

Polar phonons and intrinsic dielectric response of the ferromagnetic insulating spinel CdCr_2S_4 from first principles

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We have studied the dielectric properties of the ferromagnetic spinel CdCr_2S_4 from first principles. Zone-center phonons and Born effective charges were calculated by frozen-phonon and Berry phase techniques within LSDA+ U . We find that all infrared-active phonons are quite stable within the cubic space group. The calculated static dielectric constant agrees well with previous measurements. These results suggest that the recently observed anomalous dielectric behavior in CdCr_2S_4 is not due to the softening of a polar mode. We suggest further experiments to clarify this point.

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Multiferroics (MFs) displaying simultaneous ferroelectric (FE) and magnetic order are receiving considerable attention today.¹ Basic questions on the nature of ferroelectricity required to coexist with magnetism have been addressed,² facilitating the search for new materials.^{3,4} Much effort has been directed towards finding MFs displaying the magnetoelectric effect, due to both the desire to understand this particular fundamental manifestation of spin-lattice coupling and to the potential technological applications of controlling the magnetization (polarization) by an applied electric (magnetic) field.^{5,6}

One avenue for finding new MFs is to revisit known ferromagnetic (FM) insulators to look for ferroelectricity. CdCr_2S_4 is a member of a family of semiconducting FM chalcogenide $A\text{Cr}_2X_4$ spinels with $A=\text{Cd}, \text{Hg}$ and $X=\text{S}, \text{Se}$.^{7,8} The preponderance of evidence shows that CdCr_2S_4 crystallizes in the normal cubic spinel $Fd\bar{3}m$ space group over a wide temperature range, from 4 K (lowest temperature measured) to decomposition temperature. CdCr_2S_4 is a simple Heisenberg ferromagnet with Cr^{3+} spins ($S=3/2$) ordering at $T_c=84$ K ($\Theta_{CW}=155$ K).⁹ The valence band consists of a relatively narrow Cr t_{2g} peak hybridized with mostly sulfur $2p$ states, while Cr e_g states make up the lowest unoccupied states, across a gap of 1.6–1.8 eV, in the conduction band.^{10,11} Early interest in these materials was due to the observed coupling of the electronic structure and the lattice to the magnetic subsystem.^{12–15} While the intrinsic nature of many of these effects has subsequently been questioned,^{16–19} spin ordering has clearly been shown to have a relatively strong effect on the infrared-active and selected Raman-active phonon modes,^{15,18} making the chalcogenide spinels an attractive system to study spin-lattice effects from first principles.²⁰ Recently, CdCr_2S_4 was revisited to look for ferroelectricity, leading to the suggestion that CdCr_2S_4 is in fact a relaxor FE displaying a particularly large magnetocapacitive effect.^{21,22} A broad, frequency-dependent dielectric peak in the real part of the dielectric constant, of the type associated with relaxor behavior, was observed. The dielectric constant at 10 Hz was shown to change by 500% by application of a 5 T magnetic field, with the change decreasing rapidly with increasing excitation frequency. Finally, hysteresis loops which may indicate a nonzero polarization (P_s) were

observed below magnetic T_c (well below the dielectric peak). Octahedral-site Cr^{3+} off-centering was proposed as a possible origin of this polar behavior on the basis of a previous analysis,²³ though such off-centering is unusual for magnetic ions.² The relaxor behavior, associated in perovskites with polar nanoregions frustrated by chemical disorder,²⁴ was suggested to be due to geometrical frustration of local polar distortions which, as in the negative thermal expansion material ZrW_2O_8 ,²⁵ should result in a very-low-frequency polar phonon mode.

First-principles density functional methods have been highly successful in describing the structural, electronic, and magnetic properties of a variety of nonmagnetic and magnetic dielectrics, FEs,²⁶ and multiferroics.^{27–30} First-principles methods have emerged as an ideal technique to differentiate between extrinsic and intrinsic properties of complex dielectrics and FEs, e.g., perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$.³¹ In this paper we investigate the intrinsic FE and dielectric behavior of cubic spinel CdCr_2S_4 from first principles. We calculate all zone-center phonons, Born effective charges, and infrared-active (i.r.) mode oscillator strengths, allowing us to evaluate the static dielectric response of a single-domain, stoichiometric, defect-free crystal and to explore the possibility of a soft-mode-driven ferroelectric instability or very-low-frequency geometrically frustrated polar mode.

First-principles DFT calculations using PAW potentials were performed within LSDA and LSDA+ U as implemented in VASP.^{32,33} The wave functions were expanded in plane waves up to a kinetic energy cutoff of 500 eV. Integrals over the Brillouin zone were approximated by sums on a $6 \times 6 \times 6$ Γ -centered k -point mesh; for density of state calculations this grid was increased to $14 \times 14 \times 14$. Phonon frequencies and eigendisplacements were calculated using the direct method where each symmetry-adapted mode³⁴ was moved by approximately 0.01 Å. Born effective charge tensors were calculated by finite differences of the polarization using the modern theory of polarization³⁵ as implemented in VASP. All calculations were performed with the spin moments on the Cr ions aligned ferromagnetically.

Previous first-principles calculations¹¹ have pointed out the inadequacy of LSDA for investigation of the electronic structure of CdCr_2S_4 . In particular, LSDA fails to open a gap

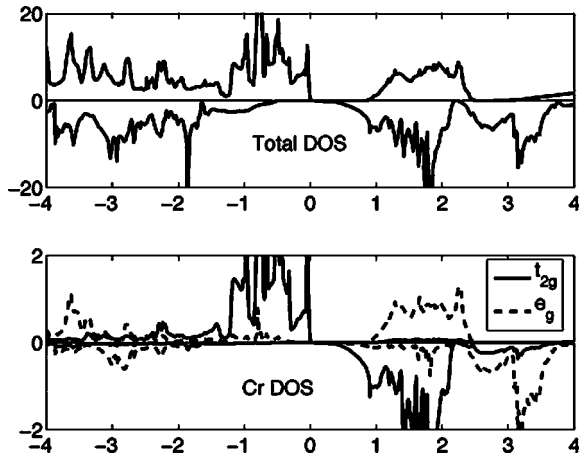


FIG. 1. LSDA total DOS (top) and site-projected DOS on the Cr t_{2g} and e_g orbitals (bottom).

and a Cr t_{2g} peak lies at the edge of the valence band. This failure, and its possible implications for the structural instabilities and dielectric response, can be addressed with LSDA+ U .³⁶ While the value of U could be calculated from first principles with constrained LSDA calculations, we use the alternative phenomenologically determined value $U = 3$ eV, which approximately reproduces the dominant feature of photoemission data,¹⁰ namely a t_{2g} peak 1.6 eV below the valence band.

We performed a full relaxation of the lattice constant, a , and anion internal parameter, u , both within LSDA and LSDA+ U . We find that the LSDA relaxed lattice constant, $a = 10.06$ Å, underestimates the experimental value by 1.8%, slightly more than that typically ($< 1\%$) found for LSDA calculations. Within LSDA+ U we find a value $a = 10.12$ Å in much better agreement ($\sim 1\%$) with the experimental value. This is consistent with other recent studies for LaMnO₃³⁷ and YMnO₃,³⁰ and is worth noting, as the LSDA+ U method has only recently begun to be applied to structural optimization.

The electronic structure of the fully relaxed system within LSDA is similar to that of previous LMTO calculations.¹¹ The total density-of-states (DOS) and site projected DOS for Cr d states are shown in Fig. 1 where a very small nonzero DOS, primarily t_{2g} states of Cr, appears at the Fermi level (note that this result is sensitive to volume where at the experimental lattice constant of $a = 10.24$ Å we find half metallicity with a majority gap of $E_{g\uparrow} = 0.77$ eV). In LSDA, it can also be seen that the t_{2g} orbitals of the valence band occupy states from approximately -0.5 eV up to the Fermi level. Taking $U = 3.0$ eV opens up a gap, $E_g = 1.5$ eV, as shown in Fig. 2, where the top valence band is primarily oxygen p states hybridized with Cr t_{2g} (now pushed down in energy ~ 1.5 eV) while the bottom of the conduction band consists of Cr e_g states with Cd s states forming a wide conduction band. We stress, given the *ad hoc* procedure used to obtain U , these results should only be read as demonstrating that a reasonably good description of the electronic structure of CdCr₂S₄ is possible within LSDA+ U . Further studies should be performed for quantitative features of the electronic structure. In both LSDA and LSDA+ U , the calculated magnetic

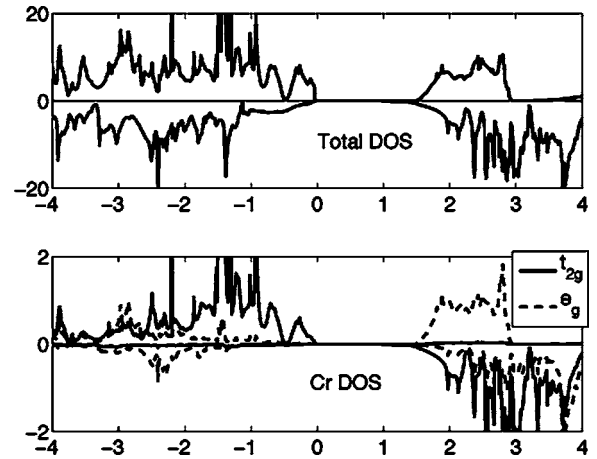


FIG. 2. LSDA+ U , $U = 3$ eV total DOS (top) and site-projected DOS on the Cr t_{2g} and e_g orbitals (bottom).

moments, $\mu = 2.80\mu_b$ and $\mu = 2.9\mu_b$, respectively, are slightly smaller than the $3\mu_b$ expected for Cr³⁺ at nominal valence. We summarize the results and compare with experiment in Table I.

Now that we have determined that a reasonably good description of the structural and electronic properties of CdCr₂S₄ can be obtained within LSDA+ U , we proceed to our main topic, the lattice dynamics and dielectric behavior. In Table II we show our calculated LSDA+ U i.r. active TO and LO modes and compare with those extracted from reflectivity experiments above and below the FM transition. We find that all i.r. modes are stable and in fact are quite hard, with the lowest frequency at 104 cm⁻¹. Agreement of our calculated phonon frequencies with experiment is within 2%, except for mode TO3, which still differs by only $\approx 3.5\%$. To further test the quality of our calculations we computed the Raman active phonons (Table III), where again agreement with experiment is within a percent. This is even better than typical for first-principles phonon calculations, where agreement to one or two wavenumbers should be considered fortuitous. To check the possible effect of the underestimation of the volume on the phonon frequencies, we repeated the calculations at the experimental volume finding very minor changes (e.g., the lowest frequency i.r. mode is now at 102 cm⁻¹). While nonzero U had a noticeable effect

TABLE I. Structural, electronic, and magnetic properties of ferromagnetic CdCr₂S₄, space group: $Fd\bar{3}m$.

	Experiment		Theory	
	300 K	40 K	$U = 3$ eV	LSDA
structure				
a (Å)	10.24	10.23	10.12	10.06
u	0.390	0.390	0.390	0.391
electronic				
E_g (eV)	1.57	1.8	1.47	0.00
magnetic				
μ (μ_b)		3	2.88	2.80

TABLE II. Infrared-active phonons frequencies, ω (cm^{-1}), effective plasma frequencies, Ω_p (cm^{-1}), and dielectric constants of ferromagnetic CdCr_2S_4 , space group: $Fd\bar{3}m$.

	Experiment ^a			Experiment ^b		Theory		LSDA
	300 K	79 K	Ω_p	300 K	15 K	$U=3$ eV		
TO	ω	ω	Ω_p	ω	ω	ω	Ω_p	ω
1				94	102	104	74	104
2				239	249	249	99	247
3	322	327	400	321	324	339	400	322
4	377	379	211	378	379	385	202	366
LO								
1				98	105	107		
2				241	251	251		
3	347	350		349	352	362		
4	390	393		392	395	398		
ϵ_{phonon}	1.9	1.8		2.8	2.8	2.3		
ϵ_{∞}	7.8 \pm 0.2			8.0	7.6			

^aReference 38.^bReference 15.

on the structural parameters, we find that the effect of non-zero U on the phonon frequencies is minimal (with an overall improved agreement with the experimental values) compared with the LSDA, also shown in Table II. Therefore, LSDA+ U provides a consistent theory to compute the lattice, electronic, and magnetic structures of CdCr_2S_4 .

The intrinsic static dielectric response is calculated as

$$\epsilon_0 = \epsilon_{\infty} + \sum_m \frac{\Omega_{p,m}^2}{\omega_m^2}$$

where ϵ_{∞} is the electronic dielectric constant and the second term on the r.h.s., ϵ_{ph} , is the sum of contributions from each i.r.-active phonon, called the oscillator strength. $\Omega_{p,m}$ and ω_m are the effective plasma frequency and i.r. phonon frequency for mode m , respectively. A large dielectric response can be the result of the presence of one or more very-low-frequency polar phonons and/or anomalously large effective plasma frequencies. Although ϵ_{∞} can be calculated from first principles, most readily with density functional perturbation theory,^{39,40} our main interest here is the phonon contribution and thus we use the experimental value $\epsilon_{\infty} \approx 8$. We computed Ω_p within

TABLE III. Raman-active phonons frequencies (cm^{-1}) of ferromagnetic CdCr_2S_4 , space group: $Fd\bar{3}m$.

	Experiment ^a		Theory	
	300 K	40 K	$U=3$ eV	LSDA
$T_{2g}(1)$	101	105	100	99
E_g	256	257	262	257
$T_{2g}(2)$	280	281	282	280
$T_{2g}(3)$	351	353	352	352
A_{1g}	394	396	393	394

^aReference 18.

LSDA+ U from calculations of the Born effective charge tensors and the real-space eigendisplacements of the phonons.³⁹ The results are shown in Table II and compared with available experimental values, where again we find excellent agreement. We see that the most polar mode (TO3), i.e., the mode with the largest Ω_p , is at $\approx 300 \text{ cm}^{-1}$, thus reducing its oscillator strength to $\mathcal{O}(1)$. The lower frequency modes, TO1 and TO2, are weakly polar, as reflected by the very small value of Ω_p , which may be why Ref. 38 classified these modes as nonpolar. Also note, the relative value of Ω_p , low for TO1 and TO2, high for TO3 and TO4, is due to the fact that the eigendisplacements of these modes are qualitatively different. TO1 and TO2 modes consist mainly of Cd^{2+} ions moving against both Cr^{3+} and S^{2-} ions while TO3 and TO4 are dominated by Cr^{3+} moving against S^{2-} . We point out that this qualitative difference of the eigendisplacements is also responsible for the mode-dependent phonon anomalies observed at T_c , which we will explore in a future publication.²⁰ The total contribution to the phonon part of the calculated dielectric constant, $\epsilon_{ph}=2.3$, agrees well with that extracted from reflectivity measurements, $\epsilon_{ph}=2.8$.¹⁵ Note that $\epsilon_{ph}=1.9$ measured in Ref. 38 contains only contributions of TO3 and TO4. This should be compared with our calculations $\epsilon(\text{TO3}) + \epsilon(\text{TO4})=1.7$. Combining ϵ_{ph} with the experimental value of ϵ_{∞} , the computed intrinsic value of the static dielectric constant of CdCr_2S_4 , ϵ_0 , is found to be ≈ 10 . This is completely consistent with the values obtained by reflectivity measurements and the capacitor measurements at 3 GHz of Refs. 21 and 22.

Our first-principles calculations of the phonons and dielectric response clearly show that CdCr_2S_4 has neither a FE instability nor very-low-frequency polar modes, which might be indicative of geometric frustration.⁴¹ In fact, the intrinsic dielectric response of CdCr_2S_4 is found to be that of a normal dielectric. Further, the lack of a zone-center FE instability implies that no P_s is expected at low temperatures. These results are in direct contrast to previous first-principles cal-

culations of perovskite relaxors (on ordered supercells) where FE instabilities and anomalously large Born effective charges, yielding large oscillator strengths for certain modes, are found.^{42,43}

We considered the possibility of other structural instabilities, in particular a Cr-off-centering antiferroelectric transition to the $F\bar{4}3m$ space group. In our 14-atom unit cell, this would be produced by the freezing-in of a silent zone-center A_{2u} phonon. The possibility of a phase transition of this type has been the subject of previous speculation (but never experimentally demonstrated) for many spinels.^{23,44} Our calculation reveals that both A_{2u} modes are quite hard, with frequencies greater than 300 cm^{-1} . In addition, the frequencies of the other silent zone-center phonon modes, E_u , T_{1g} , and T_{2u} , were all calculated to be greater than 100 cm^{-1} .

What then could be the origin of the anomalous dielectric response reported for CdCr_2S_4 ? While our results clearly rule out soft polar modes, one possibility might be the coupling of a polar mode to a zone-boundary mode, as we previously have suggested happens for YMnO_3 (note, unlike that of YMnO_3 , symmetry would require this transition to be first order). A related mechanism might involve coupling to an incommensurate structural distortion. Although most previous experiments are inconsistent with such a picture, we suggest that detailed structural experiments should be per-

formed. From the theoretical side, first-principles calculations of the phonons throughout the Brillouin zone will provide further insight into this type of scenario. Another possibility our work suggests is that the dielectric response and polarization observed in Refs. 21 and 22 may not be intrinsic.³¹ While experimentally the issue of contacts has been explored, less has been done (to our knowledge) to characterize the defect structure.⁴⁵ This is important given the recent claims that the low-temperature polarization and the relaxor behavior disappears in annealed single crystals and polycrystalline samples.⁴⁶ We suggest controlled defect experiments be performed to gain a more precise understanding of this effect.

To summarize, the computed dielectric constant of 10 is consistent with the measurements at frequencies $\mathcal{O}(\text{GHz})$, while no i.r. active phonon of the cubic spinel structure can account for the larger responses observed at lower frequencies. This suggests that the origin for the observed relaxor behavior in CdCr_2S_4 is something other than a dispersive polar soft mode.

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