Spin phonon coupling in frustrated magnet CdCr$_2$O$_4$

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The infrared phonon spectrum of the spinel CdCr$_2$O$_4$ is measured as a function temperature from 6 K 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 Cr$^{3+}$ 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$_2$O$_4$ 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$_2$O$_4$.

I. INTRODUCTION

Due to geometric frustration antiferromagnetically coupled Heisenberg spins in the pyrochlore lattice do not order at any finite temperature. 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 or further neighbor exchange coupling, and the possibility of exotic ground states. These features have led to great interest in this class of materials. Their properties are being extensively studied theoretically and experiments are dedicated to look for materials that do not order, the so-called spin-ice materials.

The family of spinel compounds $A$Cr$_2$O$_4$ ($A =$ Zn, Cd or Hg) is a good example of the Heisenberg 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 in both ZnCr$_2$O$_4$ and CdCr$_2$O$_4$ 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 $(c-a)/a = 5 \times 10^{-3}$ and $= -1.5 \times 10^{-3}$ for CdCr$_2$O$_4$ and ZnCr$_2$O$_4$, 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 that the distortion in ZnCr$_2$O$_4$ 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. 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$_2$O$_4$ is not uniform (i.e. $q \neq 0$), 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$_2$O$_4$ as well. It is particularly noteworthy that even though the structural differences between ZnCr$_2$O$_4$ and CdCr$_2$O$_4$ are minimal at high temperatures, 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 paper we report the temperature dependence of the IR reflectivity spectra in the phonon frequency range of the frustrated antiferromagnet CdCr$_2$O$_4$. 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$_2$O$_4$. 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. Large surfaces of the (111) plane were polished for reflection measurements, typical sizes were $3 \times 3 \times 0.5$ 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 ($\hbar \omega = 15\text{–}100$ meV) was obtained using a Fourier transform spectrometer with the sample in vacuum in an optical cryostat with continuous He flow.
for cooling. We fitted the spectra with a sum of Lorentzians model for the dielectric constant

\[ \varepsilon(\omega) = \varepsilon_{\infty} + \sum_j \frac{S_j}{\omega_j^2 - \omega^2 - i\omega\gamma_j} \]  

(1)

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

In the paramagnetic phase the spectra contains only the four triply degenerate IR modes allowed by symmetry (4\(T_{1u}\)). Below \( T_N \) five modes are observed as seen in figure. In the ordered phase, due to the tetragonal distortion, the phonon triplets should split into doublets and singlets, but only the phonon at 365 cm\(^{-1}\) splits significantly below \( T_N \). This phonon mode contains the largest component of the symmetry coordinate 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 (\( \sim 150 \) 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 \( \sim 150 \) K the behavior of the frequency of the Cr phonon, shown in the main panel of figure, 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\(_2\)O\(_4\). 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. However, 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 figure. 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 in ZnCr\(_2\)O\(_4\), where the doublet softens and the singlet hardens. The different behaviors of this phonon in ZnCr\(_2\)O\(_4\) and CdCr\(_2\)O\(_4\) will be explained as a consequence of the spin phonon coupling effects on their different magnetic order.

Figure (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 origin of the this behavior is the same; coupling of these phonons to the antiferromagnetic fluctuations in the paramagnetic phase. Even though we could not fit the lineshape 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 \( T_N \) (figure (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 \( T_N \).
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 stages stretching and contraction along one axis in neighboring tetrahedra. Each of these distortions is accompanied by different spin configurations, and are displayed in figures 5 and 6 of Tchernyshyov et al.

Based on this model we can qualitatively explain the phonon splitting and how the spectral weight is redistributed below $T_N$. Chen et al. proposed a model to explain the observed spin configuration in CdCr$_2$O$_4$, wherein the major contribution to the lattice distortion comes from the phonon with $E_g$ symmetry with a smaller contribution from the $E_u$ 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 [1010] are fully satisfied (i.e. neighboring spins are always antiparallel), whereas the bonds along [011], [001], [101] and [1010] alternate between frustrated and satisfied bonds as shown in the left side of figure [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 figure [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 figure [4]. This model serves as a natural explanation to 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. $\langle S_i \cdot S_j \rangle = 0$), while the phonon singlet would reduce its frequency since the bond is fully satisfied ($\langle S_i \cdot S_j \rangle = -1$). This picture is illustrated by the results in figure [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.

This simple explanation also helps us understand the results obtained in ZnCr$_2$O$_4$. 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 [1010] bonds are fully frustrated, and [011], [001], [101] and [1010] bonds are always satisfied. The doublet then ($xz$ and $yz$) has lower frequency than the singlet ($xy$) as observed in the IR measurements and indicated on the right side of figure [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, that 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 $\langle S_i \cdot S_j \rangle = -1/3$, 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 non-collinear states play near the phase transition that is not captured by the model we have used.

It is also important to note that the observation in CdCr$_2$O$_4$ (ZnCr$_2$O$_4$) 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$_2$O$_4$) 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$_2$O$_4$) the force constant diminishes, making the singlet frequency to go down and the doublet $xy$ 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$_2$O$_4$) the force constant diminishes, making the singlet frequency to go down and the doublet $xy$ 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$_2$O$_4$) the force constant diminishes, making the singlet frequency to go down and the doublet $xy$ 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.

We summarize the experimental observation in figure [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$_2$O$_4$, softening above $T_N$ on cooling, is similar to the Cr phonon triplet reported for...
λ the ratio of the total exchange constants \( J = 4 \text{ cm}^{-1} \) obtained from the Curie-Weiss fit to susceptibility data. The Peierls order parameter, doublet-singlet splitting order above ordinate. Even though there is no magnetic long range order, the spin-spin correlation function is not responding to the phonon triplet splitting induced by the spin ordering corresponding to each distortion.

\[ \lambda_{Zn} \approx 9 \text{ cm}^{-1} \]

\[ \lambda_{Cd} \approx 4 \text{ cm}^{-1} \]

**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.

\[ \lambda_{Zn}/\lambda_{Cd} \approx 1.3 \]

\[ \lambda_{Zn}/\lambda_{Cd} \approx 4/3 \]

ZnCr\(_2\)O\(_4\). 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, \( \omega = \omega_0 + \lambda \langle S_i \cdot S_j \rangle \), where \( \lambda \) 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. Unfortunately there are no specific heat data for CdCr\(_2\)O\(_4\) that would allow a direct comparison of the value of the phonon constant \( \lambda \) among the chromates. We can also estimate the value of \( \lambda \) from the doublet-singlet splitting, \( \Delta \approx 9 \text{ cm}^{-1} \). Using the spin-Peierls order parameter, \( \langle S_1 \cdot S_2 - S_2 \cdot S_3 \rangle = 9/4 \), we obtain \( \lambda = 4 \text{ cm}^{-1} \) which is somewhat smaller than the value in ZnCr\(_2\)O\(_4\) obtained before. The value of the ratio of \( \lambda_{Zn}/\lambda_{Cd} \) is much smaller than the 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 \( \lambda \) was obtained for the collinear configurations of reference 3. Since the magnetic structure of ZnCr\(_2\)O\(_4\) is noncollinear, we expect that the spin-Peierls order parameter be much smaller than the value used here, which would make the value of \( \lambda_{Zn} \) and the ratio \( \lambda_{Zn}/\lambda_{Cd} \) correspondingly larger. A comparison of our estimate of \( \lambda \) with the value obtained from the magnetic specific heat as done earlier for ZnCr\(_2\)O\(_4\) would provide a test of these ideas. Therefore, the measurement of magnetic specific heat in CdCr\(_2\)O\(_4\) 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. 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\(_2\)O\(_4\) 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\(_2\)O\(_4\). Based on the model of the soft pyrochlore lattice2,3 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\(_2\)O\(_4\) and ZnCr\(_2\)O\(_4\). We found as well the value of the spin-phonon coupling constant to be smaller in CdCr\(_2\)O\(_4\) than in ZnCr\(_2\)O\(_4\). 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.

**V. ACKNOWLEDGEMENTS**

We thank O. Tchernyshyov, G-W. Chern and C.ennie for useful discussions. This work was supported in part by the National Science Foundation MRSEC grant DMR-0520471.

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1 P. W. Anderson, Phys. Rev. 102, 1008 (1956).

2 O. Tchernyshyov, R. Moessner, and S. L. Sondhi, Phys. Rev. Lett. 88, 067203 (2002).
3 O. Tchernyshyov, R. Moessner, and S. L. Sondhi, Phys. Rev. B 66, 064403 (2002).
4 A. P. Ramirez, in Handbook of Magnetic Materials, edited by K. H. J. Buschow (North Holland, 2001), vol. 13, p. 423.
5 A. P. Ramirez, A. Hayashi, R. J. Cava, R. Siddharthan, and B. S. Shastry, Nature 399, 333 (1999).
6 S.-H. Lee, C. Broholm, T. H. Kim, W. Ratcliff II, and S.-W. Cheong, Phys. Rev. Lett. 84, 3718 (2000).
7 J. H. Chung, M. Matsuda, S.-H. Lee, K. Kakurai, H. Ueda, T. J. Sato, H. Takagi, K.-P. Hong, and S. Park, Phys. Rev. Lett. 95, 247204 (2005).
8 A. B. Sushkov, O. Tchernyshyov, W. Ratcliff II, S. W. Cheong, and H. D. Drew, Phys. Rev. Lett. 94, 137202 (2005).
9 S.-H. Lee, G. Gasparovic, C. Broholm, M. Matsuda, J.-H. Chung, Y. J. Kim, H. Ueda, G. Xu, P. Zschak, K. Kakurai, et al., J. Phys.: Condens. Matter 19, 145259 (2007).
10 H. A. Dabkowska, J. Cryst. Growth 54, 607 (1981).
11 R. Valdés Aguilar, A. B. Sushkov, S. Park, S.-W. Cheong, and H. D. Drew, Phys. Rev. B 74, 184404 (2006).
12 We use the program ReffIT by Alexey Kuzmenko. Available at http://optics.unige.ch/alexey/reffit.html.
13 C. J. Fennie and K. M. Rabe, Phys. Rev. Lett. 96, 205505 (2006).
14 J. Himmrich and H. D. Lutz, Sol. St. Comm. 79, 447 (1991).
15 G.-W. Chern, C. J. Fennie, and O. Tchernyshyov, Phys. Rev. B 74, 060405(R) (2006).
16 M. Matsuda, M. Takeda, M. Nakamura, K. Kakurai, A. Oosawa, E. Lelievre-Berna, J.-H. Chung, H. Ueda, H. Takagi, and S.-H. Lee, Phys. Rev. B 75, 104415 (2007).
17 S.-H. Lee, W. Ratcliff II, Q. Huang, T. Kim, and S.-W. Cheong, Phys. Rev. B 77, 014405 (2008).
18 T. Rudolf, C. Kant, F. Mayr, J. Hemberger, V. Tsurkan, and A. Loidl, N. J. Phys. 9, 76 (2007).