Magnetic-induced phonon anisotropy in ZnCr$_2$O$_4$ from first principles

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We have studied the influence of magnetic order on the optical phonons of the geometrically frustrated spinel ZnCr$_2$O$_4$ from first-principles. By mapping the first-principles phonon calculations onto a Heisenberg-like model, we developed a method to calculate exchange derivatives and subsequently the spin-phonon coupling parameter from first-principles. All calculations were performed within LSDA+U.

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The interplay between spin and lattice degrees of freedom give rise to an amazing variety of different phenomena, including the spin-Teller and the magneto-electric effects. Perhaps the simplest example of a spin-lattice coupling is the influence of magnetic order on phonons. Though first-principles density functional methods have been highly successful in describing the structural and magnetic properties of dielectrics, little has been done to address the coupling of spins and phonons. In this letter we present for the first time an approach to predict the influence of magnetic order on optical phonons from first-principles and apply this approach to the strongly geometrically frustrated spinel zinc chromite. Our method is general and has also been recently applied to provide a new understanding of the phonon anomalies observed at the ferromagnetic (FM) transition in the chalcogenide spinels [4].

Zinc chromite, ZnCr$_2$O$_4$, crystallizes in a spinel structure. The Cr$^{3+}$ ions (S= 3/2) form a network of vertex-sharing tetrahedra (a pyrochlore lattice) with strong antiferromagnetic (AFM) interactions between nearest neighbor spins, $\Theta_{CW} \approx 400$K. As a result, zinc chromite is strongly geometrically frustrated as evidenced by the rather low $T_N = 12.5$K (compared to $\Theta_{CW}$). The physics of ZnCr$_2$O$_4$ at $T_N$ involves a first-order cubic-to-tetragonal (c-t) structural transition (to relieve geometric frustration) as it enters the Neel state, bypassing a tetragonal (c-t) structural transition (to relieve geometric frustration). The Cr-O-Cr superexchange and to a large extent, which one wins can be attributed to volume and electronegativity of the anion. For zinc chromite, the nearest neighbor (n.n.) exchange constant, $J$, is an order of magnitude greater than all next nearest neighbor interactions. $J$ is determined by a balance between AFM direct Cr-Cr exchange and FM 90° Cr-O-Cr superexchange and to a large extent, which one wins can be attributed to volume and electronegativity of the anion. Exchange constants can be extracted by mapping first-principles calculations of the total energy for different spin configurations at $T=0$ onto a classical Heisenberg model: $E_{\text{spin}} = -2J \sum_{\text{n.n.}} \mathbf{S}_i \cdot \mathbf{S}_j$ (sum over $z=6$ n.n’s). This gives for the energy of the primitive unit cell (4 Cr-ions): $E_{FM}=E_0 - 24JS^2$ and $E_{AFM}=E_0 + 8JS^2$. From this we calculate $J = -2.1$ meV.

We develop an approach where for the first time experimentally accessible quantities of this theory can be calculated from first-principles. Finally, we apply this method to calculate the coupling parameter, $\lambda$, for ZnCr$_2$O$_4$. We find it to be in excellent agreement with that measured, providing confirmation of a strong spin-phonon mechanism responsible for the large phonon splitting.

First-principles density-functional calculations using projector augmented-wave potentials were performed within LSDA+U (local spin-density approximation plus Hubbard U) as implemented in the Vienna ab initio Simulation Package [10] with a plane wave cutoff of 500 eV and a 6x6x6 Γ-centered k-point mesh. All calculations were performed with collinear spins and without LS-coupling (inclusion of LS-coupling does not change the results). We performed full optimization of the lattice parameter, $a=8.26$ Å (exp: $a=8.31$ Å), and anion parameter, $u=0.386$ (exp: $u=0.387$), in space group Fd$3m$, where we find excellent agreement with experiment. The Cr on-site Coulomb, $U=3$ eV, and exchange, $J=0.9$ eV, parameters are justified a posteriori from the calculation of the magnetic exchange constant as we now discuss.

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which compares well with \( J_{\text{exp}} = -2.25 \text{ meV} \) estimated from the measured \( \Theta_{\text{CW}} \).

First-Principles Phonons.—For cubic ZnCr$_2$O$_4$, group-theoretical analysis predicts that the 39 zone-center optic modes transform according to the following irreducible representations (irreps) of \( O_h \): \( \Gamma_{\text{i.r.}} = 4T_{1u}, \Gamma_{\text{Raman}} = 3T_{2g} + 1E_g + 1A_{1g}, \) and \( \Gamma_{\text{silent}} = 2A_{2u} + 2E_u + 2T_{2u} + 1T_{1g} \), and the three acoustic modes according to \( \Gamma_{\text{acoustic}} = 1T_{1u} \). With AFM spins, the ordering pattern (the “collinear model” of Ref. [1]) induces a tetragonal axis chosen here to be \( \hat{z} \). Under this tetragonal ”distortion”, the point group is lowered from \( O_h \rightarrow D_{4h} \), and the irreps previously discussed become reducible, although the Raman and i.r-active irreps still do not mix. Therefore we can continue to talk about these modes independently and although the Raman modes do split, this splitting is small and not our main concern. Still, to demonstrate the quality of the phonon calculations for zinc chromite, we present our calculated Raman-active frequencies (cm$^{-1}$): \( T_{2g}^e = 185 (186), 608 (610) \); \( E_u^e = 466 (457) \); \( A_{1g} = 687 (692) \), which are in remarkable agreement (~1%) with experiment (shown in parenthesis) [12].

We now proceed to the main part of this letter, the influence of magnetic order on the i.r. phonons. Under \( D_{4h} \) the i.r. modes split according to \( T_{1u} \rightarrow A_{2u} + E_u \), where the 1-d \( A_{2u} \) and 2-d \( E_u \) irreps transform like vectors along and perpendicular to the tetragonal axis respectively. Additionally, certain rows of the silent \( T_{2u} \) irrep become i.r.-active and can in principle mix with those originating from \( T_{1u} \). This mixing is very small and for our purposes acceptable to ignore. For the remainder of this letter we only discuss the 4 modes originating from \( T_{1u} \). The rows of \( T_{1u} \) do not mix under \( D_{4h} \) so that we can still talk about the \( x, y, (E_u) \) and \( z (A_{2u}) \) blocks of the dynamical matrix. We compute the i.r. phonons by constructing the three 5x5 blocks (4 i.r-active, 1 acoustic) of the dynamical matrix from Hellmann-Feynman forces on the symmetry-adapted partner functions, \( f_{\alpha n,\alpha} \), where \( n=1,5 \) and \( \alpha = x,y,z \) label the partner function and the row of \( T_{1u} \), respectively. These partner functions transform like vectors along \( \hat{\alpha} \) under \( O_h \). The partner functions, \( f_{1,\alpha}, f_{2,\alpha}, \) and \( f_{4,\alpha} \), involve atomic displacements along \( \hat{\alpha} \) of the entire zinc, chromium, and oxygen sublattices, respectively. Nontrivial displacements within the chromium and oxygen sublattices, whose partner functions we label \( f_3 \) and \( f_5 \) respectively, are also possible. Although \( f_{3,\alpha} \) and \( f_{5,\alpha} \) both transform like vectors along \( \hat{\alpha} \), atomic displacements associated with these partner functions take place in the plane perpendicular to the \( \alpha \)-axis. In Fig. 1 we show \( f_{3,z} \) and \( f_{3,x} \) which are seen to strongly modulate the Cr-Cr bond length. Their importance to the present problem will soon become apparent.

Our calculated i.r. phonons for crystallographically cubic ZnCr$_2$O$_4$ with AFM are shown in Table I labeled \textit{ab initio}. We see that AFM order induces a large tetragonal anisotropy in the phonon sector (\( \omega_z = \omega_y \neq \omega_x \)) with large splitting (\( \Delta \omega \equiv \omega_z - \omega_x \)) occurring for modes (1) and (2), \( \Delta \omega \approx 0.12 \omega_z \), and smaller splitting for (3) and (4), \( \Delta \omega \approx 0.02 \omega_z \). (we hold off for now on comparing these results to experiment). This mode dependent behavior is reminiscent of the phonon anomalies displayed at \( T_c \) in the FM spinel CdCr$_2$S$_4$ [14] where insight was gained by looking at the eigendisplacements. We don’t repeat the analysis except to make two points. First, all four modes contain Cr-\( f_3 \) partner function (more on this below) so that the Cr-Cr bond is highly distorted in the plane perpendicular to \( \alpha \) but in (1) and (2) the total distortion is such that all Cr-O bond lengths remain fixed while in (3) and (4) the Cr-O bond lengths, particularly along \( \hat{\alpha} \), are strongly modulated (we will see what this implies). Second, the presence or absence of Zn-\( f_1 \) has no effect on the spin-phonon coupling in contrast to what is commonly proposed. We understand this from our calculations of the \( q=0 \) component of the force constant matrix, \( C_{n,\alpha n',\alpha'} \), where we find \( C_{1,x1,x} = C_{1,z1,z} \), as you would expect for cubic symmetry. We found similar results in CdCr$_2$S$_4$, CdCr$_2$Se$_4$, and HgCr$_2$Se$_4$ which suggests that the previous interpretation of phonon anomalies in these FM spinels should be revisited [3].

Our first-principles calculations clearly show that AFM spin-ordering induces a large i.r. phonon splitting as shown in Table I. Sushkov argued that the large phonon splitting of \( T_{1u}(2) \) was caused through modulation of direct Cr-Cr exchange by \( f_3 \), and since \( T_{1u}(2) \) contained the largest amount of this partner function, it was the only splitting measurable. In Fig. 1 the anisotropy imposed by the magnetic order on this mode is clear. Supporting their argument is our calculations of the \( q=0 \) component of the force constant matrix. Looking at the diagonal components we find that the anisotropy, \( C_{n,z,n,z} - C_{n,z,n,x} \) (which equals zero for a cubic system), is \( \approx 20\% \) for \( f_3 \), being 3 times larger than that due to any other partner function. Second, \( T_{1u}(2) \) contains twice as much \( f_3 \) const
pared with the other i.r. modes. But in contrast to what is seen experimentally, the phonon frequencies of all four modes are split. Additionally, the calculated splitting of $T_{1u}(2)$, $\Delta \nu = 50 \text{ cm}^{-1}$, is about 4.5 times larger than the measured splitting, $\Delta \nu = 11 \text{ cm}^{-1}$. One question then becomes how do we interpret our phonon calculations to be consistent with experiment? Also what do they teach us about the spin-phonon mechanism and the role of direct exchange? Clearly a more systematic approach to understand the first-principles calculations is desirable.

First-Principles Model.—We begin by writing the total energy, $E = E_0 + E_{ph} + E_{spin}$, of a system of i.r. phonons, $E_{ph} = \frac{1}{2} \sum_{n,n'} C_{n,n'} J_{ij} f_n f_{n'}$, $\eta \equiv [n, \alpha]$ and $C_{n,n'} = \delta_{\alpha \alpha'} C_{n,n'}$, and spins, $E_{spin} = - \sum_{ij} \langle J \rangle S_i S_j$. Without the spin-orbit interaction the spin and phonon modes are still indirectly coupled due to a positional dependence of the exchange interactions. This dependence is rather complicated because in addition to the positions of the two spins, the positions of the surrounding anions are important for the superexchange process, and may even influence direct exchange. In principle $J_{ij}$ depends on the positions of all $N$ magnetic and non-magnetic ions, $J_{ij}(r_1, r_2, \ldots r_N)$. A solution then becomes clearer if we write $J$ in terms of $f_n$ since these functions provide a complete basis to represent all possible i.r. atomic motion. For small distortions, $J$ can be expanded in $|f_n|$ leading to

$$\tilde{C}_{n,n'} = C_{n,n'} - \sum_{i,j} \frac{\partial^2 J_{ij}}{\partial f_n \partial f_{n'}} \langle S_i S_j \rangle$$

to lowest order in $S_i S_j$. In general, symmetry of the magnetic system can reduce this expression further. For spinels, $D_{4h}$ does not induce couplings between different rows of $O_h$, i.e. $\tilde{C}_{n,n'} = \tilde{C}_{n,n'}(\alpha)$, so in fact we only need to calculate derivatives of the type, $\partial^2 J_{ij}/\partial f_n \partial f_{n'}$ (magnetic order other than $D_{4h}$ could introduce derivatives connecting different rows of $O_h$ but will not change the value of the intra-row type). Now since the crystallographic group is cubic there are only two distinct changes in $J_{ij}$ depending on whether the spins lie in a plane perpendicular to $\hat{a}$ or not. With this let us define $\partial^2 J_{ij}/\partial f_n \partial f_{n'} = J''_{\perp,n,n'} \neq 0 \ \forall \ \hat{a} \cdot \alpha = 0$ and $\partial^2 J_{ij}/\partial f_n \partial f_{n'} = J''_{\parallel,n,n'} \neq 0 \ \forall \ \hat{a} \cdot \alpha \neq 0$ where $\hat{a}$ is the direction vector linking nearest neighbor spins, $S_i$ and $S_j$. Then we can write

$$\tilde{C}_{n,n'}(\alpha) = C_{n,n'}(\alpha) - J''_{\perp,n,n'} \sum_{\bar{r}} \langle S_i S_j \rangle - J''_{\parallel,n,n'} \sum_{\bar{r}} \langle S_i S_j \rangle$$

with the first sum over the two neighbors in a plane perpendicular to $\hat{a}$ and the second over the remaining four.

We have considerably reduced the problem by writing the exchange constants in terms of the partner functions and by applying symmetry, but we are still faced with the challenge to calculate $J''$. For this we propose a procedure that is similar to the approach of calculating exchange constants by mapping onto a Heisenberg-like model. As such let us write

$$\tilde{C}_{n,n'}^{FM}(\hat{z}) = C_{n,n'}^{PM} - 8 J''_{\perp,n,n'} S^2 - 16 J''_{\parallel,n,n'} S^2$$
$$\tilde{C}_{n,n'}^{AFM}(\hat{z}) = C_{n,n'}^{PM} - 8 J''_{\perp,n,n'} S^2 + 16 J''_{\parallel,n,n'} S^2$$
$$\tilde{C}_{n,n'}^{AFM}(\hat{x}) = C_{n,n'}^{PM} + 8 J''_{\perp,n,n'} S^2$$

where $\tilde{C}_{n,n'}^{FM}$ and $\tilde{C}_{n,n'}^{AFM}$ are the force constant matrices calculated from first-principles with FM and AFM order respectively. Here we have three equations and three unknowns. In Table IV we show the $T=0$ PM phonon frequencies extracted from the model which are found to be in excellent agreement (1-2%) with those measured at 13K. To test the validity of the model w.r.t. first-principles we perform additional phonon calculations with different magnetic order, for example, ferrimagnetic (FiM) order with one Cr-ion spin-down, the other three spin-up. For this spin configuration according to our model $C_{n,n'}^{FiM}(x) = C_{n,n'}^{FM}(y) = C_{n,n'}^{FM}(z) = C_{n,n'}^{PM}$. If we now perform first-principles calculations of the phonons with FiM magnetic order, we find that the frequencies are in exact agreement (<1 cm$^{-1}$) with those we extracted from the model, i.e. $\omega_{\lambda}^{FM} = \omega_{\lambda}^{FM}$. As a further test we considered additional FiM spin configurations within the conventional unit cell (eight formula units). The model reproduced the first-principles calculations to within 1 cm$^{-1}$ in every case.

Discussion.—Having established the model correctly captures the influence of magnetic order on the first-principles phonons, we turn our attention to calculating experimentally accessible quantities of the problem. First, on the role of direct exchange, it is telling that we find $\partial^2 J_{ij}/\partial f_3 \partial f_3 \approx 0.172$ meV/Å$^2$, more than ~10 times larger than any other component of $J''_{\perp}$ or $J''_{\parallel}$. This anomalously large value is consistent with the anisotropy in the force constant matrix and, as we now show, assumed correctly by Sushkov to originate from the modulation of direct exchange, $J_d$. For small displacements $J_d$ goes like $J_d(R_c) \approx J_d e^{-\alpha R_c}$, where $R_c$ is the distance between neighboring Cr-atoms. Assuming the contribution from superexchange (SE) is small, we find

| Experiment | Present Theory | ab initio |
|------------|---------------|-----------|
| Ref. | Model | $\hat{x}$ | $\hat{z}$ | $\hat{x}$ | $\hat{z}$ |
| 13K | 9K | PM | AFM | $J''_{\perp}$ | $J''_{\parallel}$ | AFM |
| 1 | 186 | 186+6 | 189 | 186 | 191 | -240 | 0 | 174 | 198 |
| 2 | 371 | 368 | 379 | 366 | 361 | 372 | -999 | 22 | 342 | 392 |
| 3 | 501 | 501 | 514 | 514 | 517 | -254 | 225 | 510 | 526 |
| 4 | 619 | 619 | 621 | 621 | 623 | -66 | 257 | 620 | 630 |

| TABLE I: Infrared-active, $T_{1u}$, phonons frequencies, cm$^{-1}$, of ZnCr$_2$O$_4$. |
\( \alpha = 0.05 \text{Å}^{-1} \) which compares well with the measured value of \( \alpha = 8.9 \text{Å}^{-1} \). This must be considered somewhat fortuitous since it is not clear that either the theoretical or the experimental approach isolates direct exchange. What does suggest the dominate role of direct exchange in \( J''_{L3} \) are our calculations for CdCr\(_2\)O\(_4\). This compound has a larger lattice constant and less negative \( J \) than ZnCr\(_2\)O\(_4\) so that direct exchange is expected to be weaker. Repeating the phonon calculations and mapping procedure for CdCr\(_2\)O\(_4\), we find \( \partial^2 J_{\perp}/\partial f \partial f_3 \approx -0.09 \text{meV/Å}^2 \). Considering a small contribution from SE is expected this compares well with \( \alpha^2 J = -0.07 \text{meV/Å}^2 \). Furthermore, no other components of \( J''_{L} \) or \( J''_{1} \) change appreciatively from those of ZnCr\(_2\)O\(_4\), consistent with the fact that the only partner function to change \( R_c \) is \( f_3 \).

The relation between \( J''_{L3} \) and direct exchange being established, we return to the discussion of the phonon splitting in ZnCr\(_2\)O\(_4\). To quantify the mode dependence and compare with experiment, let \( J''_{L} = u_{L}J'_{u_{L}} \), where \( u_{L} \) are the PM dynamical matrix real-space eigenvectors. Then we can write for the phonon anisotropy

\[
\omega_{\lambda}(\hat{z}) - \omega_{\lambda}(\hat{x}) \approx 4 \left( \frac{J''_{L} - J''_{1}}{\omega_{PM}} \right) (S_1 \cdot S_2 - S_1 \cdot S_4)
\]

where \( (S_1 \cdot S_2 - S_1 \cdot S_4) \) is defined as the spin-Peierls order parameter, \( f_{sp} \). In Table \( \text{I} \) we see that the anisotropy experienced by \( T_{uv} \) (1) and (2) is due to \( J''_{1} \), which is dominated by \( J''_{L3} \) and subsequently direct exchange. In contrast, \( J''_{L} \) plays a large role in the anisotropy of \( T_{uv} \) (3) and (4). This is due to the strong modulation of the Cr-O bonds which we suspect modifies FM superexchange and may also explain the sign. We can now compute the spin-phonon coupling constant, \( \lambda \), for \( T_{uv}(2) \). We find \( \lambda_2 = 4(J''_{L} - J''_{1})/\omega_{PM} \approx 11 \text{cm}^{-1} \) which agrees well with experiment, \( \lambda_2 = 6-10 \text{cm}^{-1} \). So from calculations of just the phonons for selected spin configurations, we are able to extract the spin-phonon coupling parameter, \( \lambda \), from first-principles. It is also now clear that the calculated splittings are significantly larger than experiment because the spin-Peierls OP for collinear AFM, \( f_{sp} = 4.5 \), is significantly larger than experiments (extracted values range from \( f_{sp} = 1.1 \) to \( 1.8 \)). In Fig. \( \text{2} \) we show how the splitting for \( T_{uv}(2) \) evolves with the spin-Peierls OP, where at \( f_{sp} = 1 \) we recover the experimentally observed splitting. If we substitute this value of the spin-Peierls OP into our model, we find that the splittings of the other modes are significantly reduced (2-5 cm\(^{-1} \)) as shown in Table \( \text{I} \). Although additional effects of the structural transition at \( T_N \) still need to be worked out, perhaps such small splittings are not easily measurable. But, it is clear, if ZnCr\(_2\)O\(_4\) could be prepared in a state where \( f_{sp} \) attained its maximum value the splitting would be 2.5 to 4 times greater than that currently measured \( f_2 \).

In summary, we have developed a method to calculate parameters of a spin-phonon theory from first-principles.

![Fig. 2: Phonon frequency of \( \omega_{2}(\hat{z}) \) and \( \omega_{2}(\hat{x}) \) as a function of the Spin-Peierls order parameter \( (S_1 \cdot S_2 - S_1 \cdot S_4) \).](image)

The method accounts for direct exchange which was shown to be responsible for the large magnetic induced anisotropy in the phonon channel of AFM ZnCr\(_2\)O\(_4\) but also equally for superexchange. As a consequence a natural solution to the problem of phonon anomalies in FM spinels is also revealed as a balance between these two processes. \( \text{3} \) We anticipate that the approach developed will also find application to magnetoelectric problems where spin fluctuations coupled to optical phonons have been proposed to explain the magnetocapacitance effect. Given the breadth of such problems today, how the spins couple to the lattice and an approach to calculate the relevant parameters of such a theory from first-principles are important questions that needed to be addressed.

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