Exchange striction induced giant ferroelectric polarization in copper based multiferroic material $\alpha$-Cu$_2$V$_2$O$_7$.

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We report $\alpha$-Cu$_2$V$_2$O$_7$ to be an improper multiferroic with the simultaneous development of electric polarization and magnetization below $T_C = 35$ K. The observed spontaneous polarization of magnitude 0.55 $\mu$Ccm$^{-2}$ is highest among the copper based improper multiferroic materials. Our study demonstrates sizable amount of magneto-electric coupling below $T_C$ even with a low magnetic field. The theoretical calculations based on density functional theory indicate the important role of spin orbit coupling on the magnetic properties of the system, however the origin of giant ferroelectric polarization is primarily due to the symmetric exchange-striction mechanism.

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Recently multiferroic materials with mutually coupled ferroelectric (FE) and magnetic orders have attracted considerable interest for their versatile technological as well as fundamental importance. A strong magneto-electric (ME) coupling is expected in improper magnetic multiferroics where ferroelectricity is induced by a specific magnetic order. In the last one decade, several magnetic multiferroics have been discovered and the examples include rare-earth manganites (TbMnO$_3$, DyMnO$_3$, HoMnO$_3$, RMnO$_3$ with R = Tb, Dy etc.), vanadates (Ni$_3$V$_2$O$_6$), chromate etc. In most of these multiferroics, FE polarization is either associated with spiral magnetic structure induced via spin-orbit coupling (SOC) or by symmetric exchange striction (SES) mechanism in case of collinear magnets. Due to the secondary nature of the electric order, the value of the FE polarization in such magnetic multiferroics is much smaller (generally $\sim 0.01 \mu$C.cm$^{-2}$) compared to the ‘proper’ FE.

It is therefore pertinent to look for materials among magnetic multiferroics where the net electric polarization ($P$) is high along with significant ME effect. Recently, giant ferroelectricity ($P \sim 0.3 \mu$C.cm$^{-2}$) and large ME coupling has been reported in case of a mixed valent manganate CaMn$_2$O$_{12}$ below about 90 K mediated by both SOC induced Dzyaloshinski- Moriya (DM) interaction as well as exchange striction mechanism working in tandem.

In order to search for a multiferroic material as an alternative to manganites with large value of $P$ and possibly mediated by a similar coupled mechanism, we investigated the Cu-based oxide Cu$_2$V$_2$O$_7$ in its orthorhombic $\alpha$ phase. Cu$_2$V$_2$O$_7$ crystallizes in at least three different polymorphs, namely (i) $\alpha$-phase which is orthorhombic and noncentrosymmetric, (ii) $\beta$-phase which is monoclinic and centrosymmetric and (iii) $\gamma$-phase which crystallizes with triclinic structure. However noncentrosymmetric $\alpha$-Cu$_2$V$_2$O$_7$ phase is only found to be important as far as the multiferroicity is concerned. It consists of magnetic Cu$^{2+}$ (3$d^9$, $S = \frac{1}{2}$) and nonmagnetic V$^{5+}$ ($3d^0$, $S = 0$) metal ions making it a system having both partially filled and empty $d$ shells similar to BiFeO$_3$, BiMnO$_3$, Pb(F$_{2/3}$W$_{1/3}$)O$_3$ etc. All Cu$^{2+}$ ions are equivalent with fivefold coordination to oxygen atoms forming a distorted [CuO$_x$] polyhedron. Each Cu-polyhedron is linked with another two via edge sharing and they together form two sets of mutually perpendicular zig zag chains (see Fig. 1). These chains are separated by V$_2$O$_7^-$ anionic group resulting from the two corner sharing VO$_4$ tetrahedra.

The magnetic behavior of $\alpha$-Cu$_2$V$_2$O$_7$ have been investigated earlier on polycrystalline samples. It was reported that $\alpha$-Cu$_2$V$_2$O$_7$ is an antiferromagnet with weak ferromagnetism at low temperature. A magnetic order was seen below 35 K ($T_C$) accompanied by a change in slope in dielectric response near $T_C$. In this letter, a combined theoretical and experimental work establish that the compound is a multiferroic with giant $P$ and ME effect where the origin of giant FE polarization is primarily due to symmetric exchange-striction mechanism.

The experimental studies including magnetic, dielectric and electric polarization measurements were performed on a well characterized sintered polycrystalline sample. Polycrystalline sample of Cu$_2$V$_2$O$_7$ was prepared by a conventional solid state reaction route in air. Highly pure CuO and V$_2$O$_5$ were mixed thoroughly in a stoichiometric ratio and homogenized with ethanol in an agate mortar. The mixture was pressed into pellets and sintered at 600°C for 90 h with several intermediate grindings. We found that any high temperature sintering results in the formation of $\beta$ phase which is non ferroelectric. Room temperature powder X-ray diffraction (XRD) pattern recorded using Cu Kα radiation ensures the single phase of the polycrystalline sample with no detectable secondary phase. Rietveld refinement analysis was performed with the help of MAUD software on the powder XRD pattern. The reliability factor of the fitting is $\sigma = 1.61$ which is reasonably good. The lattice parameters of orthorhombic crystal structure with $F\bar{d}d\bar{2}$ space group were found to be $a = 20.692$ Å, $b = 8.413$ Å and $c = 6.451$...
The Cu-O-Cu and V-O-V angles are found to be 106° and 148° respectively. These angles as well as Cu-O and V-O bond lengths agree well with the previous work on the structure of α-Cu$_2$V$_2$O$_7$.\[10\]

The magnetic measurements were performed on a Quantum Design SQUID magnetometer (MPMS-4, Evreco). The ac dielectric measurements were performed using an Agilent E4980A precision LCR meter in the temperature range 5-300 K in a helium closed cycle refrigerator. An electromagnet with maximum field strength of 9 kOe (at 5 cm pole separation) was used to apply magnetic field during dielectric measurements. The pyroelectric current of the sample was measured using a Keithley Electrometer (model 6517B) in the helium closed cycle refrigerator. Polarization hysteresis loops ($P-E$) at different constant temperatures were measured by a Ferroelectric Loop Tracer from Radiant Technology (Precision Premier-II) in a helium closed cycle refrigerator.

All the electronic structure calculations presented in this paper are performed using first principles density functional theory (DFT) within local density approximation (LDA) including Hubbard $U$\[33\] using projector augmented-wave (PAW) method\[24, 25\] encoded in the Vienna \textit{ab initio} simulation package (VASP)\[26, 27\]. The values of on-site Coulomb interaction ($U$) and Hund’s rule coupling ($J_H$) parameters were taken as $U=7.5$ eV, $J_H=1.0$ eV\[33\]. The energy cutoff for the plane wave expansion of the PAWs was taken to be 550 eV. A $(4\times4\times4)$ k-mesh has been used for self consistency. Symmetry has been switched off in order to minimize possible numerical errors. The calculation for the ferroelectric polarization with FM, AFM and NONC magnetic configuration are carried out using Berry phase method\[34\] as implemented in the Vienna \textit{ab initio} simulation package (VASP).

Fig. 2 (a) describes magnetization ($M$) vs temperature ($T$) data in zero-field-cooled-heating (ZFC), field-cooling (FC) and field-cooled-heating (FCH) protocols under magnetic field $H=100$ Oe. $M(T)$ shows a sharp rise at $T_C = 35$ K indicating the transition to a magnetically ordered state. The thermal hysteresis between FC and FCH around $T_C$ indicates the first order nature of this transition. The inverse molar susceptibility ($\chi^{-1}(T)$, where $\chi = M/H$) obeys Curie-Weiss law above 80 K (see inset of fig. 2(a)) and we get Curie-Weiss temperature ($\theta_C$) to be $\approx -78$ K which indicates the predominant antiferromagnetic (AFM) correlations in the system. The effective moment of Cu$^{2+}$ is $\approx 1.92 \mu_B$ and it is slightly higher than the spin-only value ($= 1.73 \mu_B$). At low $T$, $M$ almost saturates which is not a likely behavior of a pure AFM ordering. Possibly, the magnetic state below $T_C$ is canted AFM type. This type of spin canting often occurs due to the DM-type interaction between the neighboring spins. The isothermal $M$ vs $H$ at 5 K for $H = \pm 9$ kOe is shown in the main panel of Fig. 2 (b). The curve shows clear hysteresis which reaffirms the presence of ferromagnetic (FM) component. The coercivity of the loop is found to be about 2 kOe. The full loops both at 5 K and at 150 K (well above $T_C$) are shown in the inset. The $M-H$ curve at 5 K, however, does not show full saturation even at 50 kOe, and it once again indicates canted spin structure. We can fit the high field data (between $H = 30-50$ kOe) with an empirical relation $M(H) = \chi_{afm}H + M_S$, where $\chi_{afm}H$ is the linear term due to AFM component and $M_S$ is the saturation magnetization due to the FM part. We find $M_S$ to be $0.08 \mu_B$/f.u., which is quite small compared to the full saturation moment of two Cu$^{2+}$ ($\approx 2 \mu_B$) ions indicating the presence of weak ferromagnetism. Interestingly, the 5 K isotherm is not found to be quite smooth, and it contains signature of sharp jump whenever the field changes its sign. This may indicate the presence of uniaxial anisotropy in the system.

Fig. 3 (a) shows the $T$-variation of the real part of the complex dielectric permittivity ($\varepsilon'$) measured at different frequencies ($f$). $\varepsilon'$ is almost constant and independent of $f$ in the low-$T$ regime (below $\sim 130$ K) which signifies the static dielectric constant originating from the intrinsic contribution\[28\]. A closer look at low-$T$ part shows the existence of a small but clear hump-like anomaly around 35 K at which the canted-AFM transition occurs, which is shown prominently in the inset of Fig. 3 (a). This hump like behavior does not show any frequency dispersion, suggesting that this feature may be related to some long range electric order. It is to be noted that the imaginary part of permittivity is quite small (particularly below about 130 K) indicating that the sample is highly
resistive and the estimated resistivity at 50 K is found to be $\sim 100$ MΩ·cm.

Considering the electric anomaly near the magnetic transition, it is tempting to measure the magneto-dielectric properties of the sample. Fig. 3 (b) shows the $T$ variation of $\varepsilon'$ measured at $H = 0$ and 9 kOe. Clearly, $\varepsilon'$ shows significant effect of magnetic field below about 80 K. In the inset of fig. 3 (b), we have plotted the change in $\varepsilon'$ as a function of $T$ due to the application 9 kOe of field and we observe a significant value of magneto-dielectric effect (as high as 3.5%) at around 30 K. This is quite large considering the small value of the applied field.

In order to shed more light on the nature of the hump-like feature observed in the $\varepsilon'(T)$ coincidence with the magnetic anomaly at $T_C$, we performed the measurement of pyroelectric current ($I_P$) after cooling the sample from room temperature with different electric field ($E_{\text{cool}}$). From the $T$ variation of $I_P$, spontaneous polarization has been calculated (see fig 3 (c)), which we denote by $P_I$. Clearly $P_I$ shows a sharp increment below about 35-40 K, eventually saturating at a lower temperature. This is an indication of the development of spontaneous polarization in the system. The magnitude of $P_I$ clearly increases with the cooling field. We also measured $P_I$ with different polarity of $E_{\text{cool}}$ and $P_I$ changes sign depending on the chosen sign of $E_{\text{cool}}$ (see inset of fig. 3 (c)). Such behavior of $P_I$ confirms that the sample undergoes long range FE order below 35 K with the development of spontaneous polarization. Since, the electric order is concomitant with the magnetic order, the sample can be assigned as an improper multiferroic material. It is to be noted that even at room temperature $\alpha$-Cu$_2$V$_2$O$_7$ possesses a non-centrosymmetric crystal structure with polar point group $(mm2)$, which in general belongs to the pyroelectric class of crystals. However, a switchable spontaneous $P_I$ is only achieved below $T_C$, possibly arising from the favorable lattice distortion associated with the magnetic order. Remarkably, from the pyroelectric measurement the saturation value of the spontaneous $P_I$ is found to be as large as $0.55 \mu$C cm$^{-2}$, which is substantially high compared to the other copper based magneto-electrically driven ferroelectrics to date.

The ferroelectricity is further confirmed by the measurement of electric polarization versus electric field ($P - E$) loop using a FE loop tracer as shown in fig. 3 (d). The data recorded above $T_C$ (50 K and 80 K) do not show any loop, whilst clear loops with tendency for saturation are observed at 10 K and 30 K (which are below $T_C$). Observation of such prototypical hysteresis loop in $P$ is an essential proof for the development of FE state below $T_C$. At the value of $E = 1$ kV cm$^{-1}$ hysteresis almost closes and we get a value of polarization close to $1 \mu$C cm$^{-2}$.

The experimental results discussed above lend support to the fact that ferroelectricity is induced by magnetism in $\alpha$-Cu$_2$V$_2$O$_7$ resulting in substantially large magneto-dielectric response. It is also interesting to note that the magnetic transition at $T_C$ is first order in nature which indicates possible structural transition associated with the magnetic as well as electric orderings. In view of the above, both exchange striction as well as inverse DM effect may be the likely mechanism for the giant FE polarization in $\alpha$-Cu$_2$V$_2$O$_7$. An essential ingredient for the DM interaction is the SOC, which is not unlikely in a Cu$^{2+}$ system. From the Curie-Weiss fit to the $1/\chi$ versus $T$ data, the obtained effective moment per Cu site (1.92 $\mu_B$) is bit higher than the spin only moment (1.73 $\mu_B$). This is presumably due to the orbital contribution of the magnetic moment and hence finite SOC is justified. It is to be noted that the spontaneous polarization in $\alpha$-Cu$_2$V$_2$O$_7$ is about one order of magnitude higher than the other spiral DM type multiferroics (such as TbMnO$_3$, where $P \sim 0.5 \mu$C cm$^{-2}$). Therefore, the exact origin of FE state in the studied compound may involve more complex mechanism.

In order to understand the electronic structure, the exchange mechanism and the origin of ferroelectric polarization, we have performed first principles DFT calculations, using VASP. The non-spin polarized electronic structure calculations reveal that the oxygen $p$-states are completely occupied while the vanadium-$d$ states are empty and the Fermi level is hosted by half-filled predominantly Cu-$d_{x^2-y^2}$ states consistent with the Cu$^{2+}$V$_{5+}$O$_7$ nominal ionic formula for the system. To account for the
observed magnetism in this system, we have evaluated various symmetric spin exchange interactions between the Cu-ions by performing total energy calculations in the framework of LDA + U method for various ordered spin states and then mapping them on to the corresponding spin exchange energies of the Heisenberg model. The value of $U_{\text{eff}}(U - J)$ was taken to be 6.5 eV following the usual choice for the cuprates.\cite{32} Constraining the range of interaction to 5.42 Å, we calculated five dominant exchange interactions (the various spin-exchange paths are shown in Fig. 1(a)).

The dominant exchange interaction $J_3$ (-13.61 meV) is antiferromagnetic, followed by $J_1$ (-4.67 meV) and $J_2$ (4.07 meV) which are AFM and FM respectively. Other exchange interactions $J_4$ (0.26 meV) and $J_5$ (2.37 meV) are small and FM. The AFM exchange interactions $J_1$ and $J_3$ are mediated via Cu-O-Cu and Cu-V-O-V-Cu paths respectively [See Fig. 1(b)]. The larger bond angles in the $J_3$ exchange path make this interaction stronger compared to $J_1$. On the other hand, FM exchange interaction $J_2$ is mediated by the exchange path Cu-O-Cu. In this case, the two O atoms that mediate the exchange interaction between Cu ions are at an angle (\angle Cu-O-O) of 70.07° and thereby favoring FM interaction. Using the computed exchange parameters, the Curie-Wieess temperature $\theta_C$ for \(\alpha\)-Cu$_2$V$_2$O$_7$ is calculated to be -77.4 K which is remarkably close to the experimental value (-78 K).

In the absence of any spin frustration, the canted AFM suggested by the $M - H$ curve may be attributed to the DM-type interaction due to SOC. We have therefore considered the antisymmetric part of the spin Hamiltonian \(\mathcal{H} = \sum_{ij} \bar{D}_{ij} \cdot \bar{S}_i \times \bar{S}_j\) and calculated the three components $\bar{D}^x$, $\bar{D}^y$, $\bar{D}^z$ of the DM parameter up to 3rd nearest neighbor for \(\alpha\)-Cu$_2$V$_2$O$_7$ by performing LDA + U + SOC calculations. The ratio $|\bar{D}|$ ~ 0.5 suggests unusually strong DM interaction in \(\alpha\)-Cu$_2$V$_2$O$_7$ very similar to that reported for CaMn$_2$O$_7$ system \cite{15}. The calculation of magnetocrystalline anisotropy energies reveal $b$-axis of the conventional unit cell to be the easy axis.

In view of the importance of the SOC, in addition to FM and AFM magnetic configuration, we have considered non-collinear (NONC) magnetic configuration as shown in Fig.4. In our model NONC magnetic configuration, the nearest neighbor spins in each zig-zag chain are antiparallel where the direction of the spins are chosen to be perpendicular to the zig-zag chain direction but lying in the $bc$-plane. Our calculations reveal among the chosen magnetic configurations, the non-collinear magnetic structure has the lowest energy (See Table I) with a small magnetic moment 0.16 $\mu_B$/f.u.

| Config. | $\Delta E$ (meV) | $\Delta P_{SOC}$ ($\mu$C cm$^{-2}$) | $\Delta P_{ex}$ ($\mu$C cm$^{-2}$) |
|---------|-----------------|-------------------------------|-------------------------------|
| FM      | 0.0             | 0.01                          | 3.85                          |
| AFM     | -15             | 0.03                          | 4.33                          |
| NONC    | -30             | 0.04                          | 4.21                          |

Finally, we have calculated the FE polarization for the FM, AFM and NONC magnetic configuration using Berry phase method \cite{34} as implemented in VASP \cite{26}. In order to understand the contribution of SOC and exchange striction on ferroelectric polarization, calculations are carried out for the experimental structure including SOC and the relaxed structure without SOC respectively. The results of our calculation (Table I) although suggest...
the importance of SOC but conclusively establish that exchange striction is the primary mechanism for the giant ferroelectric polarization for this system. As shown in Fig. 1(c), as a result of exchange striction there is a compression of the CuO$_5$ polyhedron, resulting in the reduction of the bond length in the exchange path $J_1$ and increase in the bond length in the exchange path $J_2$ (See Table II). Such a modulation of the bond length induces spin-phonon coupling resulting in a giant FE polarization.

| Structure              | Change in Cu-Cu bond lengths upon relaxation (Å) |
|------------------------|-----------------------------------------------|
|                        | corresponding to the following exchange paths |  
|                        | with respect to the experimental structure     |  
|                        | $J_1$  | $J_2$  | $J_3$  | $J_4$  | $J_5$  |
| NM+U relax             | 0.0    | -0.01  | 0.0    | 0.0    | 0.0    |
| FM+U relax             | -0.07  | 0.25   | -0.01  | 0.0    | 0.0    |
| FM+SOC+U relax         | -0.07  | 0.25   | -0.01  | 0.0    | 0.0    |
| AFM+U relax            | -0.06  | 0.22   | -0.01  | 0.0    | 0.0    |
| AFM+SOC+U relax        | -0.06  | 0.22   | -0.01  | 0.0    | 0.0    |
| NONC+U relax           | -0.06  | 0.22   | -0.01  | 0.0    | 0.0    |
| NONC+SOC+U relax       | -0.06  | 0.22   | -0.01  | 0.0    | 0.0    |

In conclusion, we have found that $\alpha$-Cu$_2$V$_2$O$_7$ is a magnetic multiferroic material with sizable amount of ME coupling. The multiferroic properties of this sample is interesting due to large FE polarization as compared to other known copper based multiferroic oxides. $\alpha$-Cu$_2$V$_2$O$_7$ turns out to be an unique example of multiferroic material with single valent Cu$^{2+}$ ions where SOC is responsible for its magnetic properties while symmetric exchange striction is the primary mechanism that give rise to giant electric polarization.

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