Role of the magnetic ordering on the dielectric response of $M_2V_2O_7$ (M = Co and Cu) divanadates

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We have synthesized two divanadates $M_2V_2O_7$ ($M^{2+} = Co^{2+}$ and Cu^{2+}), that are known to show different and complex magnetic arrangements at low temperatures and have studied their dielectric behavior. We have observed a change in the slope of the dielectric constant at the magnetic transition temperature, result which confirms the existence of magnetodielectric coupling in these two divanadates. The origin of the magnetodielectric coupling seems to be different in the Cu- and Co-compounds, although in both cases it is related to their frustrated magnetic arrangement. In $Cu_2V_2O_7$, the dielectric anomaly arises from a spin canting due to the antisymmetric exchange which is allowed by structural symmetry. In the Co-divanadate, the structural symmetry does not allow antisymmetric exchange but the compound shows correlation between the behavior of the dielectric constant and inverse magnetization, which points to a dependence of its electrical polarization with the pair correlation function of neighboring magnetic spins. © 2011 American Institute of Physics. [doi:10.1063/1.3556448]

I. INTRODUCTION

The family of vanadium oxides shows a large variety of crystal structures where the main building blocks are various extended units of vanadium-oxygen polyhedra, from lowdimensional (chains, sheets) to more complex three-dimensional blocks. These vanadates exhibit a fascinating variety of functional properties whose origin is closely related to the structural and electronic peculiarities of the compounds and are therefore widely used as advanced materials like phosphors, optical switches, chemical sensors, catalysts, in solidstate batteries, etc.^{1–3} Recently, in the vanadates $M_3V_2O_8$ (M = Co, Ni) a magnetically driven ferroelectric order has been reported.^{4,5} Although the coupling between magnetic and ferroelectric order has been studied since the 1960s,^{6,7} during the last years many efforts have been devoted to finding new multiferroic materials,⁸ in which the magnetic and ferroelectric states coexist in the same compound. Among the several different classes of multiferroics,^{9,10} there is one in which ferroelectricity appears only in certain magnetically ordered states.^{11,12} In this type of multiferroic materials, the magnetic order breaks the spatial inversion symmetry and induces electric polarization as a secondary order parameter.¹⁰

In the search for new multiferroic materials and on the basis of the interesting behavior found in $M_3V_2O_8$ (M = Co and Ni),^{4,5} we have focused on another family of vanadates with formula $M_2V_2O_7$ (M = Co and Cu).

 $Co_2V_2O_7$ exhibits a dichromate structure with crystallizes in a monoclinic symmetry (S.G.: P2₁/c).¹³ One of the most remarkable structural features is that the magnetic

 Co^{2+} cations are in two different octahedral environments and that the arrays of edge-shared CoO_6 octahedra form zigzag chains along the c-axis, see Fig. 1(a). Such chains are separated by nonmagnetic bitetrahedral $(\text{V}_2\text{O}_7)^{4-}$ groups, resulting in a quasi-1D structural arrangement.

Cu₂V₂O₇ crystallizes in two different polymorphs:^{14,15} the low-temperature α -structure, that is orthorhombic and noncentrosymmetric (S.G.:Fdd2), and the high-temperature β -phase that is monoclinic and centrosymmetric (S.G.: C2/c), with the structural transition point at 985 K.

In the α -phase each copper ion is surrounded by five oxygen atoms, resulting in [CuO₅] polyhedra that link to another two by edge-sharing forming zig-zag chains, that extend approximately in two perpendicular directions, giving rise to a cross-linking chain framework, see Fig. 1(b). These chains of [CuO₅] polyhedra are separated by (V₂O₇)⁻² anion groups, consisting of corner-sharing [VO₄] tetrahedra.

As for their magnetic properties, on the basis of magnetic studies carried out on polycrystalline samples, $Co_2V_2O_7$ was initially described to consist of ferromagnetic chains that couple antiferromagnetically at low temperature with $T_C = 11 \text{ K}$.¹⁶ Nevertheless, more recent magnetic studies on single crystals of $Co_2V_2O_7$ suggest that this compound is a 3D antiferromagnet, in which two magnetic transitions occur at 6 and 13 K and also suggest a complex spin structure in a skew chain with frustration.¹⁷

On the other hand, $Cu_2V_2O_7$ shows weak ferromagnetic behavior at low temperature^{18,19} whose transition temperature has been reported to be about 35 K. The weak ferromagnetic component arises from the canting of antiferromagnetic spins through Dzyaloshinskii-Moriya (DM) interactions.²⁰

In this work, we pay special attention to the dielectric behavior of these two divanadates $M_2V_2O_7$ ($M^{2+} = Co^{2+}$

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and Cu^{2+}), at temperatures near their magnetic transitions, looking for a possible coupling between their dielectric and magnetic properties.

II. EXPERIMENTAL

 $M_2V_2O_7$ (M = Co and Cu) compounds were prepared by the ceramic method. For this purpose stoichiometric amounts of V_2O_5 (Aldrich, 98%) and CoCO₃ (Panreac), or CuO (Aldrich, 99%) were mixed, pressed into pellets, and heated in air at 600–650 °C with intermediate regrindings (see details in Table I).

The obtained samples were characterized by conventional x-ray powder diffraction (XRPD) in a Siemens D-5000 diffractometer at room temperature and using Cu (K α) = 1.5418 Å radiation. The x-ray diffraction patterns were obtained in the 2 θ range of 20–80° and were inspected using Match software²¹ to identify the present crystallographic phases.

In addition, synchrotron x-ray powder diffraction (SXRPD) studies were carried out at 300 K on the BM25A beamline ($\lambda = 0.8261$ Å) at the ESRF (Grenoble, France). For this purpose, the samples were loaded in a borosilicate capillary ($\phi = 0.3$ mm) and rotated during data collection. The Rietveld analyses were performed with the FullProf program,²² where the peak shapes were described by a pseudo-Voigt function and the background was modeled with a 6-term polynomial.

Magnetic properties were studied in a Quantum Design MPMS Squid magnetometer. Zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility data were obtained under a field of 100 Oe in the temperature range $5 \le T(K) \le 320$.

The complex relative dielectric permittivity $\varepsilon_r(\omega) = \varepsilon'_r(\omega) - i\varepsilon''_r(\omega)$ was measured in a Quadtech 1920 precision LCR-meter over the frequency and temperature ranges $20 \le v(\text{Hz}) \le 10^6$ and $5 \le T(K) \le 300$. For this purpose, the samples in form of pellets with typical areas of 25 mm² and thickness of 0.85 mm were prepared to fit in the capacitor and gold was sputtered on their surfaces to ensure good electrical contact.

III. RESULTS

A. Structural characterization

XRPD analysis show that in all cases the polycrystalline $M_2V_2O_7$ (M = Co and Cu) compounds were obtained as single phases, identified as $Co_2V_2O_7$ (JCPDS 01-070-1189) and α -Cu₂V₂O₇ (JCPDS: 01-076-0806).

The SXRPD patterns obtained at room temperature were refined by the Rietveld method in a monoclinic symmetry in the case of $Co_2V_2O_7$ (S.G: P2₁/c) and orthorhombic symmetry

TABLE I. Thermal treatments employed in the synthesis of $M_2V_2O_7$ $(M^{2+}=Co^{2+} \mbox{ and } Cu^{2+})$ divanadates.

Compound	Thermal treatments	
$\begin{array}{c} Co_2V_2O_7\\ Cu_2V_2O_7\end{array}$	600 °C/72 h 600 °C/156 h	650 °C/86 h

in the case of α -Cu₂V₂O₇ (S.G. Fdd2) (Fig. 1). The obtained cell parameters (Table II), atomic coordinates and interatomic distances are in good agreement with the data reported in the literature for these compounds.^{13–15}

B. Magnetic properties

Figure 2 shows the temperature dependence of the ZFC and FC susceptibility of these $M_2V_2O_7$ divanadates. The data confirm the presence of the transitions previously reported in the literature for these compounds.^{16,18–20}

In this context and as expected, the magnetic susceptibility of $Co_2V_2O_7$ is seen to experience a strong increase at around 11 K.¹⁶ As for $Cu_2V_2O_7$, we observe the expected transition to a weak ferromagnetic state as temperature decreases below \sim 35 K.^{19,20}

C. Dielectric properties

The temperature dependence of the real part of their complex dielectric permittivity, ε'_{r} , (the so-called dielectric constant) is shown in Figs. 3(a) and 4(a).



FIG. 1. (Color online) Crystal structure of $M_2V_2O_7$: (a) $M^{2+} = Co^{2+}$ and (b) $M^{2+} = Cu^{2+}$. Vanadium cations have been removed from the picture to clear the view of $[MO_6] M^{2+} = Co^{2+}$ or $[MO_5] M^{2+} = Cu^{2+}$ chains.

TABLE II. Cell parameters of $M_2V_2O_7$ ($M^{2+} = Co^{2+}$ and Cu^{2+}), calculated from the refinement of their SXRPD patterns at T = 300 K, and space group of these compounds.

	$Co_2V_2O_7$	α -Cu ₂ V ₂ O ₇
a(Å)	6.5951(1)	20.6754(1)
b(Å)	8.3797(1)	8.4064(1)
c(Å)	9.4814(1)	6.4460(1)
$\beta(^{\circ})$	100.226(1)	_
S.G.	P2 ₁ /c	Fdd2

In the case of $Co_2V_2O_7$, a change in the slope of the dielectric constant is observed at the temperature at which the inverse of the magnetic susceptibility starts to deviate from a Curie-Weiss law, $T \sim 40$ K, well above T_C , [Fig. 3(a)]. Such anomaly in the dielectric constant is seen to be frequency independent.

In the paramagnetic region, the ε'_r versus T curves can be fitted to the following expression [Fig. 3(a)]:

$$\epsilon_{\rm r}^{'}({\rm T}) = \epsilon_{\rm r}^{'}({\rm T}=0) + {\rm C_o}\left[\exp(\hbar\omega_{\rm o}/k_{\rm B}{\rm T}) - 1\right]^{-1},$$
 (1)

that simulates the contribution of the lattice to the dielectric constant, and that has been used by Fox *et al.*²³ to describe the dielectric behavior of BaMnF₄, where C_o is a coupling constant, ω_o is the mean frequency of the final states in the soft mode branch and ε'_r (T = 0) is the value of the dielectric constant extrapolated at T = 0 K.

If we now plot the variation of $\Delta \varepsilon'_r$, defined as the difference between the observed dielectric constant and the lattice contribution as a function of temperature, we obtain the result shown in Fig. 3(b). As it can be seen, $\Delta \varepsilon'_r$ increases markedly below ~40 K.

As for the dielectric behavior of α -Cu₂V₂O₇, a change in the slope of its dielectric constant is again observed to occur



FIG. 2. (Color online) Magnetic susceptibility of (a) $Co_2V_2O_7$ and (b) $Cu_2V_2O_7.$



FIG. 3. (Color online) (a) Dielectric properties and inverse magnetic susceptibility of $Co_2V_2O_7$ at low temperature. (b) Normalized value of the difference between the observed dielectric constant and lattice contributions.

at the temperature at which the magnetic transition takes place [Fig. 4(a)]. As in the case of the Co-compound, this anomaly in the dielectric constant of α -Cu₂V₂O₇ at the magnetic transition is frequency independent.

IV. DISCUSSION

The results shown here indicate the presence of an anomaly of the dielectric constant of the Co- and Cu-divanadates close to their magnetic transition temperatures.



FIG. 4. (Color online) (a) Dielectric properties and magnetic susceptibility of $Cu_2V_2O_7$ at low temperature. (b) Normalized value of the difference between lattice contributions and the observed dielectric constant and normalized value of magnetization.

What is the reason for this?

First, we have to note that, from the structural point of view, $Co_2V_2O_7$ exhibits a quasi-1D structural arrangement and the α -Cu₂V₂O₇ crystallizes a noncentrosymmetric structure.

With this in mind, in order to understand the coupling between the dielectric properties and the magnetization observed, it is useful to make a comparison with that of the well-known magnetodielectric compound $BaMnF_4$, with whom α -Cu₂V₂O₇ has many aspects in common. For example, both have a polar structure in which a weak ferromagnetic component arises from the canting of antiferromagnetic spins through DM interactions. And more important, both compounds show a similar dielectric anomaly at the magnetic transition.

In BaMnF₄, the dielectric anomaly is due to the presence of weak ferromagnetism in a polar crystal structure and the behavior of ε'_r as a function of temperature can be described by the Landau theory for continuous phase transitions²⁴ assuming that the magnetoelectric coupling is of the form M^2P^2 (M = magnetization, P = electric polarization). For such case, this theory predicts a nonlinear magnetoelectric coupling, where $\Delta \varepsilon'_r \propto M^2$. Moreover, as Katsufuji and Takagi have shown in $EuTiO_3$ (Ref. 25), the dielectric constant can be related to the pair correlation function of neighboring magnetic spins. Since the copper cations of α - $Cu_2V_2O_7$ are in oxidation state +2, with $3d^9$ configuration, while the vanadium cations are in state +5, with $3d^0$ configuration, the magnetic properties of α-Cu₂V₂O₇ are determined solely by its Cu²⁺ cations, which due to their canting gives rise to the weak ferromagnetic component.

The comparison of the normalized variation of the dielectric constant with respect to the normalized one of M^2 as a function of temperature [Fig. 4(b)] indicates that the hypothesis of coupling of the weak ferromagnetic component with the dielectric response is quite reasonable.

In $Co_2V_2O_7$, the situation is different because their centrosymmetric structure does not allow a magnetodielectric coupling by the same mechanism as that proposed for the Cu-divanadate. Even more, for $Co_2V_2O_7$, the deviations of the dielectric constant with respect to lattice contributions are quite evident.

By comparing the variation of dielectric constant and the inverse of magnetization with temperature, we suggest the reason might be in the different strength of the coupling among magnetic ions. Extrapolating the paramagnetic region we obtain that the Curie-Weiss temperature of $Co_2V_2O_7$ is -32(1) K. This means that the magnetic interactions in the Co-compound are stronger than suspected in principle and, as the calculated magnetic moment per Co^{2+} ion is 4.8 μ_B , in principle it could be expected that the magnetic ordering temperature were higher. In order to understand this, it must be taken into account that we are dealing with a 1D structure, where magnetic ordering is only possible due to deviations from this one-dimensional character, and therefore this ordering is quite weak.

The analysis of a 1D structure (with a logical low magnetic ordering temperature) with relatively high magnetic interactions can lead to certain errors of interpretation. From our point of view, this has happened in the calculation of the entropy of the magnetic transition in $\text{Co}_2\text{V}_2\text{O}_7$ by He *et al.*¹⁷ In fact, they recognize an underestimation of the spin entropy (they obtain only 43% of RLn(2S + 1) for spin-3/2 systems) and attribute it to an overestimation of lattice contributions or to a development of short-range ordering above T_N . Our opinion is that they might well be integrating over a too short temperature range above T_N . In case the integration window were expanded over 30 K, the expected value of spin-entropy could be recovered.

By simply taking a look at the deviations of dielectric constant with respect to the lattice contribution and the parallelism of its behavior with respect to the inverse of magnetization (which deviates from the paramagnetic regime at temperatures much higher than T_N) it is clear how strong the role of the magnetic interaction is.

Taking this result into account, we suggest that the magnetic interactions could be inducing this anomaly in the dielectric constant by a magnetostrictive effect, as defined by Katsufuji and Takagi for EuTiO₃ (Ref. 25). There, they also related the dielectric constant of a magnetic ordered region with the pair correlation function of neighboring magnetic spins. Nevertheless, given that this system does not show a polar crystal structure, we are not able to get a specific relationship between both magnitudes as in the case of α -Cu₂V₂O₇. Moreover, as Touaiher *et al.*¹⁶ have pointed out, it is not even possible to fit the experimental data of magnetization using any of the known models, probably due to the strong anisotropy of the Co²⁺ ion, that causes different g-values.²⁶

Thus, in the case of $Co_2V_2O_7$, the large magnetic moment of Co^{2+} , that in addition shows high spin-orbital coupling (magnetic anisotropy), would be giving rise to a magnetostriction effect that is strong enough to induce changes in the dielectric constant.

V. SUMMARY

In summary, in this work we have synthesized and characterized two divanadates $M_2V_2O_7$ ($M^{2+} = Co^{2+}$ and Cu^{2+}), and we report their dielectric behavior. We have observed a magnetodielectric coupling - a change of the slope of the dielectric constant at the magnetic transition temperature. In the Cu₂V₂O₇ divanadate, the magnetodielectric coupling is due to the presence of weak ferromagnetism in a polar crystal structure and the behavior of ε'_r as a function of temperature can be described with a free energy model, which suggests a nonlinear magnetoelectric coupling, with $\Delta \varepsilon'_r \propto M^2$. In the Co-compound the magnetodielectric effect appears to be due to a different mechanism: the magnetic anisotropy of Co²⁺ cations, which causes a noncollinear magnetic arrangement inside the chains and induces electrical polarization by magnetostriction.

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