Local spin resonance and spin-Peierls-like phase transition in a geometrically frustrated antiferromagnet

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Inelastic magnetic neutron scattering reveals a localized spin resonance at 4.5 meV in the ordered phase of the geometrically frustrated cubic antiferromagnet ZnCr2O4. The resonance develops abruptly from quantum critical fluctuations upon cooling through a first order transition to a co-planar antiferromagnet at $T_c = 12.5(5)$ K. We argue that this transition is a three dimensional analogue of the spin-Peierls transition.

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It appears that antiferromagnetically interacting Heisenberg spins on the vertices of a lattice of corner-sharing tetrahedra cannot order $\Gamma_4$. Characterized by weak connectivity and frustrated interactions $\Gamma_6$, this so-called pyrochlore antiferromagnet has no phase transition for spin $S = \infty \Gamma_8$ and forms a quantum spin liquid with low lying singlet excitations for $S = 1/2 \Gamma_9$ and $z = 6$ is the nearest neighbor coordination number. Experiments on Cr$^{3+}$ pairs in ZnGa2O4 $\Gamma_4$ give values for $J$ ranging from $-2.8$ meV to $-4.0$ meV and also provide evidence for biquadratic exchange $\mathcal{H}_2 = J(S_1 \cdot S_2)^2$ with $\mathcal{H}_2 = -0.21(4)$ meV.

A 25 g powder sample was prepared by solid state reaction between stoichiometric amounts of Cr2O3 and ZnO in air. Rietveld analysis of neutron powder diffraction data from the NIST BT1 diffractometer shows that ZnCr2O4 in the spinel structure (space-group $Fd\bar{3}m$, $a = 8.31273\text{Å}$ for $T = 15$ K) is the majority phase with a minority phase of 1% f. u. un-reacted Cr2O3. Elastic and inelastic neutron scattering measurements were performed at NIST on the cold neutron triple-axis spectrometer SPINS. A vertically focusing Pyrolytic Graphite (002) monochromator (PG(002)) extracted a monochromatic beam with energy $2.5$ meV $< E_i < 14$ meV from a $^{58}$Ni coated cold neutron guide. The detection system consisted of a 20 cm long polycrystalline BeO filter cooled to 77 K followed by a 23 cm $\times$ 15 cm flat PG(002) analyzer 92 cm from the sample, then a 80$'$ radial collimator, and an area sensitive detector. The energy range detected was $2.6$ meV $< E_f < 3.7$ meV with Full Width at Half Maximum (FWHM) energy resolution 0.1 meV $< \Delta E < 0.15$ meV and angular resolution $\Delta 2\theta \approx 50'$. The absolute efficiency of the instrument was measured using incoherent elastic scattering from vanadium and nuclear Bragg peaks from ZnCr2O4. The corresponding normalization factor was applied to background subtracted data to obtain measurements of the normalized magnetic neutron scattering intensity $\hat{I}(Q, \omega) = \int \frac{dQ}{4\pi} \frac{g}{2} F(Q)^2 \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta) S^{\alpha\beta}(Q, \omega)$.
Here $F(Q)$ is the magnetic form factor for Cr$^{3+}$ \cite{14} and $\kappa = 0.48(5) \, \text{Å}^{-1}$ = 0.64(6)$a^*$ indicating that the excited state involves AFM correlated nearest neighbor spins. For comparison the dashed line shows the powder-averaged magnetic neutron scattering intensity for an isolated spin dimer at the nearest neighbor separation $r_0 = 2.939 \, \text{Å}$ \cite{13}. The spin pair model produces a broader peak than the experiment indicating that the resonating spin cluster in ZnCr$_2$O$_4$ is more complex. Fig. 2 (b) also shows the wave vector dependence of inelastic scattering below the resonance integrated over energy from 1 meV to 3 meV (open symbols). Weak, non-resolution-limited peaks are visible and their locations coincide with AFM Bragg peaks (shaded). Excitations below the resonance are also apparent in the wave vector integrated data of Fig. 2 (a) where the intensity increases in proportion to energy for $h\omega < 3.5$ meV (the low energy upturn is incompletely resolved elastic scattering).

Both features are consistent with neutron scattering from spin waves in a three dimensional AFM powder with a spin gap $\Delta < 1.5$ meV. In particular the ratio of elastic to inelastic scattering is consistent with estimates based on spin wave theory in the long wavelength limit. From the width of the peaks we estimate a spin wave velocity $v = 18(2)$ meVÅ. This number is much less than the spin wave velocity for a bi-partite simple cubic AFM with $J = -2.8$ meV, $v = (2/\sqrt{3})z|J|S\alpha = 239$ meVÅ but only slightly larger than the spin wave velocity for a cubic AFM with the critical temperature of ZnCr$_2$O$_4$: $v = 2\sqrt{3}k_B T_c a/(S + 1) = 12.4$ meVÅ.

Spin wave theory provides a useful starting point for

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure2.png}
\caption{Integrated magnetic scattering intensities at $T = 1.5$ K derived from Fig. 1 (c). (a) $\omega$-dependence of the $Q$-integrated intensity: $I(\omega) = \int Q^2dQI(Q, \omega)/\int Q^2dQ$. The horizontal bar shows the instrumental energy resolution. (b) Closed symbols show the $Q$-dependence of the $\omega$-integrated resonance intensity: $I(Q) = h \int_{0.5 \, \text{meV}}^{5 \, \text{meV}} I(Q, \omega)d\omega$. Open circles show data integrated from 1 meV to 3 meV. The solid line shows the elastic scattering cross section scaled by a factor 10. Shaded peaks are magnetic Bragg peaks.}
\end{figure}
understanding the resonance. Geometrical

Fig. 3. (a)-(c) $\chi(Q_0, \omega)$ at $Q_0 = 1.5\,\text{Å}^{-1}$ derived from magnetic neutron scattering data via the fluctuation dissipation theorem. The solid lines are fits as described in the text. (d)-(e) Temperature dependence of the relaxation rate, $\Gamma_{Q_0}(T)$, and the inverse susceptibility, $\chi_{Q_0}^{-1}(T)$ derived from the fits.

frustration leads to constant energy surfaces or volumes for spin wave dispersion relations in reciprocal space. Such $Q$-space “degeneracy” in turn yields pronounced van-Hove singularities in wave vector averaged spectra. Reimers et al. [16] showed that the pyrochlore AFM has two degenerate modes for any $Q$ in the Brillouin zone. Wave vector independent excitations also exist for the kagomé AFM [17] and these have a real space interpretation in terms of the so-called weather-vane modes [18]. A real-space interpretation has yet to be found for dispersionless excitations in the pyrochlore lattice. The broad peak in Fig. 2(b) indicates that they are highly localized in the ordered phase of ZnCr$_2$O$_4$.

Turning now to excitations in the paramagnetic phase, Fig. 3 (a)-(c) show the imaginary part of the spin susceptibility, $\chi''(Q, \omega)$ for several temperatures larger than $T_c$. $\chi''(Q, \omega)$ was derived from inelastic neutron scattering data at $Q_0 = 1.5\,\text{Å}^{-1}$ via the fluctuation dissipation theorem: $\chi''(Q, \omega) = (g\mu_B)^2\pi(1 - \exp(-\beta\omega))S(Q, \omega)$.

From the spectra we derived a temperature dependent spin relaxation rate, $\Gamma_Q$, and a static staggered susceptibility, $\chi_Q$, by fitting to the following phenomenological response function: $\chi''(Q, \omega) = \chi_Q\Gamma_Q\omega^2/(\omega^2 + \Gamma_Q^2)$.

Figs. 3 (d) and (e) show the corresponding temperature dependent parameters. A power-law in $T$ describes the temperature dependence of $\Gamma_{Q_0}(T) = C \cdot k_B T(T/\theta)^{\alpha-1}$ for $T < 150\,\text{K}$ while $\chi_{Q_0}(T)$ can be described by a Curie-Weiss law: $\chi_{Q_0}(T) = (\mu_{Q_0}^2/3k_B\theta)(1 + T/\theta)$ in the entire temperature range. The best fit solid lines correspond to $\alpha = 0.81(4)$, $C = 0.6(1)$, $\mu_{Q_0} = 4.0(1)\mu_B$, and $\theta = 8.8(4)\,\text{K}$. Though we have plotted and analyzed data for $Q_0 = 1.5\,\text{Å}^{-1}$ we found similar results for $Q_0 = 2.1\,\text{Å}^{-1}$ which probe the local spin susceptibility.

At a quantum critical point, $k_B T$ is the only low energy scale for local response functions. If the lorentzian form for $\chi''(Q, \omega)$ describes the spectrum, then $\alpha$ must equal one at the critical point. This was the exponent found in Monte Carlo simulations of classical spins on a pyrochlore lattice [19]. The deviation of $\alpha$ from unity in ZnCr$_2$O$_4$ is perhaps not surprising given that the material does exhibit a magnetic phase transition. However, the fact that $\Gamma_Q$ tends to zero as $T \to 0$ rather than at $T_c$ indicates that the system may actually be approaching a quantum disordered phase with a gap $k_B T = 0.75\,\text{meV}$ before being interrupted by a first order transition to an unrelated competing phase. This idea is consistent with Fig. 4 which compares the temperature dependent lattice strain and magnetic Bragg peak intensity (frame (b)) to the inelastic neutron scattering spectrum at $Q_0 = 1.5\,\text{Å}^{-1}$ (frame (a)). Magnetic Bragg peaks, a tetragonal lattice distortion, and the spin resonance all appear abruptly, and without conventional critical fluctuations at $T_c$.

Theoretical work has shown that magnetic order can not develop in an isotropic spin pyrochlore AFM [20]. There are many possible deviations from the perfect model that could cause ZnCr$_2$O$_4$ to order nonetheless. These include further neighbor interactions and spin space anisotropy [21,22]. Because the transition in ZnCr$_2$O$_4$ is of the first order and involves a lattice distortion, we suggest that finite lattice rigidity is an important factor at the phase transition in this material. Consider the effect of tetragonal strain on magnetism in ZnCr$_2$O$_4$. It is well known that the exchange interaction between Cr$^{3+}$ ions whose oxygen coordination octahe-
dras share an edge is strongly dependent on the Cr-Cr spacing, \( r \) \(^{-1} \). Analysis of a series of chromium oxides indicates that \( dJ/dr \approx 40 \text{ meV}/A \) \(^{-1} \). This implies that tetragonal strain \( \epsilon_t > 0 \) and \( \epsilon_c < 0 \) yields weaker AFM interactions in the basal plane, \( \Delta J_\perp = \epsilon_\perp \epsilon_t dJ/dr = 0.06 \text{ meV} \), and stronger AFM interactions between all other spin pairs \( \Delta J_\parallel = r_0 (\epsilon_\parallel + \epsilon_\perp)/2dJ/dr \approx -0.04 \text{ meV} \). This asymmetry reduces the mean field energy of the ordered phase in ZnCr\(_2\)O\(_4\) by \( \Delta \langle H_s \rangle = (5\Delta J_\parallel - \Delta J_\perp)/2 \approx -0.07 \text{ meV}/\text{Cr} \) relative to the mean field ground state energy in the cubic phase \( [2] \). The result should be Néel order in tetragonal ZnCr\(_2\)O\(_4\) below an ordering temperature that we denote \( T_{N\parallel} \). Because order appears abruptly and simultaneously with the tetragonal strain we infer that \( T_{N\parallel} > T_c \). This may be possible despite the modest value of \( \Delta \langle H_s \rangle \) because of the strong local constraints present when \( T/\Theta_{CW} \ll 1 \). In addition there could be other hitherto undetected lattice modifications at \( T_c \) that also favor Néel order (see below).

The magnitude of the lattice distortion is controlled by the need to balance the increase in lattice energy and the decrease in entropy against the decrease in the energy of the spin system. Equating the free energy \( F = \langle H_t + H_s \rangle - TS \) of the competing phases at \( T_c \) implies that

\[
\Delta \langle H_s \rangle + \Delta \langle H_t \rangle - T_c \Delta S = 0
\]

(1)

when cooling through \( T_c \). We can derive \( \Delta \langle H_s \rangle \) from Fig. 1(b) and (c) using the first moment sum rule:

\[
\Delta \langle H_s \rangle = \frac{3\hbar^2}{2} \int_0^{\infty} \omega (1 - e^{-\beta\omega}) \Delta S(Q,\omega) d\omega
\]

(2)

Limiting the integral to 0.2 meV to 12 meV and averaging data for 1.3 Å\(^{-1} \) < \( Q < 2 \) Å\(^{-1} \) yields a value of \( \Delta \langle H_s \rangle = -0.40(7) \text{ meV/Cr} \). From specific heat measurements \(^{[3]} \) we find that \( \Delta S = -0.107 R \ln 4/\text{Cr} \) corresponding to \( -T_c \Delta S = 0.16 \text{ meV/Cr} \). The difference between these numbers yields an estimate for the increase in lattice energy \( \Delta \langle H_t \rangle = 0.24(7) \text{ meV/Cr} \). The energy associated with single tetragonal strain \( [23] \) only accounts for \( v_0 (c_1(c_2^2 + 2c_2^2)/2 + c_1(c_2^2 + 2c_2\epsilon_\parallel)) = 0.026 \text{ meV/Cr} \) so there are likely additional modifications to the structure of ZnCr\(_2\)O\(_4\) below \( T_c \) that help to stabilize Néel order.

There are interesting analogies between the phase transition in ZnCr\(_2\)O\(_4\) and the spin-Peierls transition. In both cases the high \( T \) phase is near quantum critical and can lower its energy through a lattice distortion. In both cases the transition occurs from a strongly correlated paramagnet: \( T_c \ll \Theta_{CW} \). And in both cases low energy spectral weight is moved into a finite energy peak. There are also important differences that render the transition in ZnCr\(_2\)O\(_4\) a distinct new phenomenon in magnetism. The lattice distortion in ZnCr\(_2\)O\(_4\) drives the spin system into an ordered phase not a quantum disordered phase. The transition in ZnCr\(_2\)O\(_4\) is of the first order while the SP transition is of the second order. And the change in entropy at \( T_c \) plays an important role in ZnCr\(_2\)O\(_4\), not in a SP transition. The central idea that finite lattice rigidity can drive a spin system away from quantum criticality however does carry over, and might be relevant for other frustrated magnets when symmetry breaking terms in the spin Hamiltonian fail to induce magnetic order.

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