Dielectric properties and electrical switching behaviour of the spin-driven multiferroic $LiCuVO_4$

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Abstract

The simultaneous existence and coupling of ferroelectric and magnetic ordering in a material, so-called multiferroicity, is of great scientific interest due to the underlying complex physical mechanisms and its possible applications. Here we present the multiferroic properties of a prototypical spin-driven ferroelectric material, the spin-1/2 chain cuprate $LiCuVO_4$. In this system, spiral spin order, with propagation in the *b* direction and a spin helix in the *ab* plane, induces ferroelectric polarization in the *a* direction when no magnetic field is applied. In an external magnetic field, the direction of the spin spiral and thus the direction of the electrical polarization can be switched. Broadband dielectric spectroscopy on a single crystalline sample oriented in two different directions was performed in applied external magnetic fields up to 9 T, demonstrating this switching behaviour of the ferroelectric polarization. Furthermore, detailed magnetic-field and temperature-dependent ferroelectric hysteresis-loop measurements reveal the switching of polarization by an electrical field, which implies the electric control of the spin helicity of $LiCuVO_4$.

Keywords: multiferroicity, $LiCuVO_4$, dielectric properties, spin-driven ferroelectricity

(Some figures may appear in colour only in the online journal)

1. Introduction

Within the different classes of multiferroic materials, those exhibiting both ferroelectric and magnetic order are the most prominent [1]. Many of these materials show a close coupling of spin and charge, which provides the possibility of controlling the magnetic order via an electric field. Systems having noncollinear spin structures, e.g. magnetic phases with a spiral or helical order, are known to reveal such behaviour [2–4]. $LiCuVO_4$ is a prototypical example of a one-dimensional spin-1/2 Heisenberg antiferromagnet [5]. At temperatures below about 2.5 K, it exhibits a three dimensional helical spiral spin order, which is accompanied by an electrical polarization [4, 6]. Microscopic mechanisms for the occurrence of multiferroicity, based on the presence of tilted spins (S_i and S_{i+1}) at neighbouring atomic sites (i and $i+1$), which leads to a helical spin order resulting in an electric polarization, were proposed in [7–9]. For this class of spin-driven multiferroics, a distinct symmetry relation for the polarization in helical magnets is predicted: $P \propto (S_i \times S_{i+1}) \times Q$, where Q denotes the propagation vector of the spin spiral and $e = (S_i \times S_{i+1})$ corresponds to the spiral axis, i.e. the normal vector of the spiral plane. In $LiCuVO_4$, this normal vector can be switched in sufficiently high magnetic fields and at even higher fields the helical spin state becomes completely suppressed. Thus, the temperature and magnetic-field dependent states of $LiCuVO_4$ result in a complex (H, T) phase diagram.

Schrettle *et al* [4] presented in detail the possible states of $LiCuVO_4$ at low temperatures: below about 2.5 K and for zero

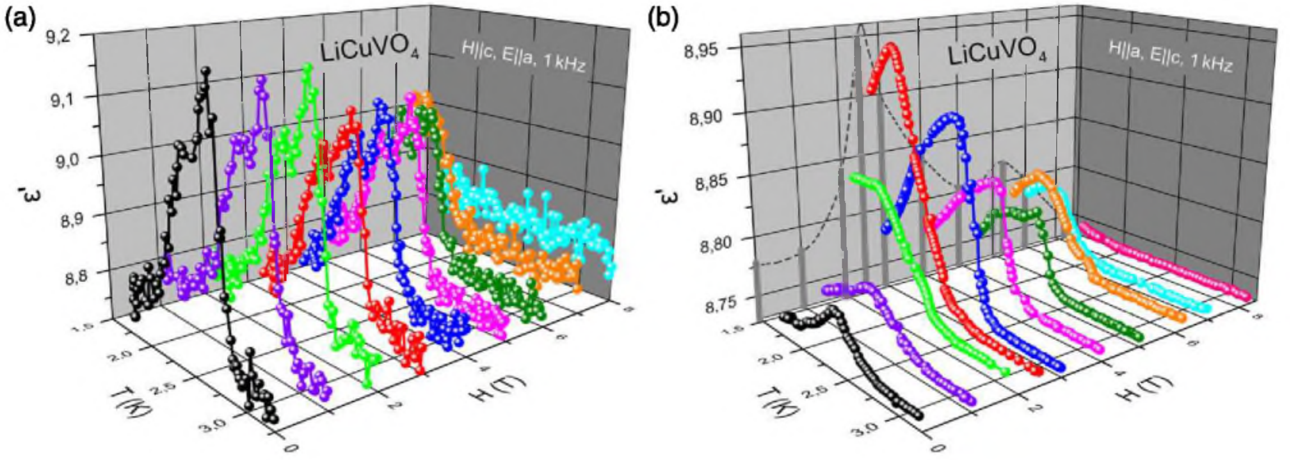

Figure 1. Temperature and magnetic-field dependent dielectric constant at 1 kHz of a LiCuVO$_4$ single crystal. (*a*) Electrical field parallel to *a* and magnetic field parallel to the *c* direction (non-switching case at $H = 2.5$ T). (*b*) Electrical field parallel to *c* and magnetic field parallel to the *a* direction (switching case at $H = 2.5$ T).

magnetic fields, the spin helix in LiCuVO$_4$ is formed in the *ab*-plane (*e* in the crystallographic *c* direction) and propagates in the *b* direction (i.e. $Q||b$). In an external magnetic field two critical H-fields can be determined: $H_1 \approx 2.5$ T and $H_2 \approx 7.5$ T. For $H > H_1$, the spiral normal vector is turned parallel to the magnetic field direction, still with $Q||b$. Above H_2, the spin helix is transformed into a modulated collinear spin structure (i.e. no spin spiral), thus preventing the development of electrical polarization according to the mechanisms discussed in [7–9]. Schrettle *et al* [4] also showed magnetic-field dependent dielectric constants of LiCuVO$_4$ at 1 kHz and 1.5 K and demonstrated that the polarization depends on the spiral spin order and can be switched in external magnetic fields, consistent with theoretical predictions [7–10]. In the present work, the temperature *and* magnetic-field dependent dielectric and polarization properties in the ferroelectric regime of a LiCuVO$_4$ single crystal are analysed in more detail. This allows us to further verify the proposed mechanisms of ferroelectricity in this material [7–10]. Moreover, we demonstrate the ability to switch the polarization and, thus, the electric control of the spin helicity in LiCuVO$_4$, a behaviour that so far has only rarely been documented in helical-spin multiferroics [2, 3, 11, 12].

2. Experimental details

The LiCuVO$_4$ single crystal was prepared as described in detail in [13, 14] and has a size of approximately $3 \times 1 \times 1$ mm^3. For the crystallographic orientation of the sample, the Laue diffraction technique was used. Magnetic susceptibility measurements reveal a transition temperature T_N for long-range magnetic order of about 2.5 K. Magnetic-field (up to 9 T) and temperature-dependent (1.5 to 10 K) dielectric spectroscopy and ferroelectric hysteresis-loop measurements were carried out in an Oxford cryomagnet equipped with a superconducting magnet. For the dielectric measurements, an Andeen-Hagerling AH2700A high-precision capacitance bridge was employed. Hysteresis-loop measurements were made using an Aixacct TF2000 ferroelectric analyser, equipped with a high-voltage booster. To perform the electrical measurements in different crystallographic directions, silver-paint contacts were applied to the plate-like sample. Two contact geometries were used: (i) sandwich geometry to test the polarization P parallel to the *c* direction and (ii) two separated caps to study P parallel to the *a* direction. For the hysteresis loop measurements we applied electric fields up to 5 kV cm^{-1}.

3. Results and discussion

Figure 1 shows the temperature-dependent dielectric constant in various external magnetic fields. The single crystal was oriented in two different directions with respect to the magnetic and electrical field, testing the two cases for which multiferroicity is expected in certain field ranges. The dielectric measurements shown in figure 1(*a*) were performed in the *a* direction of the sample and in an external magnetic field applied parallel to the *c* direction. As described in detail by Schrettle *et al* [4] this measurement configuration of LiCuVO$_4$ reveals ferroelectric signatures. In figure 1(*a*) this is evidenced by a strong increase in the dielectric constant with decreasing temperature. Moreover, with further cooling in the ferroelectric phase, the dielectric constant decreases again, leading to a peak at the ferroelectric transition temperature [15]. Similar behaviour is also found for various other spin-driven multiferroics [16–20]. For the measurements of figure 1(*a*), where the external magnetic field is parallel to the crystallographic *c* direction, at $H > H_1$ no switching of the normal vector of the helical spin structure is expected. However, at higher magnetic fields $H > H_2$, the electrical polarization vanishes and thus no peak in the dielectric constant is observed.

Figure 1(*b*) demonstrates the switching of polarization from the *a* to the *c* direction by applying an external magnetic field along the *a* direction. Against expectation, a small dielectric-constant peak at the ferroelectric transition is already observed in low magnetic fields, $H < H_1$, a small peak in the dielectric constant is present at the ferroelectric transition.

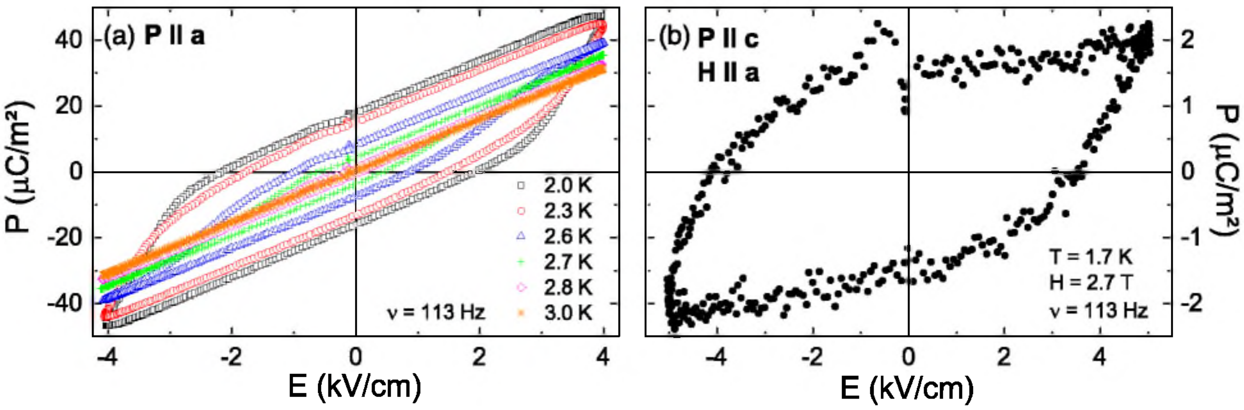

Figure 2. Polarization-field hysteresis curves of a $LiCuVO_4$ single crystal measured at 113 Hz in electrical fields up to $5\,kV\,cm^{-1}$ for two directions of P: (a) P parallel to the a direction in zero magnetic fields at temperatures above and below the ferroelectric transition. (b) P parallel to the c direction with applied magnetic field $H = 2.7$ T at $T = 1.7$ K.

Most probably, a slight misalignment of the sample in the experimental setup or residual contributions of the polarization in the a direction slightly enhanced the dielectric constant in the c direction. However, at $H_1 < H < H_2$ this peak becomes much more pronounced with the maximum in peak height close to H_1. For $H > H_1$ the normal vector of the spin spiral is switched into the a direction giving rise to polarization in the c direction [7–9]. The maxima in the dielectric constant curves (see magnetic-field dependent projections of dielectric constants to the ε'-H plane and the dashed line in figure 1(b)) are close to the critical field H_1. This indicates it is not only paraelectric to ferroelectric transitions that lead to peaks in the dielectric constant, but that a change in the polarization direction also has a strong impact on the dielectric properties. These measurements confirm and complement the magneto-current and magneto-dielectric experiments performed by Schrettle *et al* [4]. The present study of dielectric properties of $LiCuVO_4$ in an external magnetic field is fully consistent with the theoretical predictions [7–9] and demonstrates that the polarization can be switched by external magnetic fields.

We now address the following question; can an electric field switch the spin helicity of $LiCuVO_4$? Yamasaki *et al* [3] have demonstrated control of the spin helicity of $TbMnO_3$ by the direction of the polarization. This system is another prototypical example of a spin-helix system following the mechanisms considered in [7–9]. Spin-polarized neutron scattering in small electric fields applied during cooling shows that the spin helicity can be switched from a counter clockwise to a clockwise spiral magnetic structure and vice versa by an electrical field. In the following, we present a thorough characterization of the field-dependent polarization of $LiCuVO_4$ for different polarization directions, in various external magnetic fields and for different temperatures (figures 2 and 3). Figure 2(a) shows the evolution of the ferroelectric order with polarization P parallel to the a direction, measured in a zero magnetic field and at temperatures close to $T_N \approx 2.5$ K. The measurement at 3 K exhibits no significant nonlinear polarization during field modulation, i.e. as expected, no signature of ferroelectric order is found for this temperature. With decreasing temperature the shape of the curves changes significantly. At 2.7 K a hysteresis loop arises, which is typical for the ferroelectric order. To reach the remanent polarization of $5\,\mu C\,m^{-2}$ requires at least an electrical field of about $3\,kV\,cm^{-1}$. The remanent polarization increases with decreasing temperature and apparently reaches a maximum of about $18\,\mu C\,m^{-2}$ at 2 K. However, the $P(E)$ curves shown in figure 2 reveal that at low temperatures saturation has not yet been reached for the applied measurements frequency of 113 Hz. Obviously, higher electrical fields $> 4\,kV\,cm^{-1}$ would be necessary to generate a completely polarized state. This explains the deviation of the present result of $18\,\mu C\,m^{-2}$ at 2 K from the reported polarization of $30\,\mu C\,m^{-2}$ at 1.9 K [4, 21] revealed by pyrocurrent measurements using static poling fields during cooling. In any case, the performed measurements demonstrate that the ferroelectric polarization of $LiCuVO_4$ can be switched by an electrical field in zero magnetic fields, which to our knowledge has not been demonstrated before. According to the symmetry relation $P \propto e \times Q$ prevailing in this type of spin-driven multiferroics [7–9], this finding also implies that the spin helicity can be controlled by an electrical field.

Figure 2(b) demonstrates the switching of the polarization in the c direction, measured in a magnetic field of $H = 2.7\,T > H_1$ applied in the a direction. As demonstrated by the dielectric-spectroscopy results shown in figure 1(b), the polarization can be switched by an external magnetic field. The corresponding electric-field-dependent polarization measurements, corrected for linear capacitive contributions, reveal the typical non-linear ferroelectric behaviour with an apparent saturation polarization of about $2\,\mu C\,m^{-2}$ at $5\,kV\,cm^{-1}$ electrical field. This value is in reasonable agreement with the magnetocurrent measurement ($4\,\mu C\,m^{-2}$; [4]). The applied field of 2.7 T is larger than H_1 and thus the spiral normal vector e is fixed and oriented parallel to a. The result of figure 2(b) demonstrates a switching of the polarization direction. Therefore, according to the relation $P \propto e \times Q$, the spin helicity must switch too. It is a key result for spin-driven ferroelectrics that, even in an applied magnetic field, the spin helicity is switched by an electrical field.

Because the switched polarization in the c direction shown in figure 2 is relatively small, some doubts concerning the

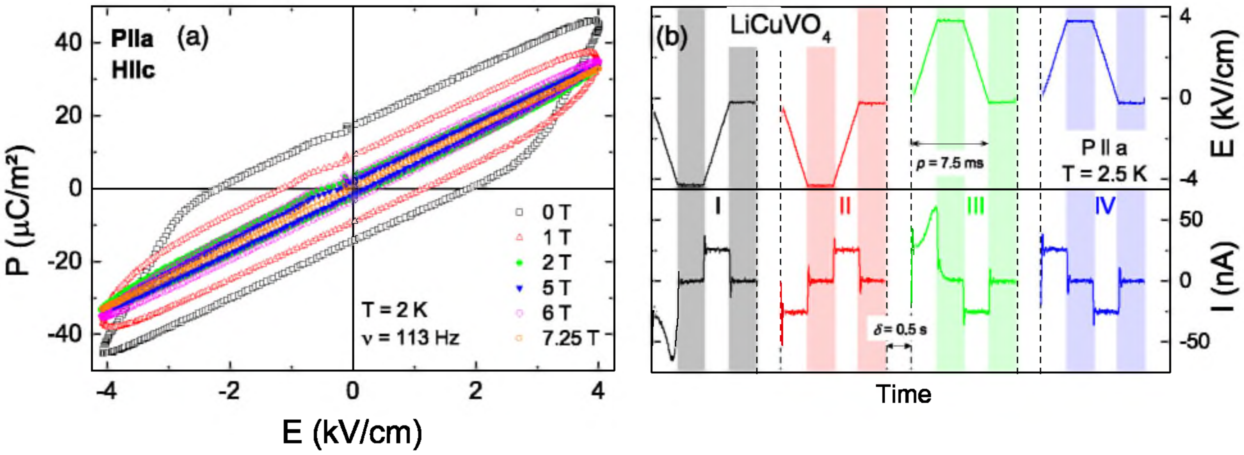

Figure 3. (*a*) Polarization-field hysteresis curves of a $LiCuVO_4$ single crystal measured at 113 Hz and 2 K in electrical fields up to 4 kV cm^{-1}. The experiments were performed for P parallel to the a direction and in magnetic fields up to 7.5 T oriented parallel to c. (*b*) Time-dependent excitation signal E and time-dependent resulting current I for P parallel to the a direction of the positive-up-negative-down measurement at 2.5 K. Polarization switching is evidenced by the spikes in the response of pulses I and III.

significance of these results may arise when assuming a slightly misaligned sample in the measurement setup or when considering artefacts that can occur during hysteresis-loop measurement [22, 23]. To further corroborate the switchability of the spin helicity by an electrical field in the presence of an external magnetic field, the ferroelectric polarization was also measured at 2 K in the a direction under magnetic fields up to 7.25 T applied in the c direction. As shown in figure 3(*a*), ferroelectric hysteresis loops also appear in this case. The remanent polarization decreases with increasing magnetic field and the 'corners' of the hysteresis loops become more rounded, i.e. the polarization does not saturate. Obviously, the maximum field of 4 kV cm^{-1} is insufficient to orient all ferroelectric domains to reach complete saturation. The positive-up-negative-down measurements shown in figure 3(*b*) provide further evidence for polarization switching: Only the current responses to the first and third electric field pulse show peaks arising from the switching of the macroscopic polarization. The intrinsic nature of this effect is strongly supported by the absence of such peaks at the second and fourth pulse as here the polarization was already switched by the preceding pulse [24]. Together with the magneto-current and pyrocurrent measurements of [4], we can exclude any non-intrinsic origin of the non-linear polarization response of $LiCuVO_4$ documented in the present work.

It can be assumed that the applied magnetic fields strengthen the orientation of the clockwise or counter clockwise spiral magnetic structure and thus the fraction of electrically polarizable domains decreases. Increasing H beyond H_1 leads to a polarization of the order of 2.5 μC m^{-2}, which corresponds to the polarizable fraction of the overall polarization of about 25 μC m^{-2} at $T = 1.95$ K, measured by magnetocurrent experiments [4]. Finally, when approaching the transition into the modulated collinear spin structure at about 7.25 T, the saturation polarization increases again (see loop at 6 T in figure 3(*a*)), which might be due to fluctuating domains or a softened spin-spiral state close to the ferro- to paraelectric transition in $LiCuVO_4$. Overall, these experiments again demonstrate that, even when applying external magnetic fields, an electric field can pole parts of the ferroelectric domains in the spin-driven ferroelectric state of $LiCuVO_4$, which is accompanied by a change of spin helicity.

4. Summary and conclusions

In summary, we have presented a thorough dielectric and polarization analysis of the spin-driven ferroelectric $LiCuVO_4$ close to the three dimensional ordering of its spiral magnetic structure at about 2.5 K. The measurements were performed as a function of the external magnetic field, temperature and field direction. Peaks in the temperature-dependent dielectric constants indicate the para- to ferroelectric transition. In the case of non-switching electrical polarization ($P||a$ and $H||c$), the dielectric constant is only slightly influenced by the strength of the external magnetic field within the regime of the spiral magnetic structure. In the switching case ($P||c$ and $H||a$), a peak of the dielectric constant shows up in the regime where the spin helix is turned in the direction of the external magnetic field ($H_1 < H < H_2$). This is consistent with the theoretical symmetry predictions for multiferroic spiral magnets [7–9], demonstrating the ability to switch the polarization by magnetic fields.

The most significant result of the present work is the detailed characterization of the field-dependent polarization of $LiCuVO_4$ as a function of temperature, magnetic field and electric field direction. There are only a few reports of the nonlinear electrically driven polarization of spin-driven multiferroics in literature [2, 11, 12] and, to our knowledge, such results were never reported for $LiCuVO_4$. Our measurements reveal the typical ferroelectric polarization hysteresis loops and thus also demonstrate the ability to electrically control the spin helicity in $LiCuVO_4$. We show that in $LiCuVO_4$, even under external magnetic fields, residual ferroelectric polarization is present and, hence, the spiral spin helicity can at least be partly switched from counter clockwise to clockwise or vice versa. These rarely documented features of spin-driven ferroelectrics indicate the close coupling of electric and magnetic order in these materials.

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