Probing Spin Correlations with Phonons in the Strongly Frustrated Magnet $ZnCr_2O_4$

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The spin-lattice coupling plays an important role in strongly frustrated magnets. In $ZnCr_2O_4$, 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 $ZnCr_2O_4$ tracks the nearest-neighbor spin correlations above T_c. The splitting of the phonon triplet below T_c provides a way to measure 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 Θ_{CW} [1–3]. 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

$$H = J\sum_{\langle ij\rangle} \mathbf{S}_i \cdot \mathbf{S}_j, \qquad (1)$$

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 [4,5]. Cubic spinel $ZnCr_2O_4$ offers a good realization of this model. Observation of magnetic order at low temperatures [6,7] has been explained in terms of a spin-driven Jahn-Teller effect [8,9] 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 $ZnCr_2O_4$ 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 [7]. The shape of the t_{2g} orbitals, pointing towards the neighboring Cr^{3+} ions, makes direct exchange the primary mechanism for magnetic interactions [10,11]. 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 $ZnCr_2O_4$ follows the Curie-Weiss law at high temperatures with $\Theta_{CW} = 390$ K, which gives the nearest-neighbor exchange coupling $J = 4.5$ meV [7]. As the temperature is lowered below Θ_{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 [12]. At $T_c = 12.5$ K the magnet undergoes a first-order transition into a phase with antiferromagnetic order and a structural distortion [7]. According to the theory [8,9,13], the phase transition is driven by local distortions of the tetrahedra that have the E symmetry in the point group T_d consistent with the observation of a tetragonal distortion below T_c [7].

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 $\langle \mathbf{S}_i \cdot \mathbf{S}_j - \mathbf{S}_k \cdot \mathbf{S}_l \rangle$, where $\langle ij\rangle$ and $\langle kl\rangle$ are nearest-neighbor bonds [13].

Experimental details.—Powders of $ZnCr_2O_4$ were prepared in air using the standard solid state reaction method.

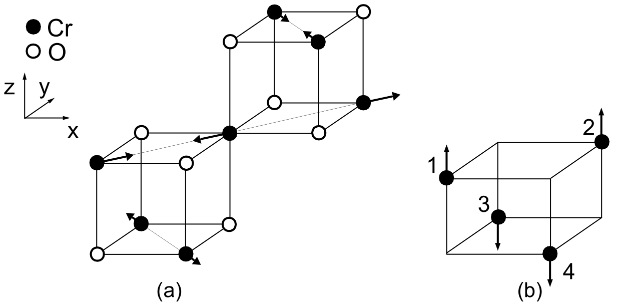

FIG. 1. (a) One (out of five) of the symmetry coordinates of the F_{1u} mode which modulates Cr-Cr exchange; arrows show displacements. (b) Spin ordering expected for a tetragonally distorted tetrahedron in $ZnCr_2O_4$; arrows indicate spins.

Small single crystals of $ZnCr_2O_4$ were grown using these powders using chemical transport method in quartz tubes sealed with Cl_2 gas as a transport agent. The working surface of our sample is tilted slightly (~3.5°) from the $\langle 111 \rangle$ plane as determined by x rays. Reflectivity measurements were performed using a Fourier-transform spectrometer and a continuous flow cryostat.

Our measurements at room temperature agree with previously published data for single crystals of $ZnCr_2O_4$ [14]. 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 also shows a magnified difference of the spectra $2(R_{\mathrm{LT}} - R_{\mathrm{HT}})$, 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 the phonon triplet splits into a doublet and a singlet (tetragonal distortion). 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].

To extract the temperature dependencies of all phonon parameters, we fit the reflectivity $R = |\frac{1-\sqrt{\epsilon}}{1+\sqrt{\epsilon}}|^2$ using a model dielectric function

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

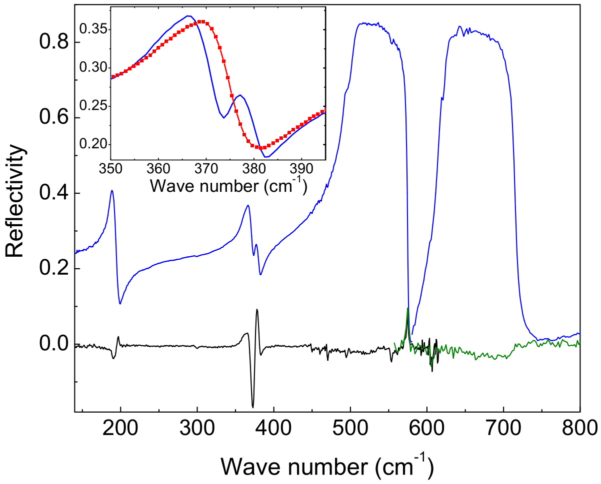

FIG. 2 (color online). Top curve: R_{LT} reflectivity spectrum of $ZnCr_2O_4$ single crystal in the low-temperature phase; bottom curve: $2(R_{\mathrm{LT}} - R_{\mathrm{HT}})$; inset: R_{LT} and R_{HT} (line + symbols) in a narrow range.

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} phonons. 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 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 only for the singlet (high frequency mode) below T_c, as can be seen from data points in the inset to Fig. 3. This mode is expected to be IR active in the $E \| z$ polarization for either tetragonal or orthorhombic distortions. The non-Malusian polarization dependence indicates that the z axis of the

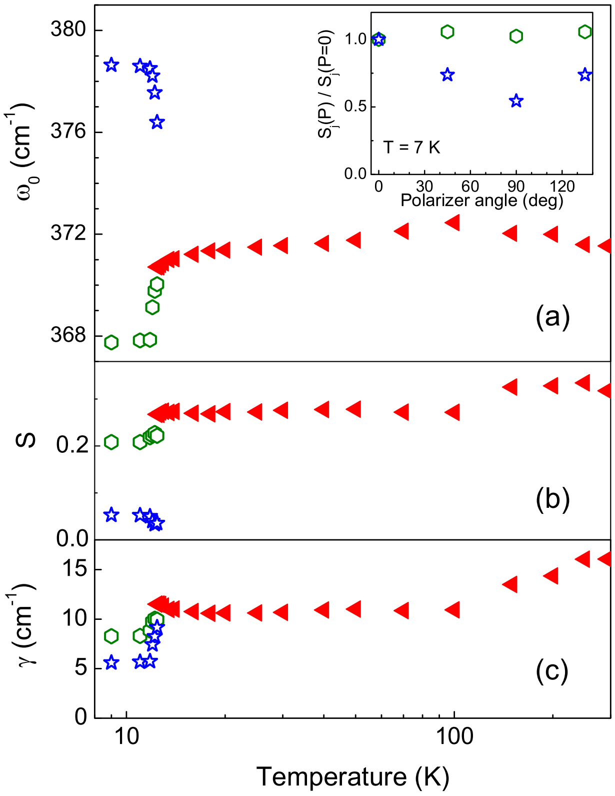

FIG. 3 (color online). Temperature dependence of the fit parameters for the split phonon in $ZnCr_2O_4$ (unpolarized spectra): solid triangles, a triplet in the 4 phonon model; hexagons and stars, a doublet and a singlet in the 5 phonon model, respectively. Inset: polarization dependence of relative intensities of a doublet and a singlet at 7 K.

distortion varies through the crystal. This variation may correspond to a nonuniform spin-Peierls order parameter or, alternatively, 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 γ is an appropriate Grüneisen 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 Grüneisen constant $\gamma \approx 30$, which must be explained. Second, the three other IR-active F_{1u} modes observed in the experiment exhibit much smaller ($\Delta\omega \leq 0.2\ \mathrm{cm}^{-1}$) frequency related changes in the tetragonal phase.

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 [18,19] and the phonon frequency is sensitive to correlations of spins of nearest-neighbor pairs:

$$\omega = \omega_0 + \lambda\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle, \tag{3}$$

where the constant λ has a typical value of a few cm^{-1} for optical phonons in oxides; 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 direct exchange [Fig. 1(a)] among the four IR-active modes [20]. 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 that produce the largest modulations of Cr-Cr distances, as observed.

To verify the linear relation (3) and to determine the proportionality constant λ, 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 $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ were determined from published data of specific heat [21]. Neglecting the magnetoelastic effects in the undistorted phase [22] we relate the spin correlations to the magnetic part of the specific heat per mole C_m:

$$\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle = \mathrm{const} + \frac{1}{6N_A J}\int_{T_c}^{T} C_m(T)\mathrm{d}T, \tag{4}$$

where $6N_A$ is the number of Cr-Cr bonds per mole. The scaling relation (3) 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 $\lambda = 6.2\ \mathrm{cm}^{-1}$. The relatively large value of λ 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.

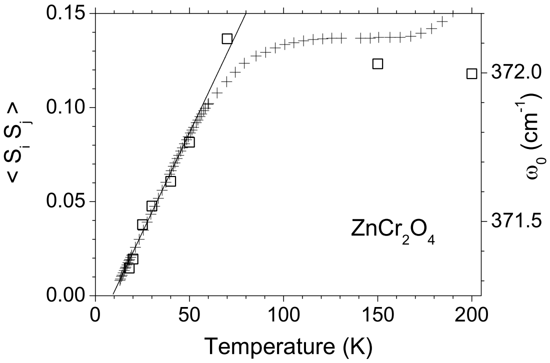

FIG. 4. Crosses: nearest-neighbor correlations $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$, up to an arbitrary additive constant, derived from the specific-heat data of Martinho *et al.* [21]; straight line fits crosses below 50 K. Squares: the phonon frequency.

To obtain a quantitative estimate of λ, 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 F_{1u} 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 $J(r)\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ on the ion separation r provides a magnetic contribution to the spring constants $k = k_0 + \delta k_{\mathrm{ex}} = k_0 + J''\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$, where $J'' = \mathrm{d}^2J(r)/\mathrm{d}r^2$. Hence $\lambda = 2J''/(m\omega_0) \approx 2\alpha^2 J/(m\omega_0)$.

The value of α can be estimated theoretically from the exchange integral for $3d$ orbitals of hydrogenlike ions, which yields $\alpha = 2Z/3a_B = 5.0$ Å^{-1} for Cr^{3+} ions ($Z = 4$) and $\lambda = 3.2\ \mathrm{cm}^{-1}$. An alternative estimate comes from the experimentally measured variation of the exchange constant with the distance giving $\alpha = -J'/J = 8.9$ Å^{-1} [7,11,23] and $\lambda = 10.0\ \mathrm{cm}^{-1}$. Our value $\lambda = 6.2\ \mathrm{cm}^{-1}$ is midway between these estimates.

The observed splitting of the triplet phonon can now be translated directly into the spin-Peierls order parameter of the distorted phase. For a tetragonal distortion with lattice constants $a = b \neq c$ [Fig. 1(b)],

$$\langle \mathbf{S}_1 \cdot \mathbf{S}_2 - \mathbf{S}_2 \cdot \mathbf{S}_3 \rangle = (\omega_z - \omega_x)/\lambda = 1.8, \tag{5}$$

where bonds 12 are along the direction (110) and bonds 23 are along (011). The bond variables $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ are averaged both over the thermal ensemble and over the location in the crystal.

Discussion.—The inferred value of the spin-Peierls order parameter (5) is only a fraction of what can be attained in a state with a uniform tetragonal distortion and collinear spins (Fig. 5 of Ref. [13]), in which bonds along the directions (110) and $(1\bar{1}0)$ are maximally frustrated: $\langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle = +S^2$, while the rest of the bonds are fully satisfied $\langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle = -S^2$. In such a state, the z component of the phonon triplet [Fig. 1(a)] would probe the frustrated bonds with spring constants $k_0 + J''S^2$, while the remaining two modes would involve bonds with $k = k_0 - J''S^2$. This significant reduction of the observed order parameter is consistent with the presence of a substantial nonuniform (nonzero wave vector) distortion in the crystal. Because the spin-Peierls order parameter is linearly coupled to the crystal distortion [13], bond averages $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ will be nonuniform as well. Even though the *local* value of the order parameter (5) may be large, averaging over the enlarged unit cell may reduce it substantially.

Indirect evidence for a nonuniform distortion has been presented by Lee *et al.* [7]. They point out that the observed uniform tetragonal distortion is too small to account for the magnetic and elastic energy released in the form of latent heat at the phase transition. Direct evidence comes from x-ray measurements of Ueda *et al.* [17]. If indeed the lion's share of the elastic and magnetic energy is hidden in the nonuniform component of the lattice distortion, even larger splittings may be found in phonons with nonzero wave vectors. For a distortion with half-integer indices, such as $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ [17], the likely candidates are phonon doublets at the wave vectors $\langle \frac{1}{4} \frac{1}{4} \frac{1}{4} \rangle$.

In conclusion, we have studied the temperature evolution of optical phonons of symmetry F_{1u} in a strongly frustrated antiferromagnet $ZnCr_2O_4$. The changes were most dramatic for the phonon with the largest amplitudes of Cr-Cr vibrations. Its frequency showed a marked softening in the strongly correlated paramagnetic regime below 100 K. It essentially tracked the temperature evolution of spin correlations inferred from magnetic specific heat allowing us to calibrate the frequency for the purposes of measuring spin correlations. Below T_c the triply degenerate phonon splits into a singlet and a doublet providing direct information about the uniform part of the spin-Peierls order parameter (5). Its magnitude is 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.

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