CdV$_2$O$_4$: A rare example of a collinear multiferroic spinel

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By studying the dielectric properties of the geometrically frustrated spinel CdV$_2$O$_4$, we observe ferroelectricity developing at the transition into the collinear antiferromagnetic ground state. In this multiferroic spinel, ferroelectricity is driven by local magnetostriction and not by the more common scenario of spiral magnetism. The experimental findings are corroborated by ab-initio calculations of the electric polarization and the underlying spin and orbital order. The results point towards a charge rearrangement due to dimerization, where electronic correlations and the proximity to the insulator-metal transition play an important role.

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FIG. 1: (Color online) Thermal expansion $\alpha$ in the whole temperature range (a) and in the vicinity of the magnetic transition (a1). The complex dielectric permittivity $\varepsilon^*$ of CdV$_2$O$_4$ is displayed as real part $\varepsilon'$ (b) and as dielectric loss $\varepsilon''$ (c) for different frequencies between 82 Hz and 0.3 MHz measured with a stimulus of $\sim$1 V/mm. The data displayed in frame b1) was measured in the vicinity of the orbital order transition at 1 Hz in external fields of zero and 10 T. Frame b2) shows the small dielectric anomaly at the structural transition below 100 K.

Results of the dielectric measurements are shown in Figs. 1 and 2. The dielectric permittivity displays a small anomaly at the structural transition temperature $T_S \approx 95$ K (Fig. 1b2) and a sharp jump-like anomaly at the magnetic transition $T_N \approx 33$ K. The latter slightly depends on an external magnetic field as demonstrated by the data for zero field and 10 T displayed in Fig. 1b1: the anomaly shifts slightly to lower temperatures under applying a magnetic field. At the same time, the permittivity possesses a distinct frequency dependent contribution superimposed on the described features: a step in $\varepsilon'(T)$ is accompanied by a peak in $\varepsilon''(T)$ shifting to lower temperatures with decreasing frequency. A very similar relaxational contribution along the $c$-axis was found in multiferroic rare earth manganites. There, it was ascribed either to the freezing of an overdamped polar lattice-mode or, alternatively, one could think of the relaxation of localized polarons at defect states [17]. In any case these data demonstrate that the dielectric properties are to some extent influenced by the experimental time window.

That the sharp dielectric anomaly at $T_N$ is connected with the onset of spontaneous electric polarization is demonstrated in Fig. 2b, displaying the electric polarization $P(T)$. The difference between the cooling data detected in the presence of an electric poling field, com-
The explanation of the appearance of polarization in CdV$_2$O$_4$ has some analogy with the mechanism proposed for E-type manganites \[13, 18\]. The distortion, in particular the shifts of oxygens, are different in the vicinity of ferromagnetic bonds and antiferromagnetic ones. The main feature of the corresponding lattice distortions is the dimerization of V-V bonds \[12\], but the shifts of the oxygens are also present, which ultimately lead to polarization. A specific feature of spinels, \textit{i.e.} the existence of \textit{two} oxygens “attached” to each V-V bond, compared to \textit{one} oxygen in E-type manganites, makes the picture more complicated, but the main physical mechanism is very similar.

In order to shed light into the origin of the ferroelectricity, we performed ab-initio calculations using the projector augmented-wave (PAW) method \[19\] with plane-wave basis sets as implemented in the VASP program \[20\]. To describe the correlation effects of V-3d electrons, we used the DFT+U method \[21\], for different values of $U_{eff} = U - J_H$ ranging between 0 and 8 eV, and the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional \[22\]. The HSE has been shown to provide an accurate treatment of solid state systems when the delicate balance between itinerancy and localization of correlated states plays an important role \[23\], as in the system under study \[12\].

Starting from the tetragonal experimental crystal structure with $I4_1/amd$ centric symmetry \[24\], we performed ionic relaxations for different values of $U_{eff}$, keeping the V magnetic moments ordered as $\uparrow\downarrow\downarrow\downarrow$ along the [101] and [011] directions (see Fig. 3a). The relaxed structure shows the formation of short (S) and long (L) bonds between $\uparrow\uparrow$ and $\downarrow\downarrow$ moments, respectively, see also \[12\]. The situation seems to be different in MgV$_2$O$_4$ \[25\]. Our relaxed structure has a $I4_1$ polar space group. For large values of $U_{eff}$, the general trend towards formation of V-V dimers is reduced. Note that, imposing the ferromagnetic spin ordering, the structure retains the inversion symmetry, and no dimerization is found for any values of $U_{eff}$. Further inspection of the relaxed polar structures shows that the spin, orbital and lattice degrees of freedom are coupled: in plane $xz, yz$ long bonds are oriented as reminiscent of a Kugel-Khomskii model \[26\] and of the experimental structure proposed for ZnV$_2$O$_4$ \[27\] (see Fig. 3b). For the relaxed structure, we evaluated the ferroelectric polarization $P_{BP}$ (see Fig. 3b) according to the Berry phase theory \[28\]. We obtained a finite $P_{BP}$, directed along the c-axis, which is strongly related to the formation of a dimerized structure at intermediate values of $U_{eff}$. The electronic charge redistribution due to dimer formation gives rise to differences between the BP and the point charge model (PCM) values of $P$. The red curve in Fig. 3b) is the total polarization, ionic plus electronic (BP) contribution, \textit{i.e.} $P_{BP}$, the grey one is the estimate of the point charge model (using the ionic nominal valencies). The fact that they are different suggests

![FIG. 3: (Color online) Schematic view of a) the V-O ionic arrangements with spin magnetic structure (see black arrows) and short (long) V-V bond lengths highlighted by dashed (bold solid) lines; a’) oxygen-induced dipoles (see ellipses) and long bond-length V-O (see black lines) - symmetry inequivalent oxygens are denoted with different symbols/colors; b) calculated polarization according to DFT+U (left) and HSE schemes (right); V and O arrangement for c’ $\uparrow\uparrow\uparrow\uparrow$ and c’) $\uparrow\uparrow\downarrow\downarrow$ spin ordering along [101] or [011]; d) values of $\alpha_1$, $\beta_2$, $\alpha_2$, $\beta_1$ angles as a function of $U_{eff}$.](https://example.com/figure3.png)
that covalency effects are relevant.

We now discuss the mechanism behind ferroelectricity. First of all, let us recall that if we consider a FM (↑↑↑↑) state with the suggested experimental $I_{41}/amd$ symmetry, all V-O angles are equivalent along the chain (see Fig. 3a). Note, however, that V-O distances are slightly different, due to the peculiar coordination of the spinel structure: each O is an “apical” one with respect to one V ion and a “planar” one with respect to the other neighboring V ion. This does not exclude a priori some degree of orbital-ordering, even in a FM spin configuration. As expected from the centrosymmetric space group, no polarization is found from our calculations for this case. However, once the magnetic order ↑↑↓↓ is imposed, (i) the angles $\alpha_1$ and $\beta_2$ ($\alpha_2$ and $\beta_1$) become inequivalent as a consequence of the formation of short/long V-V bonds; (ii) $\alpha_1$ and $\beta_1$ become different. The long V-O bonds are arranged as shown in Fig. 3b. This pattern is compatible with a weakly staggered $xz, yz$ orbital ordering. As a result, the dipole moments $P'$ and $P''$, originating from the inequivalency of oxygens, and schematically shown in Fig. 3a, appear due to different $\alpha_1$ and $\beta_2$ ($\alpha_2$ and $\beta_1$) angles; since $P'$ and $P''$ don’t compensate, they give rise to a net $P$. This picture is valid for intermediate values of $U_{eff}$. At large values of $U_{eff}$, however, the inequivalence of $\alpha_1$ and $\beta_1$ ($\alpha_2$ and $\beta_2$) V-O-V angles disappears, see point (i) above, whereas (ii) is still valid. (see Fig. 3b1); as a result, $P$ is suppressed, but is still non-zero. In other words, the ↑↑↓↓ spin ordering, imposed onto the centric $I_{41}/amd$ space group, gives rise to an electronic instability which ultimately results in a V-V dimerization and formation of short and long V-O bonds, compatible with a staggered $xz, yz$ orbital ordering. This electronic instability is already evident before ionic optimization: the two ↑ (↓) V sites are inequivalent by symmetry, and, upon ionic relaxations, this inequivalency eventually drives the V-V dimerization. Also the two oxygens bonded to ↑↑ (or ↓↓ V) become inequivalent, in turn giving rise, upon ionic relaxations, to a weakly staggered orbital ordering. Both effects cooperate to stabilize the polarization.

Thus the theoretical results confirm, first of all, the structure proposed in [12], with dimerization in V-V chains in $xz$- and $yz$-directions. Furthermore, they show that CdV$_2$O$_4$ is ferroelectric. The calculated polarization is along the $c$-direction, and its value is $P \approx 200 \mu$C/m$^2$. This is typical for multiferroics with ferroelectricity induced by magnetostriction, like HoMnO$_3$ or YMn$_2$O$_5$, see e.g. [14]. The fact that the experimentally observed value is smaller, $P \approx 5 \mu$C/m$^2$, see above, is rather common. The same happens in HoMnO$_3$: the measured value in polycrystalline material $P \approx 90 \mu$C/m$^2$ [14] is smaller than the theoretical value [14] - which however agrees with the estimates obtained from optical studies [29]. Most likely it is connected with the polycrystalline nature of the samples: first, polarization is averaged over all directions, but most important is that probably in these granular materials one does not reach full domain orientation during the poling procedure used.

Why the polarization is absent in the measured samples of ZnV$_2$O$_4$ and MgV$_2$O$_4$, is not completely clear. Theoretically we could expect that these spinels, with very similar structure, could be also multiferroic. One of the reasons could be that these materials have much smaller gaps than CdV$_2$O$_4$ and are close to the localized-itinerant crossover [16]. The finite conductivity of these samples ($\times 10^4$ times higher than in CdV$_2$O$_4$ [12]) may scramble the results of the measurements. The quality of the samples may also matter. In any case, this question deserves further study.

Summarizing, we discovered the first multiferroic ternary spinel with collinear magnetic structure, CdV$_2$O$_4$. We thus show that not only a spiral magnetic structure can produce ferroelectricity in spinels; the magnetostriction mechanism can do it as well. In the latter case, polarization is usually even larger than in spiral magnets, which is also the case here. Our study also clarifies the very controversial question about orbital ordering and structural distortions in V-spinels, confirming that there should appear a strong V-V dimerization, that is also responsible for polarization. We conclude by suggesting that similar phenomena might occur in other spinels, thus broadening the class of multiferroic systems to this important group of materials.

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