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Magnetodielectric coupling of a polar organic-inorganic hybrid Cr(II) phosphonate

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Cr[(H₃N-(CH₂)₂-PO₃)(Cl)(H₂O)] represents a rare example of a polar organic-inorganic hybrid material that exhibits a canted antiferromagnetic order below $T_N=5.5$ K. The unusual coexistence of a polar crystal structure and magnetic order triggered our investigation of the magnetodielectric coupling. The coupling is evidenced by an anomaly in the temperature dependence of the dielectric constant ϵ below the Néel temperature. The magnetocapacitance is enhanced by one order of magnitude below T_N . The main characteristics of the magnetodielectric response are interpreted by Landau theoretical coupling terms.

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I. INTRODUCTION

The design of multifunctional materials, which exhibit more than one physical or chemical property in the same structure, represents an important goal in modern solid-state sciences.¹ The study of multiproperty systems, in which magnetic properties coexist with other physical or chemical properties, has provided examples of great interest for future technological applications.^{2,3} Hybrid materials obtained from an organic framework with transition-metal ions can give a good path toward the design of new multiferroic and/or magnetodielectric materials. This means that the occurrence of a polar crystal axis in a magnetic material could provide, at least in principle, new multiferroic materials.

In this perspective, Cr[(H₃N-(CH₂)₂-PO₃)(Cl)(H₂O)] (**I**) represents a rare example of a polar organic-inorganic hybrid material containing Cr²⁺ ion ($3d^4$, $S=2$ electronic configuration), which is also magnetically ordered at low temperatures. The compound is ionic and it crystallizes in the polar space group $P2_1$ ($n^\circ 4$) with $a=5.249(1)$ Å, $b=14.133(3)$ Å, $c=5.275(1)$ Å, and $\beta=105.55(2)^\circ$. The structure is layered, made of an alternation of inorganic and organic layers along the polar b axis (see Fig. 1).⁴ The most relevant feature of the crystal structure is the almost parallel alignment of Cr[O₄Cl] units along the polar axis of the unit cell with the Cl atoms pointing in the same direction. The compound is paramagnetic and below $T_N=5.5$ K orders as a canted antiferromagnet with a coercive field and a remnant moment of 30 Oe and 0.08 μ_B , respectively, at 4.5 K.⁴ The effective magnetic moment is of 4.7 μ_B per Cr²⁺ ion. We have chosen to investigate the magnetocapacitance (MC) of **I**. The reason is twofold: first to explore the possible occurrence of interesting phenomena such as ferroelectricity or nonlinear optical effects found for other polar molecule based materials.⁵ The second one resides in the fact that magnetodielectric coupling studies of polar materials are focused mainly on pure inorganic multiferroic metal oxides.⁶⁻¹¹ The target of this work is twofold: (1) to investigate the magnetodielectric coupling in a polar organic-inorganic hybrid material and (2) to discuss the results in comparison with some well-known magnetodielectric com-

pounds. In particular, we compare our results with those found in the pure inorganic compound BaMnF₄. This material is similar to **I** because it has one unique polar axis and is antiferromagnetic with a small ferromagnetic component.

In this paper we report the study of magnetodielectric coupling of **I** as a function of temperature and magnetic field. The experimental data are discussed in terms of Landau theory.^{11,12}

II. EXPERIMENTAL SECTION

I has been synthesized according to a method described previously.⁴ The resulting light-blue microcrystalline solid is air sensitive and it was finely ground under inert atmosphere. The fine blue powder was then introduced in a stainless-steel die (Perkin Elmer) and pressed under vacuum (10^{-2} mm Hg) at a pressure of 12 tons. A cylindrical-shaped blue pellet of 1.5-mm thickness and 8-mm radius was obtained and stored under inert atmosphere.

Complex impedance measurements were performed using an Agilent AG4284A LCR meter. The measurement of the dielectric constant was carried out by using a homemade sample holder with four coaxial cables. The sample holder fits inside a commercial Quantum Design PPMS apparatus, which allows measurement of the dielectric constant between 2 and 400 K and magnetic field up to 9 T. Contacts were fabricated using silver paint. An ac voltage of 1 V was applied to the sample. The dielectric constant was extracted from the value of capacitance, taking into account the sample and contact dimensions.

Ferroelectricity of the samples was investigated using a Radiant Precision Workstation ferroelectric tester with a high-voltage interface connected to a TREK 609E-6 4-kV high-voltage amplifier. The maximum voltage applied was 400 V depending on the sample. The measurements were carried out in silicone oil.

III. RESULTS

Cr(II) phosphonate is a bad insulator at room temperature with a two-point ac resistance of the sample in the range of

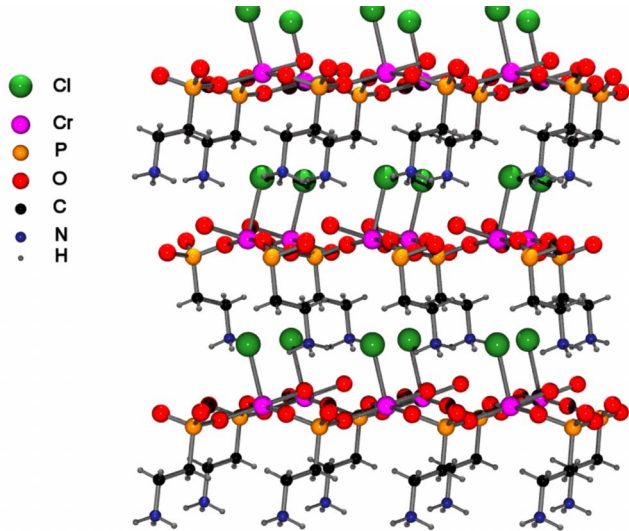


FIG. 1. (Color online) Crystal structure of $\text{Cr}[(\text{H}_3\text{N}-(\text{CH}_2)_2-\text{PO}_3)(\text{Cl})(\text{H}_2\text{O})]$.

100–400 k Ω . Therefore, the hysteresis loop measured at 1 kHz showed the typical behavior of a “lossy dielectric” at a maximum voltage of 100 V. The lossy shape of the curve changed when the applied frequency was lowered up to 100 Hz and the resulting behavior was similar to that of a resistor. Measurements performed on another pellet of Cr(II) phosphonate were found to be reproducible. Increasing the applied voltage, irrespective of the frequency, yielded “dead short” behavior for both samples (for a classification of common hysteresis artifacts, see Ref. 13). This was probably due to the occurrence of a dielectric breakdown in the sample since the lossy behavior could not be recovered when the voltage was decreased back to the starting value. Therefore, **I** cannot be considered ferroelectric, as it breaks down electrically at low electric fields, before any saturation of the polarization can be observed.

The dielectric constant ϵ of a pellet of **I** was measured as a function of temperature T with a temperature step of 0.25 K at three values of frequency f . When a frequency of 1 kHz was applied, a shift toward higher values of the dielectric constant was observed compared to measurements made with frequencies of 10 and 100 kHz. Moreover, the measurement performed at $f=1$ kHz was noisier with respect to those performed at the other two frequencies. For all the studied frequencies, the dielectric loss is quite low [$\tan(\delta) < 0.01$].

On the basis of these preliminary results, a frequency $f = 10$ kHz was chosen for the measurements. The temperature dependence of the dielectric constant ϵ measured in the temperature range $T=2$ –20 K is reported in Fig. 2. We clearly observe an anomaly at a temperature corresponding to the Néel temperature. This anomaly is evidenced by a decrease in ϵ below the Néel temperature. This result demonstrates the existence of a magnetodielectric coupling in a polar organic-inorganic hybrid material. However, this anomaly is significantly less pronounced when compared to those observed in other magnetodielectric compounds (see Table I). The variation of ϵ was normalized to the magnetic

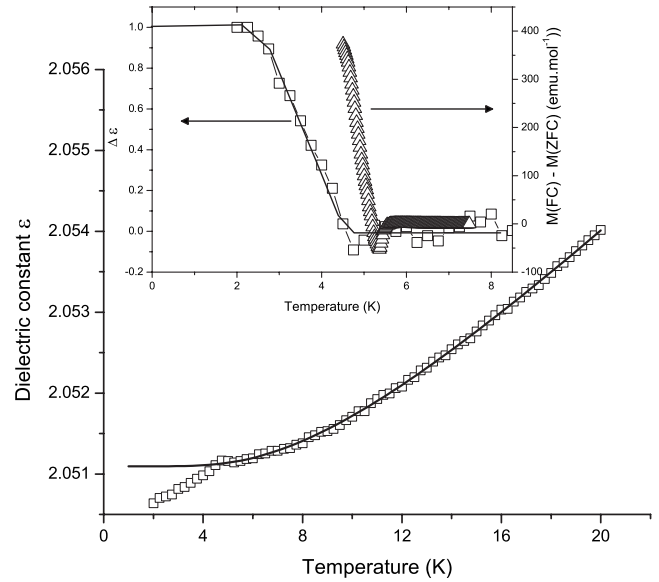


FIG. 2. Dielectric constant versus temperature of **I** showing an anomaly below T_N . The extrapolated line represents the contribution of the lattice (see text). The inset shows the magnetic contribution to $\epsilon(T)$ (left) and magnetization (right) (Ref. 5). The line in the inset is a guide to the eye.

transition temperature to permit comparison between our data and the literature.

In order to analyze the magnetic anomaly near the critical temperature T_N , the lattice contribution has been subtracted from the experimental data. This has been done using Eq. (1)

$$\epsilon(T) = \epsilon_0 + \frac{C}{\exp\left(\frac{\hbar\omega_0}{k_B T}\right) - 1}. \quad (1)$$

Equation (1) contains three fitting parameters and yields a classical form, which is linear in temperature at high temperatures.¹² The fit of the experimental data by using Eq. (1) is reported as a solid line in Fig. 2. In the inset of Fig. 2 the normalized value of the difference between the lattice contribution and the observed dielectric constant is shown. This difference corresponds to the magnetic order parameter emerging below T_N and will be discussed in Sec. IV. The fit

TABLE I. Magnetodielectric parameters for several transition-metal oxides and for Cr^{II} organophosphonate for comparison. $\frac{\Delta\epsilon}{\epsilon}$ at $H=5$ T is given below the magnetic-ordering temperature. $\frac{\Delta\epsilon}{\epsilon}$ per K is the variation of ϵ normalized to $\Delta T = T_N - T_{\text{low}}$ where T_{low} is the lowest measured temperature. $b_{T < T_N}$ corresponds to the curvature of $\Delta\epsilon / \epsilon(H=0) = a + bH^2$.

Compound	$(\Delta\epsilon/\epsilon)$ (H=5 T)	$(\Delta\epsilon/\epsilon)$ per K	$b_{T < T_N}$	T_N (K)
EuTiO ₃ (Ref. 7)	$\approx 6\%$	1%	≈ 2.6	5.5
ϵ -Fe ₂ O ₃ (Ref. 9)	0.26%	0.05%	5.2×10^{-2}	110
YMnO ₃ (Ref. 11)	0.005%	0.081%	$\approx 2 \times 10^{-4}$	77
This work	0.0275%	0.0085%	2.1×10^{-2}	5.5

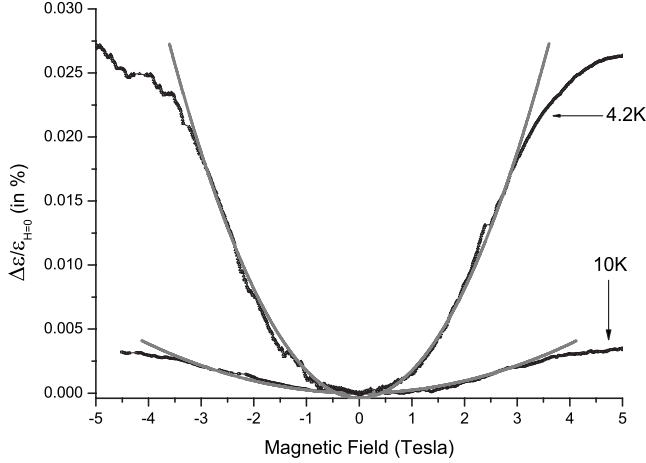


FIG. 3. MC measured below and above $T_N=5.5$ K ($f=10$ kHz). In black, we present the field dependence at 4.2 and at 10 K. In gray, we show the fit with $\Delta\varepsilon/\varepsilon_{(H=0)}=a+bH^2$.

yields the following values: $\varepsilon_0=2.05$, $C=7.8\times 10^{-3}$, and $\omega_0=114$ cm^{-1} . ε_0 is the value of the dielectric constant extrapolated at $T=0$ K and C is a constant. The value of ω_0 is the fitted frequency of the polar mode. We show in the inset of Fig. 2 the dielectric constant plotted together with the magnetic data from Ref. 4. We see that the anomaly is observed roughly at the magnetic transition. The slight difference in transition temperature is likely to be related to the handling in air necessary at the preparation of the sample (I is air sensitive⁴).

The effect of the applied magnetic field on the magnetodielectric coupling was also studied. For this purpose MC measurements under a magnetic field up to 5 T have been performed above and below T_N . The results are presented in Fig. 3. Below ($T=4.2$ K) and above ($T=10$ K) T_N both MC responses exhibit a quadratic dependence on magnetic field, at least up to a field of 3 T. The significant difference in the magnetocapacitive responses below and above T_N can be explained by the appearance of magnetic ordering (see Sec. IV). The increase in the magnetocapacitive response is almost one order of magnitude between 4.2 and 10 K ($\Delta\varepsilon/\varepsilon_{(H=0)}=a+bH^2$, $b_{T<T_N}/b_{T>T_N}=2.1\times 10^{-2}/2.4\times 10^{-3}=8.75$). This is in contrast to the observations of YMnO_3 where the magnetocapacitive response is nearly constant below and above T_N .¹¹ The increase in the magnetodielectric coupling here can be ascribed to the emergence of the magnetic ordering below T_N ; this statement will be shown in the discussion (see Sec. IV). While the field dependence observed in compound I is quite small above T_N , the magnetodielectric coupling constant $b_{T<T_N}$ in the magnetically ordered phase is two orders of magnitude larger than what has been reported for YMnO_3 (Ref. 11) but much smaller than for EuTiO_3 (Ref. 7) for a similar magnetic-ordering temperature (see Table I). It can be noticed from Table I that the values reported for $b_{T<T_N}$ are not related to the magnetic transition temperature. These observations show that strong magnetic interactions (i.e., high-ordering temperatures) are not required for a large magnetodielectric response.

IV. DISCUSSION

The behavior of ε as a function of temperature and magnetic field, $\varepsilon(T,H)$, can be described by a Landau expansion of the free energy. This approach requires an analysis of the possible magnetic symmetries of the investigated system. Unfortunately, no powder neutron data are available for I. However, we can consider the simplest case where the magnetic cell is identical to the chemical one. The presence of two Cr^{2+} sites per unit cell suggests the possibility of antiferromagnetic coupling between these two sites. In such a situation there are two possibilities for the magnetic structure: (i) the spins are confined in the (a,c) plane with a ferromagnetic component along the b axis or (ii) the spins are confined along the b axis with the ferromagnetic component in the (a,c) plane. In (i) the magnetodielectric coupling involves the order parameters—the electrical polarization $P=(0,P_y,0)$, the sublattice magnetization $L=(L_x,0,L_z)$, and a ferromagnetic component $M=(0,M_y,0)$. In (ii) the order parameters are $P=(P_x,0,P_z)$, the sublattice magnetization is $L=(0,L_y,0)$ and the ferromagnetic component is $M=(M_x,0,M_z)$. Model (i) represents the magnetic point group $2'$ while (ii) describes the magnetic point group 2. In this model (i) describes the compound BaMnF_4 while (ii) is equivalent to the findings for 1% Co doping of BaMnF_4 .¹² However, we work here with powder and thus we are not sensitive to the anisotropy of the system. Consequently we will limit our considerations to the more general case including only the relevant terms and neglecting the weak ferromagnetic component. The free energy of the system can be written as follows:

$$F = F_0 + \frac{\alpha}{2}L^2 + \frac{\beta}{4}L^4 + \frac{a}{2}P^2 + \frac{\sigma}{2}P^2L^2 + \frac{\gamma}{2}P^2H^2 - EP. \quad (2)$$

In Eq. (2), L designates the magnetic order parameter, P the electrical polarization, H the magnetic field, and E the electric field. We remind the reader that P and E are polar vectors while L and H are axial vectors. All the terms of Eq. (2) are invariant by time inversion and satisfy the symmetry of the system. Considering the equilibrium conditions of the system, we find

$$\frac{\partial F}{\partial P} = aP + \sigma PL^2 + \gamma PH^2 - E = 0.$$

$$\frac{\partial F}{\partial L} = \alpha L + \beta L^3 + \sigma P^2 L = 0. \quad (3)$$

Using the relationships shown in Eq. (3) and taking into account that the dielectric constant $\varepsilon - 1 = \frac{\partial P}{\partial E}$, we find:

$$\text{If } L = 0, \quad \frac{\partial P}{\partial E} = (a + \gamma H^2)^{-1}.$$

$$\text{If } L \neq 0, \quad \frac{\partial P}{\partial E} = \left(a - \frac{\alpha\sigma}{\beta} - \frac{3\sigma^2 P^2}{\beta} + \gamma H^2 \right)^{-1}. \quad (4)$$

The emergence of antiferromagnetic order L thus renormalizes the electric susceptibility by $-\frac{(\alpha\sigma+3\sigma^2P^2)}{\beta}$. For small values of the magnetic field, we can use a series expansion as function of H . If we do so, we find

$$\begin{aligned} \text{If } L=0, \quad \frac{\partial P}{\partial E} &\simeq \frac{1}{a} - \frac{\gamma}{a^2}H^2. \\ \text{If } L \neq 0, \quad \frac{\partial P}{\partial E} &\simeq \frac{1}{a - \frac{\alpha\sigma}{\beta} - \frac{3\sigma^2P^2}{\beta}} \\ &\quad - \frac{\gamma}{\left(a - \frac{\alpha\sigma}{\beta} - \frac{3\sigma^2P^2}{\beta}\right)^2}H^2. \end{aligned} \quad (5)$$

We can rewrite the formulas of Eq. (5) as $\varepsilon = a + bH^2$ where b is the coefficient in H^2 in Eq. (5). This explains the quadratic magnetic-field dependence for low values of H . Additionally the additional terms in Eq. (5) for $L \neq 0$ account for the renormalization of the magnetodielectric coefficient b in the magnetically ordered phase as observed experimentally. Furthermore, close to the Néel temperature, taking into account that $L^2 = \frac{-\alpha - \sigma P^2}{\beta}$, the b coefficient can be expressed as

$$b \simeq \frac{8\sigma\gamma}{\left(a - \frac{2\sigma^2P^2}{\beta}\right)^3}L^2. \quad (6)$$

Consequently, according to Eq. (6) the magnetodielectric coupling constant b mirrors the temperature dependence of $L^2(T)$.

The field dependence of ε below and above T_N is governed by the term $\frac{\gamma}{2}P^2H^2$. This term is not restricted by the symmetry and is generally allowed. More importantly, this term is also allowed in nonmagnetic and nonpolar dielectric materials. Consequently, this term not only explains the quadratic magnetic-field dependence for compounds such as YMnO_3 (polar ferroelectric),^{8,11} EuTiO_3 (nonpolar ferromagnetic),⁷ and $\text{Co}_3\text{V}_2\text{O}_8$ (nonpolar antiferromagnetic)¹⁴ but also Si:P, which was the first example reported for MC.¹⁵ In the latter example, it has been shown that the magnetic-field dependence of the MC arises from the effect of intrastate interaction within an Anderson-localized state.¹⁶

The necessity for a biquadratic coupling term in P and L (or M in the case of a ferromagnet) was already realized by Smolenskii and others.^{10,17,18} This term has been generalized by Lawes *et al.*¹⁹ by taking into account the q -dependent fluctuations $P^2 \sum_q g(q) \langle M_q M_{-q} \rangle$ with $g(q)$ as a q -dependent coupling term. Smolenskii's approach expects the largest contribution of the magnetic coupling at lowest temperatures. The suppression of $\varepsilon(T)$ mirrors the temperature dependence of $L^2(T)$ [or $M^2(T)$]. This is exactly what has been observed for BaMnF_4 ,¹² YMnO_3 ,¹¹ and DyMnO_3 .²⁰ On the other hand, the Lawes *et al.*¹⁹ approach accounts for the fact that at the magnetic ordering temperature, where L (or M) is zero, the dielectric constant exhibits a maximum as a function of temperature. This behavior was observed for SeCuO_3 .

The origin of the magnitude of these contributions still needs to be established in detail despite several contributions.^{21–25} The coupling term P^2H^2 accounts for the MC varying proportional to H^2 . The MC is very system dependent—in materials with magnetism-induced polarization, MC is maximized near phase transitions such as the polarization-flop transition for DyMnO_3 with MC=600%. In materials in which P arises at much higher temperature than L , as in YMnO_3 and present hybrid material, MC is expected to be quadratic in field and temperature independent once $P(T)$ is temperature independent. Nevertheless, this is very material dependent. Very abrupt temperature dependence of MC is observed close to T_N for YbMnO_3 .²⁶ In the present hybrid, we observe that MC increases below the magnetic ordering. The origin of this effect requires more detailed analysis as the MC is measured very close to T_N . As the MC brings the value of $\varepsilon(T)$ back in high magnetic fields toward the extrapolated high-temperature behavior, we assume that MC is related to suppression of L or T_N by the applied magnetic field. However, this goes beyond the scope of the present analysis.

For a linear magnetoelectric effect coupling terms of the type LMP are necessary.²⁷ This kind of term is allowed in our case and thus a magnetically induced electrical polarization could be observed. However, the experimental observation is difficult on powders due to anisotropy and it is also difficult to make good electrical contacts on this hybrid system.

V. CONCLUSION

The magnetodielectric coupling of the polar organic-inorganic hybrid material $\text{Cr}[(\text{H}_3\text{N}-(\text{CH}_2)_2-\text{PO}_3)(\text{Cl})(\text{H}_2\text{O})]$ has been investigated. The magnetodielectric response is enhanced by almost one order of magnitude below T_N between 4.2 and 10 K. This is due to the appearance of long-range magnetic ordering. The comparison with other magnetodielectric materials suggests that strong magnetic interactions are not necessary in order to obtain a high magnetodielectric response. Using Landau theoretical arguments, we are able to explain the quadratic dependence in magnetic field and the increase in the magnetodielectric coupling below T_N . In conclusion we have studied a different example of a polar hybrid organic-inorganic compound, which shows significant magnetodielectric coupling. This work opens magnetodielectric materials to another class of compounds.

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