Spin-phonon coupling in frustrated magnet $CdCr_2O_4$

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The infrared phonon spectrum of the spinel $CdCr_2O_4$ is measured as a function of temperature from 6 to 300 K. The triply degenerate Cr phonons soften in the paramagnetic phase as temperature is lowered below 100 K and then split into a singlet and doublet in the low temperature antiferromagnetic phase, which is tetragonally distorted to relieve the geometric frustration in the pyrochlore lattice of ions. The phonon splitting is inconsistent with the simple increase (decrease) in the force constants due to decreasing (increasing) bond lengths in the tetragonal phase. Rather they correspond to changes in the force constants due to the magnetic order in the antiferromagnetic state. The phonon splitting in this system is opposite of that observed earlier in $ZnCr_2O_4$ as predicted by theory. The magnitude of the splitting gives a measure of the spin-phonon coupling strength, which is smaller than in the case of $ZnCr_2O_4$.

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I. INTRODUCTION

Due to geometric frustration antiferromagnetically coupled Heisenberg spins in the pyrochlore lattice do not order at any finite temperature.[1] Geometric frustration also has the consequence of creating very large degeneracy in the ground state giving a finite entropy at zero temperature. This degeneracy makes them susceptible to ordering due to perturbations such as magnetoelastic[2,3] or further neighbor exchange coupling, and the possibility of exotic ground states. These features have led to great interest in this class of materials.[4] Their properties are being extensively studied theoretically and experiments are dedicated to looking for materials that do not order, the so-called spin-ice materials.[5]

The family of spinel compounds ACr_2O_4 (A=Zn, Cd, or Hg) is a good example of the Heiseinberg antiferromagnet in the pyrochlore lattice, where the only magnetic ion is the non-Jahn-Teller active Cr^{3+} (with spin $S=3/2$). The Cr ions sit at the vertices of the corner sharing tetrahedra spanned by the lattice with space group $Fd\bar{3}m$. This arrangement causes geometric frustration of the primarily antiferromagnetic interactions. It has been shown that magnetoelastic coupling leads to a structural distortion[6,7] in both $ZnCr_2O_4$ and $CdCr_2O_4$ and that in this distorted lattice a complex antiferromagnetic order is established below $T_N=12$ and 7.8 K, respectively. The uniform component of the lattice distortions is tetragonal with $(c-a)/a=5\times10^{-3}$ and $=-1.5\times10^{-3}$ for $CdCr_2O_4$ and $ZnCr_2O_4$, respectively. The opposite sign of the observed distortion in these very similar materials is unexpected, making their differences significant and worthy of investigation. It has been also observed[8] that the distortion in $ZnCr_2O_4$ leads to splitting of one of the infrared (IR) active phonons and that the size of the splitting gives a measure of the spin correlations both above and below T_N.

A Landau theory of the magnetoelastic interaction in the pyrochlore lattice for the case of uniform distortions has been developed by Tchernyshyov *et al.*[2,3] They found a correlation between the lattice distortions, or bond order, and the spin order of the ground state. Since it is known that the lattice distortion in $ZnCr_2O_4$ is not uniform[9] (i.e., $\mathbf{q}\neq0$), this theory does not apply directly. It is, nevertheless, a good starting point in the explanation of some experimental facts and, as we will show below, it allows an understanding of certain features of the behavior of the IR phonons in $CdCr_2O_4$ as well. It is particularly noteworthy that even though the structural differences between $ZnCr_2O_4$ and $CdCr_2O_4$ are minimal at high temperatures,[6,7] significant differences appear in the IR spectra of the two upon magnetic ordering, suggesting that the magnetic interactions are very sensitive to subtle lattice changes.

It is important therefore to compare these two materials in order to elucidate how the subtle differences in the radius of the A site ion leads to characteristically different distortions and phonon splittings in the ground state. In this Brief Report we present the temperature dependence of the IR reflectivity spectra in the phonon frequency range of the frustrated antiferromagnet $CdCr_2O_4$. We find that only one of the triply degenerate modes in this compound splits significantly below the Néel temperature, similar to the splitting in $ZnCr_2O_4$.[8] However, some important differences are observed. We discuss these effects in terms of the lattice distortion that relieves frustration and its associated spin configuration.

II. RESULTS

Single crystals were grown by a flux method as described elsewhere.[10] Large surfaces of the (111) plane were polished for reflection measurements; typical sizes were $3\times3\times0.5$ mm^3. The samples were characterized by magnetic susceptibility measurements and showed the antiferromagnetic transition temperature to be $T_N=7.8$ K. The temperature dependence from 6 to 300 K of the reflectivity spectra ($\hbar\omega=15-100$ meV) was obtained using a Fourier transform spectrometer with the sample in vacuum in an optical cryostat with continuous He flow for cooling.[8,11] We fitted[12] the spectra with a model of Lorentz oscillators for the dielectric constant

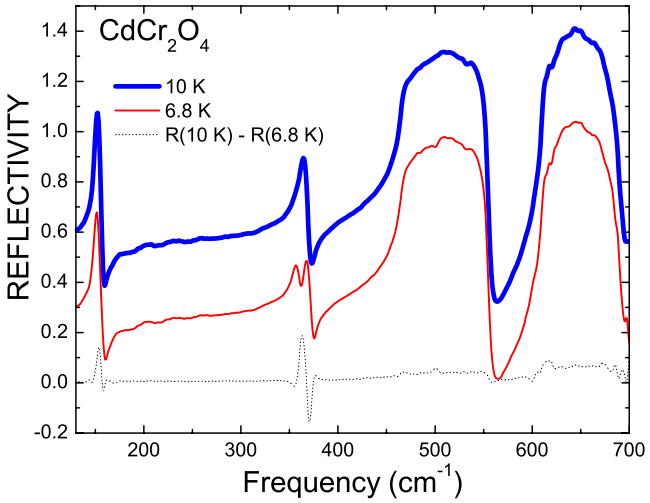

FIG. 1. (Color online) 10 K (thick line) and 6.8 K (thin line) reflectivity spectra of $CdCr_2O_4$ (offset for clarity). Also shown is the difference spectra in thin dotted line.

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{S_j}{\omega_j^2 - \omega^2 - i\omega\gamma_j}, \quad (1)$$

using the reflectivity formula $R=|\sqrt{\varepsilon}-1|^2/|\sqrt{\varepsilon}+1|^2$. Then we extracted the parameters of the Lorentzian oscillators as a function of temperature: S_j (cm^{-2}) spectral weight, ω_j (cm^{-1}) phonon frequency, and γ_j (cm^{-1}) the linewidth.

In the paramagnetic phase the spectra contains only the four triply degenerate IR modes allowed by symmetry ($4T_{1u}$). Below T_N five modes are observed as seen in Fig. 1. In the ordered phase, due to the tetragonal distortion, the phonon triplets should split into doublets and singlets,[13] but only the phonon at 365 cm^{-1} splits significantly below T_N. This phonon mode contains the largest component of the symmetry coordinate[14] that modulates the Cr-Cr distance and, thus, the direct exchange between neighbors. Therefore we expect the effects of the transition into the antiferromagnetic state to be much more pronounced on this mode. We note, however, that by taking the difference between spectra above and below T_N we see that the low frequency (~150 cm^{-1}) phonon also shows signature of splitting. We also point out that the motion involved in the two high frequency phonons modulates the superexchange path Cr-O-Cr but we do not observe any splitting on these phonons, even though these phonons also contain a small component of the Cr-Cr mode that dominates the low frequency phonons. We can conclude then that the main component of the magnetic interaction is the direct exchange between Cr ions.

Above ~150 K the behavior of the frequency of the Cr phonon, shown in the main panel of Fig. 2, is as expected due to anharmonic processes, but below this temperature the phonon softens by 3 cm^{-1}. As we will discuss below, we understand this effect as a signature of the coupling of this phonon to the spin fluctuations in the paramagnetic phase and it is similar to the behavior in $ZnCr_2O_4$. Below T_N the phonon splits into a doublet and a singlet. The singlet frequency softens significantly and the doublet frequency hardens. The low temperature limit of the doublet frequency is close to the expected value in the paramagnetic state in the presence of anharmonic hardening of the lattice, but with the absence of softening due to spin liquid effects as indicated by the dashed line in Fig. 2. By comparing their spectral weights, we conclude that the singlet shifts down and the doublet shifts up in frequency upon cooling below T_N, with a final splitting $\Delta=9$ cm^{-1}. This value of the splitting is close to $\Delta_{ZCO}=11$ cm^{-1} reported before[8] in $ZnCr_2O_4$, where the doublet softens and the singlet hardens. The different behaviors of this phonon in $ZnCr_2O_4$ and $CdCr_2O_4$ will be explained as a consequence of the spin-phonon coupling effects on their different magnetic order.

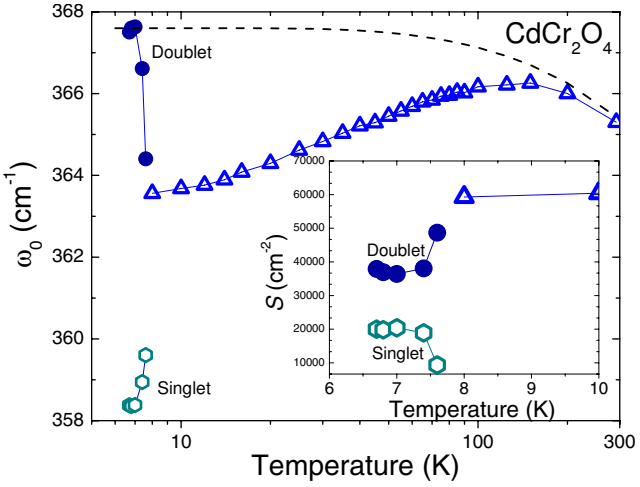

FIG. 2. (Color online) Temperature dependence of the Cr phonon frequency. The dashed line indicates the anharmonic behavior of the frequency. The inset shows the spectral weight of this phonon and its distribution below T_N.

Figure 3(a) shows the temperature dependence of the frequency of the lowest energy IR active phonon. This phonon also shows anomalous softening below 100 K, the frequency shifts by 1.5 cm^{-1} from above T_N to approximately 100 K. This temperature dependence is similar to the behavior of the Cr phonon triplet at 365 cm^{-1}, therefore we suspect that the

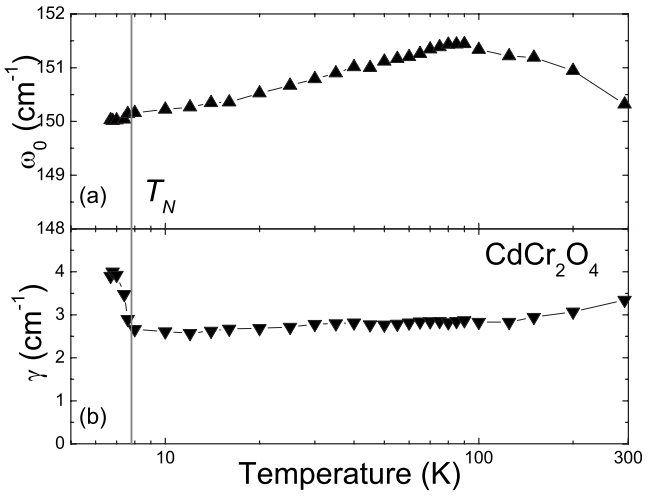

FIG. 3. Temperature dependence of the lowest energy phonon (a) frequency and (b) linewidth.

origin of this behavior is the same; coupling of these phonons to the antiferromagnetic fluctuations in the paramagnetic phase. Even though we could not fit the line shape of this phonon with two separate oscillators significantly better than with a single oscillator, it is evident from the sudden increase of the linewidth at T_N [Fig. 3(b)] that this phonon also splits. The high frequency phonons show the expected increase on cooling of its frequency due to anharmonic processes and do not show any evidence of splitting below T_N.

III. DISCUSSION

The lattice distortions that effectively couple to the spins, and release the frustration, belong to the E (doublet) representation of the point group of the tetrahedron T_d. These distortions correspond to tetragonal and orthorhombic modifications of the unit cell. When the full translational symmetry of the lattice is taken into account, the E representation becomes E_u and E_g according to whether the distortion is odd or even under inversion symmetry. The E_g distortion is then a uniform stretching of all tetrahedra, while the E_u distortion staggers stretching and contraction along one axis in neighboring tetrahedra. Each of these distortions is accompanied by different spin configurations; the latter are displayed in Figs. 5 and 6 of Tchernyshyov *et al.*[3]

Based on this model we can qualitatively explain the phonon splitting and how the spectral weight is redistributed below T_N. Chern *et al.*[15] proposed a model to explain the observed[7,16] spin configuration in $CdCr_2O_4$, wherein the major contribution to the lattice distortion comes from the phonon with E_u symmetry with a smaller contribution from the E_g phonon. The distortion is such that the contraction occurs along the x axis in one tetrahedron and in the y axis in the neighboring one. The bonds along [110] and $[1\bar{1}0]$ are fully satisfied (i.e., neighboring spins are always antiparallel), whereas the bonds along [011], $[0\bar{1}1]$, [101], and $[\bar{1}01]$ alternate between frustrated and satisfied bonds as shown in the left side of Fig. 4 with full lines for satisfied bonds and dashed lines for frustrated bonds. These bonds are formed along chains of up-up-down-down spins around which one can form left and right handed screws of fully frustrated and fully satisfied bonds.

In this case the phonon triplet T_{1u} mode (motion indicated in the middle panel of Fig. 4) involves different bonds in each of its components: the xy motion probes the fully satisfied bonds, and the yz and xz motions probe the mixed bonds, as illustrated at the top of Fig. 4. This model serves as a natural explanation for the splitting of the phonon frequencies, the doublet (yz and xz) should not change its frequency with respect to the paramagnetic phonon triplet since the contribution from frustrated and satisfied bonds would cancel (i.e., $\langle S_i S_j \rangle = 0$), while the phonon singlet would reduce its frequency since the bond is fully satisfied ($\langle S_i S_j \rangle = -1$). This picture is illustrated by the results in Fig. 2. These considerations are consistent with observation when the spin glass phonon softening effects are included. Therefore, in the Néel phase the phonon doublet shifts to the position it would have in the absence of any spin correlations at low temperatures.

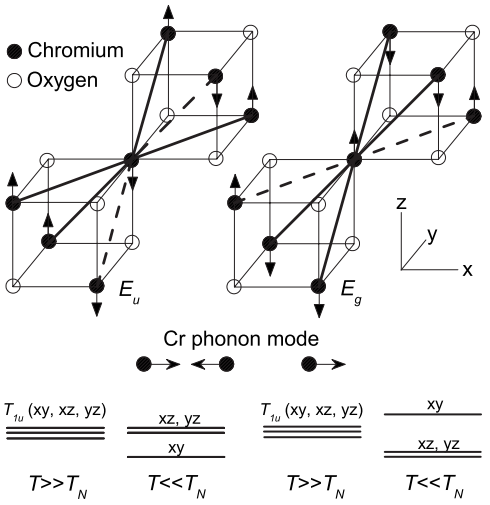

FIG. 4. Expected spin order effect on the frequencies of the Cr phonon triplet. (Top) Spin and bond orders induced by the E_u (left) and E_g (right) distortions, solid (dashed) lines represent satisfied (frustrated) bonds. (Bottom) Schematic representation of the phonon triplet splitting induced by the spin ordering corresponding to each distortion.

This simple explanation also helps us understand the results obtained in $ZnCr_2O_4$. In this compound the observed uniform distortion is given by a simple lattice contraction along the [001] direction. So the E_g distortion is dominant. The bond order is such that [110] and $[1\bar{1}0]$ bonds are fully frustrated, and [011], $[0\bar{1}1]$, [101], and $[\bar{1}01]$ bonds are always satisfied. The doublet then (xz and yz) has lower frequency than the singlet (xy) as observed in the IR measurements[8] and indicated on the right side of Fig. 4.

If we compare the split phonon frequencies with the phonon triplet just above T_N, and not with the paramagnetic state as done above, we expect the frequency shifts to have a definite behavior. Just above the transition individual tetrahedra cycle through different spin configurations, which we assume to be collinear, so that each bond spends 1/3 of the time with parallel spins and 2/3 of it with antiparallel spins. Then on average we will have $\langle S_i S_j \rangle = -1/3$, which means that the phonon doublet shifts up $1/3\Delta$ and the singlet shifts down $2/3\Delta$ with respect to the frequency just above T_N. The experimental observation does not agree with this prediction. This could be an indication of the role that the noncollinear states play near the phase transition that is not captured by the model[2,3] we have used.

It is also important to note that the observation in $CdCr_2O_4$ ($ZnCr_2O_4$) is in opposition to what is expected from a simple tetragonal distortion that elongates (contracts) the c axis when the distortion does not couple to the spins. For a simple elongation along the c axis (as it would correspond to $CdCr_2O_4$) we expect the frequency of the singlet (xy motion) to go up since the effective force constant of the bond is increased in proportion to the distortion, and the doublet (xz,yz motions) would have lower energy. For the contraction case (as in $ZnCr_2O_4$) the force constant diminishes, making the singlet frequency go down and the doublet go up. This makes clear the crucial role in relieving frustra-

tion that the spin-phonon coupling plays in these materials. We summarize the experimental observation in Fig. 4, where the splitting of the phonon triplet is shown schematically.

The behavior of the phonon frequencies of the two lowest energy phonons in $CdCr_2O_4$, softening above T_N on cooling, is similar to the Cr phonon triplet reported[8] for $ZnCr_2O_4$. This effect could be explained as the consequence of spin-phonon coupling due to the short range magnetic order in the spin glass state at low temperatures and how it affects the phonon frequency. Since direct exchange between Cr ions dominates the magnetic interactions, the dependence of the exchange on bond separation induced by the spin correlations modifies the phonon frequency with a term proportional to the nearest neighbor spin-spin correlation function, $\omega=\omega_0+\lambda\langle S_iS_j\rangle$, where λ is proportional to the second derivative of the direct exchange constant with respect to the phonon coordinate. Even though there is no magnetic long range order above T_N, the spin-spin correlation function is not zero. Its value could be estimated from the magnetic specific heat.[8] Unfortunately there are no specific heat data for $CdCr_2O_4$ that would allow a direct comparison of the value of the spin-phonon constant λ among the chromates. We can also estimate the value of λ from the doublet-singlet splitting[13] $\Delta=9$ cm^{-1}. Using the spin-Peierls order parameter, $\langle S_1S_2-S_2S_3\rangle=9/4$, we obtain $\lambda=4$ cm^{-1}, which is somewhat smaller than the value in $ZnCr_2O_4$ obtained before.[8,13] The value of the ratio of $\lambda_{Zn}/\lambda_{Cd}(\approx 1.3)$ is much smaller than that expected from the ratio of the total exchange constants $J_{Zn}/J_{Cd}\approx 4$ as obtained from the Curie-Weiss fit to susceptibility data.

This apparent discrepancy is likely a consequence of the oversimplification of our representation of the magnetic order in these materials. The value of the spin-Peierls order parameter used for the estimation of λ was obtained for the collinear configurations of Ref. 3. Since the magnetic structure of $ZnCr_2O_4$ is noncollinear,[17] we expect that the spin-Peierls order parameter be much smaller than the value used here, which would make the value of λ_{Zn} and the ratio $\lambda_{Zn}/\lambda_{Cd}$ correspondingly larger. A comparison of our estimate of λ with the value obtained from the magnetic specific heat as done earlier for $ZnCr_2O_4$ (Ref. 8) would provide a test of these ideas. Therefore, the measurement of magnetic specific heat in $CdCr_2O_4$ is a priority.

The effects of the competition between direct exchange and superexchange in the spin-lattice interaction in the magnetic chromium spinels has been recently studied using IR spectroscopy by Rudolf *et al.*[18] Their results demonstrate that the simple picture presented here needs modification if it is to be applied to systems where the direct antiferromagnetic exchange is not the dominant interaction. We note, however, that their measurements in $CdCr_2O_4$ do not agree with ours completely, and we believe that their use of polycrystalline samples might be a factor for the differences.

IV. CONCLUSIONS

We have presented measurements of the IR phonon spectra of frustrated antiferromagnet $CdCr_2O_4$. Based on the model of the soft pyrochlore lattice[2,3] we have explained the behavior of the frequency in the Cr-motion-dominated phonon triplet as it enters into the antiferromagnetic phase. This model also allows an understanding of the different spectral weight distributions between $CdCr_2O_4$ and $ZnCr_2O_4$. We found as well the value of the spin-phonon coupling constant to be smaller in $CdCr_2O_4$ than in $ZnCr_2O_4$. The comparison between these two materials demonstrates our understanding that direct exchange is the most relevant interaction for these systems and of the main features of the interplay between frustrated magnetism and spin-lattice coupling in the pyrochlore lattice.

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