Magnetically Induced Phonon Anisotropy in $ZnCr_2O_4$ from First Principles

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We have studied the influence of magnetic order on the optical phonons of the geometrically frustrated spinel $ZnCr_2O_4$ within density-functional theory. By mapping local spin density approximation plus Hubbard U (LSDA + U) 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.

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The interplay between spin and lattice degrees of freedom give rise to an amazing variety of phenomena, including the spin-Teller [1] and the magnetoelectric [2] 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 [3], 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, $ZnCr_2O_4$, crystallizes in a spinel structure. The Cr^{3+} ions ($S = 3/2$) form a network of vertex-sharing tetrahedra 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 the Curie-Weiss temperature, Θ_{CW}). The physics of $ZnCr_2O_4$ 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 bond-ordered state [1,5]. Recently, Sushkov *et al.* [6] measured the reflectivity spectrum of $ZnCr_2O_4$ and found a large infrared-active (ir) phonon splitting (11 cm^{-1}) at T_N. They invoke a coupling between phonons and spins to argue that ir phonons provide a quantitative measure of the spin-Peierls order parameter [1]. Yet, *a priori*, it is unclear whether this spin-phonon mechanism can account for the size of the effect.

We study the influence of magnetic order on the phonon frequencies of $ZnCr_2O_4$ within the LSDA + U method. We give evidence that anisotropy induced by AFM ordering of spins can account for the large anisotropy measured in the ir phonons [6]. We decouple the macroscopic elastic degrees of freedom from those of the spins by calculating the phonons of crystallographically cubic $ZnCr_2O_4$. This approach is similar to that taken by Massidda *et al.* [7] for MnO and naturally decouples the tetragonality induced by the lattice strain at T_N from that generated by the spin pattern alone. In order to understand the calculations, we revisit the long-standing problem of how spins couple to optical phonons [8]:

$$\omega \approx \omega_0 + \lambda\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle.$$

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, λ, for $ZnCr_2O_4$. 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.

Within density-functional theory, the failure of the local spin density approximation (LSDA) properly to capture the physics of strongly correlated systems is well established. The LSDA + U method is a widely successful approach beyond LSDA [9]. In this Letter we perform density-functional calculations using projector augmented-wave potentials within LSDA + U as implemented in the Vienna *ab initio* simulation package [10,11] with a plane wave cutoff of 500 eV and a $6 \times 6 \times 6$ Γ-centered k-point mesh. All calculations were performed with collinear spins and without LS coupling. As expected for Cr^{3+} which lacks orbital degrees of freedom, inclusion of LS coupling does not change the results. We performed full optimization of the lattice parameter, $a = 8.26$ Å (expt: $a = 8.31$ Å), and anion parameter, $u = 0.386$ (expt: $u = 0.387$), in space group Fd$\bar{3}$m, where we find excellent agreement with experiment. Values of the Cr on-site Coulomb, $U = 3$ eV, and exchange, $j = 0.9$ eV, parameters were used that reproduce the dominant features of the photoemission and band gap data in sulfur Cr^{3+} spinels [12]. Although we expect U to be slightly higher in the oxides, these values give a reasonable account of the magnetic exchange constant as we now discuss.

For zinc chromite, the nearest neighbor (nn) 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 [13]. Exchange constants can be extracted by mapping LSDA + U calculations of the total energy for different spin configurations at $T = 0$ onto a classical Heisenberg model; $E_{\rm spin} = -2J\sum_{\langle nn\rangle}\mathbf{S}_i \cdot \mathbf{S}_j$ (sum over $z = 6$ nn's). This gives for the energy of the primitive unit cell (4 Cr ions): $E_{\rm FM} = E_0 - 24JS^2$ and $E_{\rm AFM} = E_0 + 8JS^2$. From this we calculate $J = -2.1$ meV, which compares well with $J_{\rm expt} = [3k_B\Theta_{\rm CW}/2zS(S+1)] = -2.25$ meV.

LSDA + U phonons.—For cubic $\mathrm{ZnCr_2O_4}$, group-theoretical analysis predicts that the 39 zone-center optic modes transform according to the following irreducible representations (irreps) of O_h: $\Gamma_{\rm ir} = 4T_{1u}$, $\Gamma_{\rm Raman} = 3T_{2g} \oplus 1E_g \oplus 1A_{1g}$, and $\Gamma_{\rm silent} = 2A_{2u} \oplus 2E_u \oplus 2T_{2u} \oplus 1T_{1g}$, and the three acoustic modes according to $\Gamma_{\rm acoustic} = 1T_{1u}$. 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 ir-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 ($\mathrm{cm^{-1}}$): T_{2g}: 185 (186), 521 (515), 608 (610); E_g: 466 (457); A_{1g} 687 (692), which are in remarkable agreement ($\sim$1%) with experiment (shown in parenthesis) [14].

We now proceed to the main part of this Letter, the influence of magnetic order on the ir phonons. Under D_{4h} the ir modes split according to $T_{1u} \rightarrow A_{2u} \oplus E_u$, where the 1D A_{2u} and 2D E_u irreps transform like vectors along and perpendicular to the tetragonal axis, respectively. Additionally, certain rows of the silent T_{2u} irrep become ir-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 ir modes originating from T_{1u}. We compute the ir phonons by constructing the three 5×5 blocks (4 ir active, 1 acoustic) of the dynamical matrix from Hellmann-Feynman forces on the symmetry-adapted partner functions, $f_{n,\alpha}$, where $n = 1, 5$ and $\alpha = x, y, z$ label the partner function and the row of T_{1u}, respectively. 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 α 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 ir phonons for crystallographically cubic $\mathrm{ZnCr_2O_4}$ with AFM are shown in Table I labeled LSDA + U. We see that AFM order induces a large tetragonal anisotropy in the phonon sector ($\omega_x = \omega_y \neq \omega_z$) 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), $\Delta\omega = 0.02\omega_z$. (We hold off for now on comparing these results to experiment.) Insight can be gained by looking at the eigendisplacements. 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 α 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 [15]. We understand this from our calculations of the $q = 0$ component of the force constant matrix, $C_{n,\alpha;n',\alpha'}$, where we find $C_{1,x;1,x} = C_{1,z;1,z}$, as you would expect for cubic symmetry. We found similar results in $\mathrm{CdCr_2S_4}$, $\mathrm{CdCr_2Se_4}$, and $\mathrm{HgCr_2Se_4}$ which suggests that the previous interpretation of phonon anomalies in these FM spinels should be revisited [4].

Our LSDA + U calculations clearly show that AFM spin ordering induces a large ir phonon splitting (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, $C_{n,z;n,z}$-$C_{n,x;n,x}$ (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 compared with the other ir modes. But in contrast to what is seen experimentally, the phonon frequencies of all four modes are split.

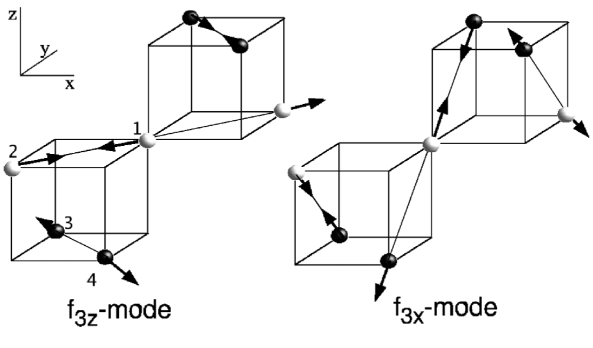

FIG. 1. T_{1u}partner functions f_{3z} (left) and f_{3x} (right). Cr up-spins (white spheres) and Cr down-spins (black spheres) are shown while oxygen atoms sit at the unoccupied corners are not shown for clarity.

TABLE I. Infrared-active T_{1u} phonons frequencies in cm^{-1}.

	Experiment			Present Theory						
	Ref. [6]			Model					LSDA + U	
	13 K	9 K		PM	AFM		$\mathcal{J}''_{\perp}$	$\mathcal{J}''_{\parallel}$	AFM	
		$\hat{x}$	$\hat{z}$		$\hat{x}$	$\hat{z}$			$\hat{x}$	$\hat{z}$
(1)	186	$186 + \delta$		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

Additionally, the calculated splitting of $T_{1u}(2)$, $\Delta\omega = 50\ \mathrm{cm}^{-1}$, is about 4.5 times larger than the measured splitting, $\Delta\omega = 11\ \mathrm{cm}^{-1}$. 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, $E = E_0 + E_{\mathrm{ph}} + E_{\mathrm{spin}}$, of a system of ir phonons, $E_{\mathrm{ph}} = \frac{1}{2}\sum_{\eta\eta'} C_{\eta,\eta'} f_\eta f_{\eta'}$, $\eta \equiv \{n, \alpha\}$ and $C_{\eta,\eta'} = \delta_{\alpha\alpha'} C_{n,n'}$, and spins, $E_{\mathrm{spin}} = -\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$. Without the spin-orbit interaction the spin and phonon sectors are still indirectly coupled due to a positional dependence of the exchange interactions [8]. 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 [13]. In principle J_{ij} depends on the positions of *all* N magnetic and nonmagnetic ions, $J_{ij}(r_1, r_2, \ldots, r_N)$. A solution then becomes clearer if we write J in terms of f_η since these functions provide a complete basis to represent all possible ir atomic motion. For small distortions, J can be expanded in $|f_\eta|$ leading to

$$\tilde{C}_{\eta,\eta'} = C_{\eta,\eta'} - \sum_{ij} \frac{\partial^2 J_{ij}}{\partial f_\eta \partial f_{\eta'}} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$$

to lowest order in $\mathbf{S}_i \cdot \mathbf{S}_j$. 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., $\tilde{C}_{\eta,\eta'} = \tilde{C}_{n\alpha,n'\alpha} \equiv \tilde{C}_{n,n'}(\alpha)$, so in fact we only need to calculate derivatives of the type, $\partial^2 J/\partial f_n \partial f_{n'}$ (magnetic order other than D_{4h} could introduce derivatives connecting different rows of O_h but will not change the value of the intrarow 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 $\hat{\alpha}$ or not. With this let us define $\partial^2 J_{ij}/\partial f_\eta \partial f_{\eta'} \equiv J''_{\perp n,n'} \neq 0 \quad \forall\ \hat{r}_{ij} \cdot \alpha = 0$ and $\partial^2 J_{ij}/\partial f_\eta \partial f_{\eta'} \equiv J''_{\parallel n,n'} \neq 0 \quad \forall\ \hat{r}_{ij} \cdot \alpha \neq 0$, where $\hat{r}_{ij}$ is the direction vector linking nearest neighbor spins, $\mathbf{S}_i$ and $\mathbf{S}_j$. Then we can write

$$\tilde{C}_{n,n'}(\alpha) = C_{n,n'}(\alpha) - J''_{\perp n,n'} \sum_{\hat{r}_\perp} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle - J''_{\parallel n,n'} \sum_{\hat{r}_\parallel} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle,$$

with the first sum over the two neighbors in a plane perpendicular to $\hat{\alpha}$ 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

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

where $\tilde{C}^{\mathrm{FM}}$ and $\tilde{C}^{\mathrm{AFM}}$ are the force constant matrices calculated from first-principles with FM and AFM order, respectively. Here we have three equations and three unknowns. *Notice that this approach now gives a method to approximate paramagnetic (PM) phonon frequencies within* LSDA + U [16]. In Table I we show the $T = 0$ PM phonon frequencies extracted from the model. They are found to be in excellent agreement (1–2%) with those measured at 13 K. To test the validity of the model with respect to 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 $\tilde{C}^{\mathrm{FiM}}(x) = \tilde{C}^{\mathrm{FiM}}(y) = \tilde{C}^{\mathrm{FiM}}(z) = C^{\mathrm{PM}}$. If we now perform LSDA + U calculations of the phonons with FiM magnetic order, we find that the frequencies are in exact agreement ($< 1\ \mathrm{cm}^{-1}$) with those we extracted from the model, i.e., $\omega^{\mathrm{FiM}}_\lambda = \omega^{\mathrm{PM}}_\lambda$ [17]. As a further test we considered additional FiM spin configurations within the conventional unit cell (eight formula units). The model reproduced the LSDA + U calculations to within $1\ \mathrm{cm}^{-1}$ in every case.

Discussion.—Having established that 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 $\partial^2 J_\perp/\partial f_3 \partial f_3 \approx -0.172\ \mathrm{meV/\AA^2}$, more than $\sim$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 $J_d(R_c) \approx J_d e^{-\alpha \Delta R_c}$, where R_c is the distance between neighboring Cr atoms. Assuming the contribution from superexchange (SE) is small, we find $\alpha = 9.05\ \mathrm{\AA}^{-1}$, which compares well with the measured value of $\alpha = 8.9\ \mathrm{\AA}^{-1}$. 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 dominant role of direct exchange in $J''_{\perp 3,3}$ are our calculations for $CdCr_2O_4$. This compound has a larger lattice constant and less negative J than $ZnCr_2O_4$ so that direct exchange is expected to be weaker. Repeating the phonon calculations and mapping procedure for $CdCr_2O_4$, we find $\partial^2 J_\perp/\partial f_3 \partial f_3 \approx -0.09$ meV/Å^2. Considering a small contribution from SE is expected this compares well with $\alpha^2 J = -0.07$ meV/Å^2. Furthermore, no other components of $J''_\perp$ or $J''_\parallel$ change appreciably from those of $ZnCr_2O_4$, consistent with the fact that the only partner function to change R_c is f_3.

The relation between $J''_{\perp 3,3}$ and direct exchange being established, we return to the discussion of the phonon splitting in $ZnCr_2O_4$. To quantify the mode dependence and compare with experiment, let $\mathcal{J}''_\lambda = u^\dagger_\lambda J'' u_\lambda$, where u_λ are the PM dynamical matrix real-space eigenvectors. Then we can write for the phonon anisotropy

$$\omega_\lambda(\hat{z}) - \omega_\lambda(\hat{x}) \approx 4\left(\frac{\mathcal{J}''_{\lambda\parallel} - \mathcal{J}''_{\lambda\perp}}{\omega_{\rm PM}}\right)\langle \mathbf{S}_1 \cdot \mathbf{S}_2 - \mathbf{S}_1 \cdot \mathbf{S}_4 \rangle,$$

where $\langle \mathbf{S}_1 \cdot \mathbf{S}_2 - \mathbf{S}_1 \cdot \mathbf{S}_4 \rangle$ is defined as the spin-Peierls order parameter, $f_{\rm sp}$, [1]. In Table I, we see that the anisotropy experienced by T_{1u} (1) and (2) is due to $\mathcal{J}''_\perp$, which is dominated by $J''_{\perp 3,3}$ and subsequently direct exchange. In contrast, $\mathcal{J}''_\parallel$ plays a large role in the anisotropy of T_{1u} (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, λ, for $T_{1u}(2)$. We find $\lambda_2 = 4(\mathcal{J}''_\parallel - \mathcal{J}''_\perp)/\omega_{\rm PM} \approx 11$ cm^{-1}, which agrees well with experiment, $\lambda_2 = 6$–10 cm^{-1}. Although we may be slightly overestimating λ_2 due to a slight underestimation of the Hubbard-U parameter as discussed, a more detailed study of the dependence of λ on U [4] shows that the agreement with experiment is not sensitive to this underestimation. So from calculations of just the phonons for selected spin configurations, we are able to extract the spin-phonon coupling parameter, λ. It is also now clear why the calculated splittings are significantly larger than those measured. To extract λ we considered the simplest collinear AFM spin structure ($q = 0$) relevant to that observed experimentally. For this uniform spin system (Fig. 5 of Ref. [1]), the spin-Peierls order parameter (OP) obtains its maximum value, $f_{\rm sp} = 4.5$. Experimentally, however, the Néel state involves a nonuniform ($q \neq 0$) distortion and subsequently the extracted value of the spin-Peierls OP (averaged over the unit cell) is much lower, ranging from $f_{\rm sp} = 1.1$ to 1.8. For the calculated value of λ, a value of $f_{\rm sp} = 1$ recovers 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 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.

In summary, we have developed a method to calculate parameters of a spin-phonon theory from first principles. The method accounts for direct exchange which was shown to be responsible for the large magnetic induced anisotropy in the phonon channel of AFM $ZnCr_2O_4$ 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 [4]. 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 prevalence 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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[17] This is not completely correct. The symmetry induced by FiM1 is D_{3h}, and components of the dynamical matrix connecting different rows of the irreps of O_h are not zero. The first-principles phonons were calculated by projecting into the T_{1u} subspace which has the effect of zeroing these "off-diagonal" terms. If one wanted to capture this physics we must include terms like $\partial^2 J/\partial f_{n,\alpha}\partial f_{n',\alpha'}$ with $\alpha \neq \alpha'$, which are not important in the present problem.