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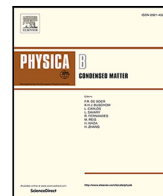
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## The magnetoelectric effect in $\text{LiFePO}_4$ – revisited

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### ABSTRACT

We study the magnetoelectric effect in  $\text{LiFePO}_4$  using the pyrocurrent method to determine the magnetic-field-induced electric polarization as a function of temperature for various applied magnetic field strengths. We discover a diagonal magnetoelectric tensor element not previously reported. This new coupling reflects the emergence of an electric polarization along  $a$  induced by a magnetic field along the same direction and is consistent with the symmetry-imposed requirements for the small canting components of the magnetic ground state reported for this compound. Our observation is thus further evidence for a ground state which is not supported by the space group  $Pnma$  as originally assigned to  $\text{LiFePO}_4$ .

### 1. Introduction

In magnetoelectric (ME) materials, a magnetization is induced upon applying an electric field or similarly, an electric polarization is induced upon applying a magnetic field [1–4]. Electric polarization and magnetization in these materials are not necessarily spontaneous but regardless of whether they are spontaneous or induced, manipulating one property affects the other and vice versa. The linear ME effect is described by a tensor,  $\alpha$ , coupling the polarization and magnetic field as  $\mathbf{P} = \alpha\mathbf{H}$  and likewise, the magnetization and electric field as  $\mu_0\mathbf{M} = \alpha^T\mathbf{E}$ . The magnetic point group symmetry of the system determines which tensor elements may be non-zero [5,6].

Here we revisit the ME effect in  $\text{LiFePO}_4$  with crystal structure reported to belong to the space group  $Pnma$ .  $\text{LiFePO}_4$  becomes antiferromagnetic below  $T_N = 50$  K with the ordered moments primarily along the  $b$  axis and the magnetic unit cell coinciding with the crystallographic one [7–9]. Previous measurements show that the non-zero ME tensor elements are  $\alpha_{ab}$  and  $\alpha_{ba}$  [10,11], in agreement with the magnetic point group ( $mmm'$ ) [12] as first proposed for the magnetic structure in  $\text{LiFePO}_4$  [7,13]. However, more recent neutron diffraction studies demonstrate that the magnetic ground state of  $\text{LiFePO}_4$  involves two different irreducible representations [9,14] and that the structure is not entirely collinear. The consequence is a lowering of the magnetic point group symmetry and additional ME tensor elements are permitted, i.e. the diagonal elements  $\alpha_{aa}$ ,  $\alpha_{bb}$  and  $\alpha_{cc}$  [12].

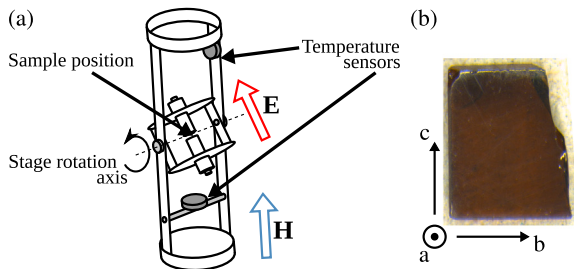
In this work, we measure the pyroelectric current as a function of temperature at different field strengths up to 12 T in order to further investigate, the ME effect in  $\text{LiFePO}_4$ . We discover that indeed the diagonal ME tensor element,  $\alpha_{aa}$ , is non-zero and this observation is consistent with the recently proposed low-symmetry ground state of the compound [9]. Consequently, the crystal symmetry may be lower than  $Pnma$ .

### 2. Methods

The magnetic-field-induced electric polarization was derived from the pyroelectric current (pyrocurrent). The measurements were performed at the Helmholtz-Zentrum Berlin using a Physical Property Measurement System (PPMS) by Quantum Design with a custom insert, see Fig. 1(a) [15]. A high quality  $\text{LiFePO}_4$  single crystal was grown by a flux method and from this a plate-like sample with dimensions  $a \times b \times c = 0.45 \times 3 \times 4.3$  mm<sup>3</sup> was cut, see Fig. 1(b). For each cut, the crystal was aligned within 0.5° perpendicular to the desired crystallographic direction using X-ray Laue diffraction. Gold was sputtered on both large (100) faces to ensure good electrical contact. The sample holder rotates with respect to the vertical field direction and thus permits probing off-diagonal ME tensor elements. The stage rotation is fixed before inserting the stick into the PPMS, i.e. only *ex-situ* rotations are possible. This way the experimental setup allows for probing  $\alpha_{aa}$ ,  $\alpha_{ab}$  and  $\alpha_{ac}$ . For

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**Fig. 1.** Pyrocurrent setup. (a) Sample holder allows for sample rotation with respect to the vertical magnetic field direction (after Ref. [15]). Only *ex-situ* rotations are possible. (b) Optical microscopy image of the sample used in the experiment with crystal axes indicated.

$H||b$  and  $H||c$ , the sample is aligned by eye inside the holder using the cut sides as a reference. This means that the sample alignment with respect to the magnetic field direction is within  $\sim 2^\circ$  for these two settings. For  $H||a$  and with respect to the electric field direction, the alignment is determined by the precision of the cut, i.e. within  $0.5^\circ$ .

The pyrocurrent was measured as a function of temperature in the range 4–60 K and with applied magnetic field up to 12 T using the quasi-static method [16]. The magnetic field direction is always vertical in the PPMS but with the sample aligned such that the magnetic field is parallel to either of the three crystallographic axes. An electric potential corresponding to  $\sim 200$  V/mm was applied in the paramagnetic phase at 60 K to ensure formation of a single domain for the electric polarization. The electric field was always applied along the  $a$ -axis of the sample. The sample was electric and magnetic field cooled to base temperature where the potential was switched off but the magnetic field was kept constant at the desired field strength. The pyrocurrent,  $I(T)$ , was recorded upon heating with a constant ramp rate of  $\frac{dT}{dt} = 2$  K/min.

The electric polarization,  $P(T_1)$ , at temperature  $T_1$  is calculated as follows:

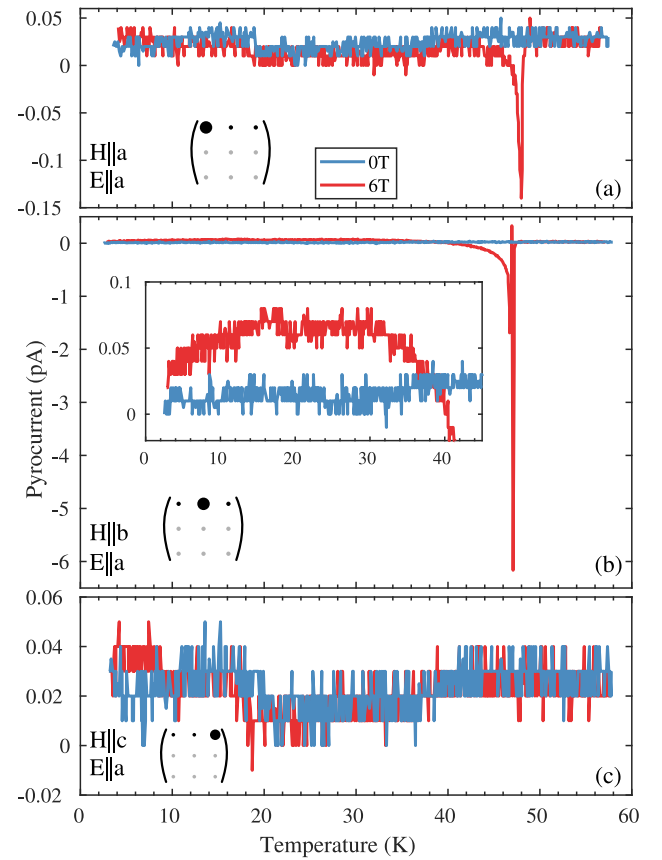
$$P(T_1) = P(T_0) - \frac{1}{A} \int_{T_0}^{T_1} I(T) \left( \frac{dT}{dt} \right)^{-1} dT, \quad (1)$$

where  $A$  is the surface area of the sample and the integration constant  $P(T_0)$  is chosen such that the polarization is zero in the paramagnetic phase.

### 3. Results and discussion

**Fig. 2** displays the pyrocurrent as measured at zero field and at 6 T for magnetic fields applied along respectively the  $a$ ,  $b$  and  $c$  axes from top to bottom panel. Note that the first field-induced phase transitions in  $\text{LiFePO}_4$  are reported at 29 and 32 T [17] and hence 6 T may be considered in the low-field limit. Note also that for  $\text{LiFePO}_4$  the ME effect is not allowed in zero field and we therefore do not expect a signal in the pyrocurrent in zero field. For  $H||b$  there is a strong signal and for  $H||c$  there is no signal. This is as expected if the magnetic point group is  $mmm'$  [12] as previously suggested [7,11]. However, we also observe a weak but significant signal for  $H||a$ , i.e. for the diagonal component of the ME tensor,  $\alpha_{aa}$ . Note that the temperature profile of the current below the transition is markedly different for  $H||a$  and  $H||b$  at 6 T [compare **Fig. 2(a)** and the inset in panel (b)]. For  $H||a$  the current at 6 T is close to the zero-field background below 40 K. For  $H||b$  there is a clear finite contribution over the background below 40 K. This indicates that the signal for  $H||a$  is not simply created by a small misalignment with respect to the magnetic field direction in combination with the strong signal for  $H||b$ .

The electric polarization as derived from the pyrocurrent using Eq. (1) is shown in **Fig. 3** for various applied field strengths. The temperature profile of the pyrocurrent as measured at zero field is used

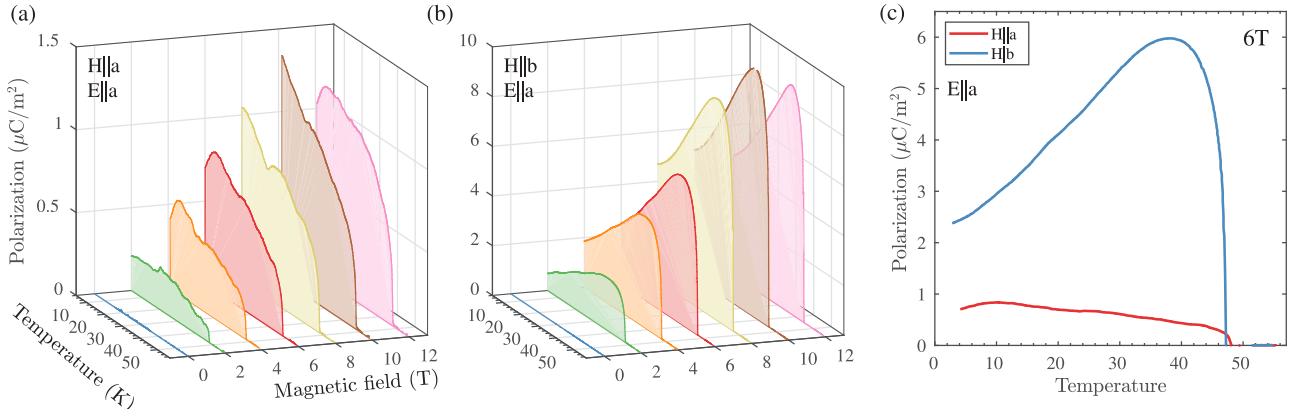


**Fig. 2.** Raw pyrocurrent data for zero field (blue line) and at 6 T (red line) for (a)  $H||a$ , (b)  $H||b$  and (c)  $H||c$ . At zero field the ME effect is prohibited in  $\text{LiFePO}_4$  and the pyrocurrent here may therefore serve as background as described in the text. In each panel a matrix is shown which indicates the probed ME tensor element. The inset in panel (b) shows the pyrocurrent for  $H||b$  below 45 K on a similar scale to panel (a) to highlight the difference in the temperature dependence between the data with  $H||a$  and  $H||b$  in this region. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

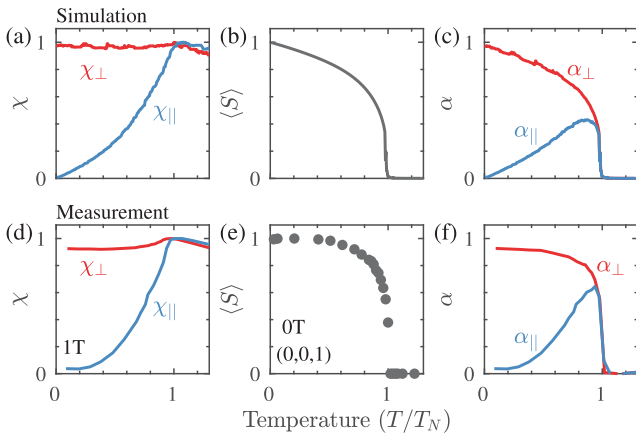
as background and subtracted prior to integration. In addition, we subtract a field-induced upwards shift of the current in the paramagnetic phase as we expect no signal in this phase. It is apparent that the temperature profiles for the polarization with  $H||a$  and  $H||b$  are very different and we discuss this in the following.

In the simplest picture of an easy-axis collinear antiferromagnet [18, 19] only ionic spin contributions are considered and the ME coefficients may be expressed as  $\alpha_{||,\perp} \propto \langle S \rangle \chi_{||,\perp}$ . Here  $\langle S \rangle$  is the sublattice magnetization and corresponds to the order parameter,  $\chi$  is the magnetic susceptibility and  $||$  ( $\perp$ ) denotes the parallel (transverse) direction with respect to the moment direction which is along  $b$  for  $\text{LiFePO}_4$ . For the transverse direction,  $\chi_{\perp}$  is constant below  $T_N$  and hence the temperature dependence of  $\alpha_{\perp}$  resembles that of the order parameter. However, for fields parallel to the spin direction,  $\chi_{||}$  goes to zero at low temperatures. Therefore, in this simple picture,  $\alpha_{||}$  first increases below  $T_N$  but then displays a maximum before going to zero at low temperatures. This behavior is illustrated in **Fig. 4** which shows  $\chi$ ,  $\langle S \rangle$  and  $\alpha$  as obtained with Monte Carlo simulations for a standard easy-axis antiferromagnet (top panels) and corresponding measurements for  $\text{LiFePO}_4$  (bottom panels).

Going back to our measurements on  $\text{LiFePO}_4$ , the ME tensor element  $\alpha_{ab}$  (i.e.  $\alpha_{||}$ ) displays a temperature profile similar to that predicted by this simple picture except for a finite  $T = 0$  contribution which may be explained when taking into account orbital moment [21]. The sister compound  $\text{LiMnPO}_4$  has an entirely quenched orbital moment



**Fig. 3.** Electric polarization as derived from the pyrocurrent and collected at different magnetic field strengths for (a)  $H||a$  and (b)  $H||b$ . Note the different scales on the vertical axes. Panel (c) shows a comparison of the polarization for  $H||a$  and  $H||b$  at 6T, corresponding to the pyrocurrent curves shown in Fig. 2.

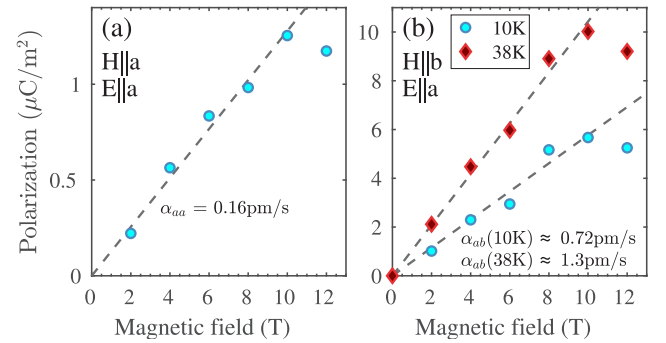


**Fig. 4.** Magnetoelectric effect in the simplest picture. Top panels show the simulated results for a standard easy-axis collinear antiferromagnet and the bottom panels show the corresponding measurements for  $\text{LiFePO}_4$ . (a),(d) Magnetic susceptibility [20],  $\chi$ , (b),(e) order parameter [9],  $\langle S \rangle$  and (c),(f) ME coupling coefficients calculated as  $\alpha_{||\perp} \propto \langle S \rangle \chi_{||\perp}$ .

and indeed here  $\alpha_{||} \rightarrow 0$  for  $T \rightarrow 0$  [10]. In  $\text{LiFePO}_4$ , the temperature dependence of the  $\alpha_{aa}$  component follows that of the order parameter as expected for collinear antiferromagnets in transverse field (i.e.  $\alpha_{\perp}$ ). This is also the case for  $\alpha_{ba}$  as shown in Ref. [9].

The existence of  $\alpha_{aa}$  (and by extension also  $\alpha_{bb}$  and  $\alpha_{cc}$ ) implies that the magnetic point group symmetry of  $\text{LiFePO}_4$  in its ground state is  $2_z/m'_z$  rather than  $mmm'$  [12]. This is consistent with neutron diffraction intensity being observed at magnetic Bragg peak positions corresponding to components in the ground state belonging to two different irreducible representations [9]. Consequently the space group of  $\text{LiFePO}_4$  is most likely not  $Pnma$  as otherwise reported by several studies [7,13,22–24]. A high-resolution synchrotron X-ray diffraction experiment is needed to look for the possibility of a monoclinic distortion.

Next, we examine the field dependence of the electric polarization. In Fig. 5 we show the average polarization at  $10 \pm 1\text{K}$  and  $38 \pm 1\text{K}$  as a function of field. The value 38K is chosen because this is where the temperature profile of the polarization has its maximum for  $H||b$ . The other value, 10K, was chosen to represent the low-temperature behavior. Below this temperature the polarization displays a dip for certain field values and directions, see Fig. 3(a) and 3(c) [also seen for the data collected with  $H||c$ ]. Since no phase transition was previously reported at this temperature, we assign the dip as an artifact of the experimental setup. Fig. 5 shows that the polarization increases linearly



**Fig. 5.** Field dependence of the polarization at 10K (blue circles) and 38K (red diamonds) for (a)  $H||a$  and (b)  $H||b$ .

with field as expected. However, at 12T the polarization decreases. It is unclear from our measurements whether this is a real effect, but since the first field-induced phase transitions in  $\text{LiFePO}_4$  are reported at 29 and 32T [17] we do not expect a non-monotonous behavior of the polarization as a function of field at 12T. It would be interesting to investigate the ME effect in  $\text{LiFePO}_4$  at higher fields.

#### 4. Conclusions

We revisited the magnetolectric effect in  $\text{LiFePO}_4$  using the quasistatic pyrocurrent method and discovered a non-zero magnetolectric tensor element,  $\alpha_{aa}$ , not previously reported. This diagonal element is consistent with the magnetic ground state as determined from neutron diffraction and which involves two different irreducible representations. Consequently, both studies suggest that the crystal structure of  $\text{LiFePO}_4$  is not orthorhombic in the antiferromagnetically ordered phase.

#### CRedit authorship contribution statement

**Ellen Fogh:** Conceptualization, Sample preparation, Data analysis, Interpretation, Figure preparation, Writing – original draft. **Bastian Klemke:** Pyrocurrent measurements, Data analysis, Interpretation. **Alexandre Pages:** Sample preparation, Data analysis, Interpretation. **Jiying Li:** Crystal growth. **David Vakin:** Crystal growth. **Henrik M. Rønnow:** Interpretation, Writing – original draft. **Niels B. Christensen:** Conceptualization, Interpretation, Writing – original draft. **Rasmus Toft-Petersen:** Conceptualization, Interpretation, Writing – original draft.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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