{2+}, Zn^{2+}, Mg^{2+}) and $ZnAl_2O_4$ are shown in the lower inset. The upper inset shows one of the hexagon-loop structures formed by linked tetrahedra.

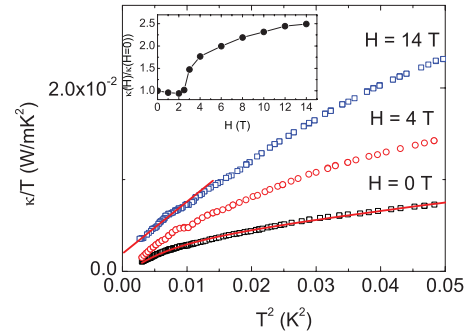FIG. 2. (Color online) Temperature dependence of the thermal conductivity for $ZnCr_2O_4$ at different magnetic fields. The solid line over $H = 0$ data is a fit to Eq. (1). The straight line over the $H = 14$ T data is a T^3 dependence, as discussed in the text. Inset: Field dependence of the thermal conductivity at 92 mK. The result is representative of the behavior at any temperature below $T_{N,S}$.

is a broad maximum followed by the characteristic reduction of $k(T)$ at $T > T_{max}$ due to Umklapp scattering.

The behavior changes drastically for Mg and Zn ($f \approx 30$): $k(T)$ increases continuously with temperature as it is commonly observed in amorphous solids.[16] This is also seen in single-crystal $ZnCr_2O_4$, so it must be an intrinsic effect not simply related to grain boundary scattering. Given the large frustration of $(Mg,Zn)Cr_2O_4$, strong spin fluctuations can be anticipated between T_N and Θ_{CW}. The increase of k below $T_{N,S}$ and the smaller value than in Cd and nonmagnetic samples, shows that the temperature dependence of $k(T > T_{N,S})$ in $(Zn,Mg)Cr_2O_4$ is due to magnetic or magnetoelastic scattering. In fact, the importance of spin-lattice interactions to understand the low-energy excitations in $ZnCr_2O_4$ has been established both experimentally and theoretically.[9] In the spin-liquid regime $T_{N,S} < T < \Theta_{CW}$, this coupling manifests for example in the deviation of the anharmonic temperature dependence of some infrared (IR) and Raman modes.[13] Correlated spin fluctuations at $T_{N,S} < T < \Theta_{CW}$, plus the coupling to the lattice degrees of freedom, may generate bond-length fluctuations that shorten the mean free path of acoustic phonons to a constant value. From an analogy with the kinetic theory of gases, the thermal conductivity of a crystalline solid can be expressed as $k(T) = (1/3)C_v v\Lambda$, where C_v is the lattice heat capacity and v and Λ are the mean acoustic phonon velocities and mean free path, respectively.[15] Using the experimental $C_v(T)$, $v = 5750$ ms^{-1} (Ref. [17]), and the theoretical density obtained from the x-ray diffraction data, this approach gives a satisfactory description of the glasslike thermal conductivity above $T_{N,S}$ using a phonon mean free path $\Lambda \approx 17 \pm 4$ Å (see Fig. 1). Consequently, in this picture spin-bond fluctuations above $T_{N,S}$ scatter the phonons effectively, reducing their effective mean free path to a few lattice parameters in the highly frustrated members of this series. The value of the mean free path is of the order of the size of the hexagonal loop structures reported by Lee *et al.*[10] (Fig. 1, inset), which could be responsible for phonon scattering above $T_{N,S}$.

A similar effect was reported in the spin-liquid phase of the frustrated ferroelectric $YMnO_3$ (Ref. [18]) and in the orbital-liquid phase of $La_4Ru_2O_{10}$.[19] However, in these

systems, bond order removes the magnetic frustration, and $k(T)$ recovers the Debye temperature dependence below T_N. In contrast, although the thermal conductivity of $ZnCr_2O_4$ also increases sharply at the first-order phase transition at $T_{N,S}$, it does not follow a phonon $k(T) \approx \beta T^3$ dependence in the symmetry broken phase. Instead, it shows a convex trend in the $k/T \approx \beta T^2$ plot, as well as a clear effect of the magnetic field (Fig. 2). This proves that magnetic excitations carry heat at low temperatures (down to 50 mK) in $ZnCr_2O_4$. In fact, the ordered magnetic moment per Cr^{3+} measured by neutron diffraction below $T_{N,S}$ is $2.03\mu_B$.[20] This is considerably smaller than the fully polarized value, suggesting that strong spin fluctuations still survive below T_N.

Therefore, to fit the $k(T, H = 0)$ curve, we used the following equation:

$$k(T) = \alpha \exp\left(\frac{\Delta E}{k_B T}\right) + \beta T^3, \qquad (1)$$

that considers the existence of a spin gap, plus a Debye term for phonons. The results are satisfactory below ≈ 0.3 K for $k(H = 0)$ (see Fig. 2), giving $\alpha = 0.0015(5)$ Wm^{-1}K^{-1}, $\Delta E = 0.20(2)$ K and $\beta = 0.10(3)$ Wm^{-1}K^{-4} (roughly 2/3 of the heat at 0.2 K is carried by phonons).

As shown in the inset of Fig. 2, the thermal conductivity does not increase monotonously with magnetic field. For small fields, k is almost independent or a slightly decreasing function of H. Then it rises suddenly above ≈ 2.5 T, approaching saturation at ≈ 14 T, at more than twice its zero field value. The existence of a critical field $H_C \approx 2.5$ T is consistent with the behavior of the magnetic susceptibility (Fig. 3), which also shows a nonlinear behavior above $H \approx 1.5$ T, reminiscent of a metamagnetic transition.

Glazkov *et al.*[21] proposed that this subtle effect corresponds to a spin reorientation along the $\langle 111\rangle$ and $\langle 110\rangle$ directions of the crystal. The coplanar AF structure of $ZnCr_2O_4$ cannot be stabilized by isotropic nearest neighbor magnetoelastic interactions alone, showing the importance of considering further nearest neighbor exchange interactions.[20] Fitting the $M/H(T)$ data to a quantum tetrahedron model proposed by Garcia-Adeva and Huber resulted in values of J_1 between 39 and 19 K and J_2 ranging from 1.7 to 4.4 K.[13,22] A critical field
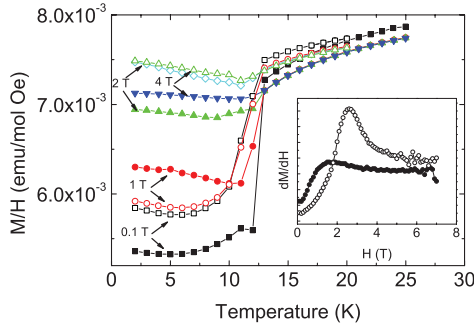
FIG. 3. (Color online) Field dependence of the magnetization in $ZnCr_2O_4$ (closed symbols) and $MgCr_2O_4$ (open symbols) below $T_{N,S}$, under zero field cooling conditions. Inset: Field derivative of M for $ZnCr_2O_4$ (closed symbols) and $MgCr_2O_4$ (open symbols) at 5 K.

FIG. 4. (Color online) Fitting of $k(H = 14\text{T})$ of $ZnCr_2O_4$ to Eq. (2).

of $H_C \approx 2.5$ T corresponds to ≈ 1.7 K, which is of the order of the energy scale of the next nearest neighbor interaction J_2.[13] The magnetoelastic coupling energy λ is also of the same order of magnitude, of about 5–7 K (Ref. [13]). As a consequence, a field of 2.5 T can easily rearrange spins and/or domains. Therefore, we suggest that the magnetic field destabilizes the zero field magnetic ground state, when $H_C \approx J_2 \approx \lambda$. This is consistent with the large effect over M/H observed below $T_{N,S}$ at $H > H_C$, as well as with the larger H_C for $MgCr_2O_4$ than for $ZnCr_2O_4$ (Fig. 3), owing to the smaller lattice parameter (larger J_2) in the Mg sample.

This behavior is very similar to a spin-liquid material, in which the thermal conductivity increases steeply above a characteristic magnetic field that closes the spin gap of fermionic-like excitations.[3]

For spin excitations to be responsible for carrying this amount of heat, there must be an acoustic magnon branch with a large velocity and a small zero field gap, of the order of ≈ 2.5 T (≈ 0.15 meV), that can be closed by the application of $H \approx H_C$.

Glazkov et $al.$[21] observed several gapped resonance modes in the antiferromagnetic resonance spectrum of $ZnCr_2O_4$. In particular, they measured a 25 GHz (≈ 0.15 meV) zero field gap at $k = 0$, that softens at $H \approx 1.5$ T along the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions. This substantial reduction of the acoustic magnon gap could increase the density of magnons that can be excited to participate in the transport of heat, producing the large change observed in $k(H = 2.5$ T). However, this should produce a peak in the thermal conductivity, and therefore the enhancement of k at high field is most probably due to the reduction of paramagnetic scattering of phonons.

We should mention also that the coexistence of a tetragonal and a orthorhombic phase was recently observed in $(\text{Zn,Mg})Cr_2O_4$ below T_N.[23] A preferential coupling of the field to one of the two phases could provide a different explanation for the sudden increase of $k(H \approx 2.5$ T), although it is not at all evident why the thermal conductivity of these two phases should be so different.

The temperature dependence of the high-field thermal conductivity is not trivial either. At very low temperature, the thermal conductivity of the high-field phase follows a T^3 behavior with a nonzero intercept (see Fig. 2). This may s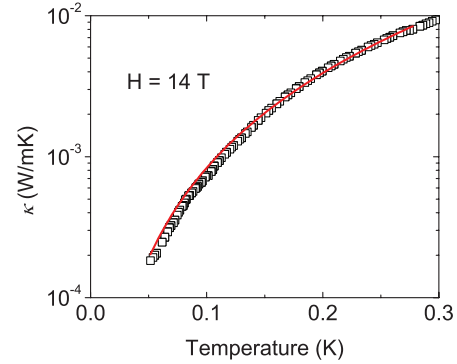uggest the magnetic field is increasing magnon thermal conductivity by closing a gap for fermionic-like excitations, similar to what happens at zero field in a quantum spin liquid, except in the symmetry broken phase. As the magnetic field destabilizes the spin-bond structure, spin frustration is partially restored so that gapped and gapless excitations may coexist in this structure. However, the T^3 law is only followed in a very restricted temperature interval, and the fitting may not be completely reliable.

Another possibility is explored in Fig. 4. The $k(H = 14$ T) curve can be fitted in a wide temperature interval using Eq. (2):

$$k(T) = \beta T^3 + \delta T^2, \tag{2}$$

the best fitting being for $\beta = 0.15$ (W/mK^4) and $\delta = 0.07$ (W/mK^3) that is, replacing the exponential term in Eq. (1) by T^2.

A T^2 dependence of $C_p(T)$ is characteristic of two dimensional antiferromagnetic correlations, and it was reported previously in the low-temperature regime of magnetic spinels and other frustrated systems[24,25] and could be pointing to the existence of AF correlations within the Cr^{3+} hexameric rings.

IV. CONCLUSIONS

The thermal conductivity in spin frustrated $ZnCr_2O_4$ is completely dominated by strongly correlated spin fluctuations in the whole temperature range. Above $T_{N,S}$, in the spin-liquid phase, coupling of magnetic fluctuations to acoustic phonons suppresses the thermal conductivity, which shows a glasslike temperature dependence. The approximately constant mean free path of $\Lambda \approx 17 \pm 4$ Å corresponds roughly with the precursors of the molecular structures formed below $T_{N,S}$.[26] In the symmetry broken phase below $T_{N,S}$, the magnetic contribution dominates $k(T)$ even at the lowest temperature probed (50 mK). This shows that the structural distortion is not able to remove the magnetic frustration completely, and strong spin fluctuations persist below $T_{N,S}$. This study shows that high-field destabilization of the ordered phase may give place to novel excitations in frustrated magnets.

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