Probing spin correlations with phonons in the strongly frustrated magnet ZnCr$_2$O$_4$

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The spin-lattice coupling plays an important role in strongly frustrated magnets. In ZnCr$_2$O$_4$, an excellent realization of the Heisenberg antiferromagnet on the “pyrochlore” network, a lattice distortion relieves the geometrical frustration through a spin-Peierls-like phase transition at $T_c = 12.5$ K. Conversely, spin correlations strongly influence the elastic properties of a frustrated magnet. By using infrared spectroscopy and published data on magnetic specific heat, we demonstrate that the frequency of an optical phonon triplet in ZnCr$_2$O$_4$ tracks the nearest-neighbor spin correlations above $T_c$. The splitting of the phonon triplet below $T_c$ provides a way to measure of the spin-Peierls order parameter.

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Geometrically frustrated magnets can resist magnetic ordering and remain in a strongly correlated paramagnetic state well below the Curie-Weiss temperature $\Theta_{CW}$. Particularly strong frustration is found in the Heisenberg antiferromagnet on the “pyrochlore lattice”, wherein magnetic sites form a lattice of corner-sharing tetrahedra. The dynamics of the magnet is determined by the spin Hamiltonian

$$H = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j,$$

with the interaction restricted to nearest-neighbor bonds $\langle ij \rangle$. Theoretical investigations indicate that classical spins on this lattice may not order down to zero temperature. Cubic spinel ZnCr$_2$O$_4$ offers a good realization of this model. Observation of magnetic order at low temperatures has been explained in terms of a spin-driven Jahn-Teller effect that is reminiscent of the spin-Peierls instability in spin chains. The coupling between spin and lattice degrees of freedom thus plays a major role in relieving the geometrical frustration.

The B sites of ZnCr$_2$O$_4$ are occupied by magnetic ions Cr$^{3+}$ with spin $S = 3/2$ [Fig. 1(a)]. A crystal field of a nearly cubic symmetry splits the five $3d$ orbitals of Cr$^{3+}$ into a $t_{2g}$ triplet and an $e_g$ doublet. By Hund’s rules, the three electrons of Cr$^{3+}$ have aligned spins ($S = 3/2$) and occupy all of the three $t_{2g}$ states. The lack of orbital degeneracy precludes the ordinary Jahn-Teller effect common to spinels and ensures a very small spin anisotropy. The shape of the $t_{2g}$ orbitals, pointing towards the neighboring Cr$^{3+}$ ions, makes direct exchange the primary mechanism for magnetic interactions. As a result, interactions beyond nearest neighbors are negligibly small, while the nearest-neighbor interactions are highly sensitive to the motion of Cr$^{3+}$ ions creating a strong spin-phonon coupling.

The magnetic susceptibility of ZnCr$_2$O$_4$ follows the Curie-Weiss law at high temperatures with $\Theta_{CW} = 390$ K, which gives the nearest-neighbor exchange coupling $J = 4.5$ meV. As the temperature is lowered below $\Theta_{CW}$, the magnet gradually enters a paramagnetic state with strong correlations between spins but no magnetic order: the spins remain liquid but their motions are highly coordinated. At $T_c = 12.5$ K the magnet undergoes a first-order transition into a phase with antiferromagnetic order and a structural distortion. According to the theory, the phase transition is driven by local distortions of the tetrahedra that have the $E$ symmetry in the language of the tetrahedral point group $T_d$. This is consistent with the observation of a tetragonal distortion below $T_c$.

In this work we demonstrate that lattice vibrations can provide quantitative information about spin correlations. We have measured the frequencies of IR-active phonons and found, below the magnetoelastic phase transition, a large splitting of a phonon mode involving magnetic ions.
From the magnitude of the splitting we have inferred the absolute value of the spin-Peierls order parameter $|S_i \cdot S_j - S_{i\perp} \cdot S_{j\perp}|$, where $\langle ij \rangle$ and $\langle kl \rangle$ are nearest-neighbor bonds.

**Experimental details.** Powders of ZnCr$_2$O$_4$ were prepared in air using the standard solid state reaction method. Small single crystals of ZnCr$_2$O$_4$ were grown using these powders using chemical transport method in quartz tubes sealed with Cl$_2$ gas as a transport agent. The crystals were of regular habit with the ⟨111⟩ face clearly visible. The working surface of our sample is tilted slightly (∼3.5°) from the ⟨111⟩ plane as determined by X-rays. Reflectivity measurements were performed using a Fourier-transform spectrometer in the frequency range from 100 to 5000 cm$^{-1}$. The temperature dependence from 6 to 300 K was measured using liquid helium in a continuous flow cryostat (sample in vacuum) with optical access windows.

The room temperature phonon spectrum of cubic spinels is well studied. Our measurements at room temperature agree with previously published data for single crystals of ZnCr$_2$O$_4$ [24]. As expected on symmetry grounds, the spectrum consists of four phonon triplets of the $F_{1u}$ symmetry (point group $O_h$, space group $Fd\bar{3}m$). Figure 2 shows the reflectivity spectrum $R_{LT}$ for the low-temperature (LT) phase averaged over the temperature range from 9 to 11 K. It shows a magnified difference of the spectra $2(R_{LT} - R_{HT})$, where $R_{HT}$ is the reflectivity spectrum averaged between 13 and 14 K. The most prominent difference is observed at 370 cm$^{-1}$ below $T_c$ this phonon splits into two components. In addition, there is a slight modification of the vibrational mode at 186 cm$^{-1}$, which cannot be fit with two slightly split oscillators. Several new modes with small oscillator strengths are seen above 300 cm$^{-1}$ in the low-temperature IR spectra. Most likely, these are phonons with nonzero wave vectors in the cubic phase that become visible in the LT phase due to Brillouin zone folding [15, 16]. This is consistent with a recent observation of an enlarged structural unit cell below $T_c$ [17]. Raman spectra also contain a set of new phonons in the LT phase [18].

To extract the temperature dependencies of all phonon parameters, we fit the reflectivity $R = |1 + \epsilon(T)|^2$ using a model dielectric function

$$\epsilon(\omega, T) = \epsilon_\infty + \sum_j S_j \omega_j^2 \left( \frac{\omega_j^2}{\omega^2 - \omega_j^2 - i \omega \gamma_j} \right)$$

where $\epsilon_\infty(T) \equiv \epsilon(\infty, T)$ is the dielectric constant well above all phonons, $j$ enumerates the phonons, $S_j(T)$ is an oscillator strength, $\omega_j(T)$ is a phonon frequency, and $\gamma_j(T)$ is a damping rate.

Figure 3 presents temperature dependences of the phonon frequency, oscillator strength, and damping rate for the 370 cm$^{-1}$ phonon. The symbols show the best-fit parameters for the model dielectric function (2) with four phonon modes above $T_c$ and five phonons below. Upon cooling from room temperature, the resonance frequency of the 370 cm$^{-1}$ phonon hardens first, as do the other three IR-active modes. In contrast, it softens significantly below 100 K [Fig. 3(a)]. Just below $T_c = 12.5$ K, this phonon splits into two modes with a frequency difference of 11 cm$^{-1}$. The total oscillator strength is approximately conserved. There is no polarization dependence of the reflectivity spectrum at 14 K. Some polarization dependence appears on the split phonon below $T_c$ as can be seen from data points in Fig. 3 at 7 K. A clear observation of the expected polarization effects in the tetragonal phase was not found most likely because of multiple domains in the sample. No hysteresis effect is observed.

**Theoretical model.** The splitting of the 370 cm$^{-1}$ phonon is consistent with the lowering of the crystalline symmetry from cubic to tetragonal. What physical mechanism is responsible for the magnitude of splitting? Anharmonic effects unrelated to magnetism could cause the splitting; however, there are two arguments against this interpretation. First, the magnitude of the anharmonic effect can be estimated as $\Delta \omega/\omega = \gamma \Delta a/a$, where $\gamma$ is an appropriate Gr"uneisen parameter. To reconcile the observed splitting $\Delta \omega/\omega = 0.030$ with the magnitude of the tetragonal distortion $\Delta a/a \approx 10^{-3}$ [7], we must assume a rather large Gr"uneisen constant $\gamma \approx 30$, which must be explained. Second, the three other IR-active $F_{1u}$ modes observed in the experiment exhibit much smaller ($\Delta \omega \leq 0.2$ cm$^{-1}$) frequency related changes in the tetragonal phase. These objections cast doubts on anharmonic (and nonmagnetic) origins of the splitting.

Most likely, the splitting of the triplet is caused by the same effect that triggers the spin-Peierls instability.
— the spin-phonon coupling. It is well known that the elastic constants in magnetic materials are affected by the spins \[^{11,20}\]. As a consequence, the phonon frequency is sensitive to correlations of spins of nearest-neighbor pairs \((ij)\):

\[
\omega = \omega_0 + \lambda(S_i \cdot S_j),
\]

where the constant \(\lambda\) has a typical value of a few cm\(^{-1}\) when optical phonon frequency is well above all magnons and phonon is not a zone folding mode; in addition to taking a thermal average, the spin correlations must also be averaged over the crystal with the weights appropriate for a given phonon.

A strong argument in favor of the magnetoelastic mechanism is the nature of the 370 cm\(^{-1}\) phonon: it features by far the largest contribution of the symmetry coordinate modulating Cr–Cr bonds (Fig. 1A) among the four IR-active modes \[^{21}\]. The particular geometry of the occupied 3\(d\) orbitals in chromium makes the direct Cr–Cr exchange the primary source of magnetic interactions \[^{10,11}\]. In the case of direct exchange, the strength of magnetic interactions is particularly sensitive to the distances between the magnetic ions (rather than the bond angles in the case of superexchange). Therefore we expect to find the largest splitting in those modes which produce the largest modulations of Cr–Cr distances, as indeed observed.

To verify the linear relation \(^{4}\) and to determine the proportionality constant \(\lambda\), we have compared the temperature dependences of the spin correlations and phonon frequency in the high-temperature phase (Fig. 4). The nearest-neighbor spin correlations \((S_i \cdot S_j)\) were determined from published data of specific heat \[^{22}\]. Neglecting the magnetoelastic effects in the undistorted phase \[^{23}\] we relate the spin correlations to the magnetic part of the specific heat per mole \(C_m\):

\[
(S_i \cdot S_j) = \text{const} + \frac{1}{6N_A J} \int_{T_c}^T C_m(T) \, dT,
\]

where \(6N_A\) is the number of Cr–Cr bonds per mole. The scaling relation \(^{4}\) works fairly well in the temperature range between 18 and 150 K. (The phonon softening above 100 K is likely due to thermal expansion.) This procedure yields the scaling constant \(\lambda = 6.2\) cm\(^{-1}\).

The relatively large value of \(\lambda\) can be ascribed to the strong sensitivity of direct exchange to atomic displacements: the exchange constant \(J\) varies with the Cr-Cr distance approximately exponentially,

\[
J(r + \Delta r) \approx J(r)e^{-\alpha \Delta r},
\]

on the scale of the Bohr radius \(a_B\). In contrast, the spin-phonon coupling in the case of superexchange comes from variations of bond angles, which have a less dramatic effect on magnetic energy.

![FIG. 3: (Color online) Temperature dependence of the fit parameters for the split phonon in ZnCr\(_2\)O\(_4\); symbols — fit; squares, circles, and triangles at 7 K — fits of polarized spectra with \(P = 0^\circ, 45^\circ, 90^\circ\), respectively.](image)

![FIG. 4: Crosses: nearest-neighbor correlations \((S_i \cdot S_j)\), up to an arbitrary additive constant, derived from the specific-heat data of Martinho et al. \[^{22}\]; straight line fits crosses below 50 K. Squares: the phonon frequency.](image)

To obtain a quantitative estimate of \(\lambda\), consider a simplified lattice model in which magnetic ions of mass \(m\) are connected by springs of stiffness \(k\) (the rest of the atoms are discarded). The resulting “pyrochlore” lattice has only one optical mode that transforms as the irreducible triplet \(\Gamma_1\) under the operations of the point group \(O_h\). The spins move along a \(\langle 110 \rangle\) direction [Fig. 1(a)] with the frequency \(\omega_0 = 2\sqrt{k_0/m}\). The dependence of the
magnetic energy $J(r)(\mathbf{S}_i \cdot \mathbf{S}_j)$ on the ion separation $r$ provides a magnetic contribution to the spring constants $k = k_0 + \delta k_x = k_0 + J''(\mathbf{S}_i \cdot \mathbf{S}_j)$, where $J'' = d^2J(r)/dr^2$. Hence $\lambda = 2J''/(m\omega_0) \approx 2\alpha^2J/(m\omega_0)$.

The value of $\alpha$ can be estimated theoretically from the exchange integral for 3d orbitals of hydrogenlike ions, which yields $\alpha = 2Z/3a_B = 5.0 \text{ Å}^{-1}$ for Cr$^{3+}$ ions ($Z = 4$) and $\lambda = 3.2 \text{ cm}^{-1}$. An alternative estimate comes from the experimentally measured value of the exchange constant with the distance giving $\alpha = -J'/J = 8.9 \text{ Å}^{-1}$ and $\lambda = 10.0 \text{ cm}^{-1}$. Our value $\lambda = 6.2 \text{ cm}^{-1}$ is midway between these estimates.

The observed splitting of the triplet phonon can now be translated directly into the spin-Peierls order parameter $\alpha$ only a fraction of what could be attained in a state with a uniform tetragonal distortion and collinear spins described in Ref. [13]. It is therefore likely that the lattice distortion and the spin-Peierls order parameter are nonuniform. The nonuniform component of the distortion may produce an even larger splitting of a phonon doublet with a wave vector $\frac{\pi}{a}$. We thank G. Blumberg and C. L. Broholm for useful discussions. This work was supported in part by the National Science Foundation under Grants No. DMR-0080008 and DMR-0348679.

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