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How to cite

KHARCHENKO, N. F. et al. Weak ferromagnetism in the antiferromagnetic magnetoelectric crystal LiCoPO4. In: Low temperature physics, 2001, vol. 27, n° 9-10, p. 895–898. doi: 10.1063/1.1414584

This publication URL:https://archive-ouverte.unige.ch/unige:31080Publication DOI:10.1063/1.1414584

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Weak ferromagnetism in the antiferromagnetic magnetoelectric crystal LiCoPO₄

N. F. Kharchenko and Yu. N. Kharchenko*

B. Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine, pr. Lenina 47, 61103 Kharkov, Ukraine

R. Szymczak and M. Baran

Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, PL-02-668 Warsaw, Poland

H. Schmid

University of Geneva, Department of Inorganic, Analytical and Applied Chemistry, CJ-1211 Geneva 4, Switzerland

(Submitted August 3, 2001)

Fiz. Nizk. Temp. 27, 1208–1213 (September–October 2001)

A study of the magnetization of the antiferromagnetic magnetoelectric crystal $LiCoPO_4$ as a function of temperature and the strength of a magnetic field oriented along the antiferromagnetic vector reveals features due to the presence of a weak ferromagnetic moment. The value of the magnetic moment along the **b** axis at 15 K is approximately 0.12 G. The existence of a ferromagnetic moment can account for the anomalous behavior of the magnetoelectric effect observed previously in this crystal. © 2001 American Institute of Physics. [DOI: 10.1063/1.1414584]

Cobalt lithium orthophosphate is a well-known magnetoelectric crystal of the family of orthorhombic antiferromagnets with the olivine structure and having the general formula LiMPO₄ (where $M = Fe^{2+}$, Mn^{2+} , Co^{2+} , Ni^{2+}). It has been attracting attention because it has large values of the constants α_{xy} and α_{yx} of the linear magnetoelectric effect^{1,2} and unusual and as yet unexplained behavior of the magnetoelectric effect in a magnetic field.²⁻⁴ The magnetoelectric effect in this crystal is the largest among the compounds of 3d elements. The crystal structure of LiCoPO₄, like that of the other lithium phosphates of transition elements of the olivine family, has a symmetry described by the space group *Pnma* (D_{2h}^{16}) (Refs. 5,6). In this structure the unit cell (a 10.20 Å, b = 5.92 Å, c = 4.70 Å) contains four formula units, and the magnetic ions are crystallographically equivalent and occupy four c positions. According to the results of neutron-diffraction studies⁷ carried out on polycrystalline samples of LiCoPO₄, upon antiferromagnetic ordering (T_N) $= 21.9 \text{ K})^2$ the number of formula units in the unit cell remains unchanged (z=4), and the magnetic moments of the Co^{2+} ions are collinear and directed along the **b** axis, completely compensating each other. The magnetic structure of the crystal is described in a collinear four-sublattice model with the Shubnikov symmetry group Sh_{62}^{445} (*Pnma'*) (Ref. 7).

In studying the magnetoelectric effect in LiCoPO₄, it was found^{2,3} that for preparation of a homogeneous (singledomain) antiferromagnetic state of the crystal, as must be done in order to measure the magnetoelectric effect, it is sufficient to decrease the temperature of the sample from $T>T_N$ to $T<T_N$ in a magnetic field **H** oriented along the **B** axis, or to apply a sufficiently strong magnetic field along the **b** axis at temperatures $T<T_N$. This is atypical for all of the compensated antiferromagnetic magnetoelectric crystals that have been studied, for which it is necessary to apply magnetic and electric fields simultaneously in order to prepare a single-domain state. The behavior of the magnetoelectric effect observed by the authors of Refs. 1–3 could be due to the existence of a weak ferromagnetic moment in the crystal. However, previous studies of the magnetic properties of both polycrystalline^{7,8} and single-crystal⁹ LiCoPO₄ have not detected weak ferromagnetism.

The creation of a homogeneous magnetic state in a compensated antiferromagnet in the presence of only a magnetic field may also be caused by quadratic (in the field) magnetization effect.¹⁰ In this case the magnetic field induces in the crystal a magnetic moment that is even with respect to the field strength. In antiferromagnetic (AFM) states with oppositely directed sublattice moments, oppositely directed magnetic moments will be induced. Therefore, when a magnetic field is applied in a certain direction, the energy of the collinear antiferromagnetic domains will be different. When the difference of the energies of the antiferromagnetic domains, which varies in proportion to H^3 , reaches a threshold value determined by the coercivity of the antiferromagnetic domain wall, the crystal will go to a single-domain state or a magnetization reversal of its antiferromagnetic state will occur.¹¹ A quadratic magnetization effect is allowed by symmetry only in AFM crystals which are not symmetric with respect to the operation of anti-inversion (or complete inversion): $\overline{1}' = \overline{1} \cdot 1'$. However, the group mmm' that has been established for LiCoPO₄, although it does not contain the operation of spatial inversion, does have a center of antiinversion. Consequently, the quadratic magnetization and weak ferromagnetic moment (WFM) should be forbidden in LiCoPO₄.

Magnetooptic studies¹² of $LiCoPO_4$ have revealed new features of the behavior of this antiferromagnetic crystal in a

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FIG. 1. Temperature dependence of the magnetization of the LiCoPO₄ crystal in an external magnetic field $\mathbf{H} \| \mathbf{b}$ with a field strength of 1 T (a) and 0.05 T (b); the M(T) curves near the Néel temperature at H=0.05 T (c). FC (H=1 T) — the value of the magnetic field in which the sample was cooled.

magnetic fields. It was found that the birefringence of linearly polarized light induced by a magnetic field $\mathbf{H} \| \mathbf{b}$ is comparable to the spontaneous magnetic linear birefringence at a value of the external field much smaller than the value of the effective exchange field. This property suggests the presence of transverse projections of the magnetic moments in the crystal and, hence, a noncollinear magnetic structure in it.

Given this situation, it is advisable to make highly sensitive measurements of the magnetization of the LiCoPO₄ crystal. In this paper we report the results of measurements of the magnetization M as a function of temperature and magnetic field strength. All of the measurements were made with a SQUID magnetometer (Quantum Design MPMS-5). The sample studied had a mass of 7.46 mg and was in the form a parallelepiped with dimensions of $0.96 \times 1.22 \times 1.76$ mm.

The experimental results are presented in Figs. 1–3. Figure 1 shows the curves of the temperature dependence of the magnetization obtained in magnetic fields H of 1.0 and 0.05 T. The behavior of the magnetization in the 1.0 T field is similar to that which was observed previously in Ref. 9 at H=1.2 T. The temperature dependence of M is similar to the typical behavior for 2D antiferromagnets in which the interaction between magnetic ions in the plane is dominant over the interaction between ions belonging to neighboring planes.¹³ For M(T) there is a broad hump, the top of which lies above T_N (at $T \sim 25$ K).

In the 0.05 T field the M(T) curves is qualitatively different from that discussed above. It clearly displays the following features.



FIG. 2. Magnetization of the LiCoPO₄ crystal as a function of the internal magnetic field H_{int} in an external magnetic field $H \parallel b$ (a); the M(H)/H curves at crystal temperatures of 15 K (b) and 21.3 K (c).

a) In the temperature interval 5–10.5 K the projection of the magnetic moment of the sample on the magnetic field direction is negative. With increasing temperature its absolute value initially increases and then, at T>8 K, decreases to zero, changes sign, and increases monotonically with temperature out to the neighborhood of T_t (see Fig. 1b and 1c).

b) At a temperature $T_i = 20.9$ K there is a jump in the magnetization (occurring in a single interval between experimental points, which in this part of the curve is 0.1 K).

c) Near the Néel temperature at 21.6 K (see Fig. 1c) a weak but clearly registered peak is observed. The increase of the magnetization with further increase in temperature begins only at $T > T_N$.

All of these anomalies can be explained by assuming that the sample in the initial state had a ferromagnetic moment directed oppositely to the direction of the applied magnetic field. Thus the sample was initially cooled in "zero" field (ZFC) and then a field H=0.05 T, in which the measurements were made, was applied. The residual field of the superconducting solenoid can be as high as 0.002 T. The direction of that field could accidentally be directed opposite to the direction of the applied magnetic field in the M(T)measurement. It follows from the trend of the M(T) curve that the orientation of the spontaneous moment, directed opposite to the field, persists to a temperature T_t , at which the "switching" of the antiferromagnetic state of the sample occurred. In a narrow temperature interval 21-21.9 K the spontaneous moment is directed along the field. When the temperature approaches T_N the spontaneous moment rapidly decreases to zero, and a peak appears on the M(T) curve (see Fig. 1d).



FIG. 3. Hysteresis of the magnetization in the LiCoPO₄ crystal: the M(H) curve in the neighborhood of zero field at temperatures of 15 and 21.3 K (a); the M(H) curve after subtraction of the linear contribution χH ; the dashed curve shows a dependence of the type βH^3 (b); the M(H) curve after subtraction of the linear and cubic contributions: $M(H) - (\chi H + \beta H^3)$ (c).

Further confirmation of the presence of a weak ferromagnet moment in the LiCoPO₄ crystal was obtained in a study of the field dependence of the magnetization at different temperatures. Figure 2 shows the M(T) curves obtained at 15 and 21.3 K. The temperature 21.3 K was chosen so as to lie in the narrow temperature interval between the jump and the peak on the M(T) curve for H=0.05 T (see Fig. 1c).

Figure 2a shows the field curves of the magnetization, obtained for a completely cycle of variation of the field from

+5 to -5 T and back to +5 T. The M(H) curves are well approximated by the function $M(H) = M_s \chi + H + \beta H^3$. This function is shown by the solid curve in Fig. 2a for T=15 K. The presence of a nonzero spontaneous moment M_s is demonstrated by the M(H)/H curves in Figs. 2b, 2c. The position of the experimental points obtained at T=15 K are well described by the function $\chi + \beta H^2 + M_s/H$, where $M_s =$ ± 0.12 G, $\chi = 5.06$ G/T, and $\beta = 3.2 \times 10^{-2}$ G/T³. They are shown by the solid and dotted curves in Fig. 2.

Because of the nonzero value of M_s , as H goes to zero the quantity $M(H)/H = \chi + \beta H^2 + M_s/H$ increases by a hyperbolic law, M_s/H changes sign when the direction of the field is switched, and then it decreases by the same law. One can see that when the field reaches certain threshold values $(H_c^+ = +1.7 \text{ T and } H_c^- = -3.8 \text{ T})$ a jumplike transition of the experimental points from one branch of the M(H)/H curve to the other occurs. The M(H)/H curve obtained at 21.3 K differs from that described above in that the sign of M(H)/Hin the field interval from 5 to 0.1 T is always positive. Only in the field interval from -0.1 to 0.1 T is the behavior of M(H)/H at 21.3 K sign-varying and similar to that observed at 15 K in a wider field interval. This means that at that temperature the spontaneous moment M_s can be directed counter to the field only in a narrow field interval.

The hysteresis of the magnetization of the sample is more clearly demonstrated in Fig. 3. In Fig. 3a the part of the curve shown in Fig. 2a is shown in an enlarged scale in the field interval from -0.1 to +0.1 T. It is seen that a linear extrapolation of M(H) to H=0 near zero gives a nonzero spontaneous magnetization for both temperatures. The field dependence of that part of the magnetic moment of the sample which is not due to a simple field-independent susceptibility, i.e., $M(H) - \chi(H)$, is shown in Fig. 3b. The hysteresis loop is seen against the background of a cubic dependence. It is even more clearly seen after subtraction of the cubic contribution βH^3 (Fig. 3c). The revealed hysteresis of the magnetization convincingly attests to the presence of a weak spontaneous magnetic moment in the sample. Its value, determined as $M_s = (M_s^+ - M_s^-)/2$, is 0.12 G at 15 K and around 0.015 G at 21.3 K.

Other features can also be seen in Fig. 3c. The most intriguing of them is the change in magnetization in the field interval from -0.1 T to +0.1 T, which has a diamagnetic character. Such behavior of the sample is unusual. It brings to mind "superdiamagnetism,"^{14,15} which is allowed by symmetry in this antiferromagnetic magnetoelectric crystal, where the symmetry of the leading magnetic ordering admits the existence of a toroidal moment.⁴ In the presence of a density gradient of the toroidal moment (e.g., near defects of the system to a magnetic field.¹⁵ However, before drawing any conclusions about the causes of the observed feature it is necessary to carry out special experiments and to eliminate possible artifacts.

As to the causes of the weak ferromagnetism (or, more precisely, weak ferrimagnetism), there are several possible mechanisms for its appearance in the $LiCoPO_4$ crystal. Using the well-known methods of constructing invariants of the thermodynamic potential,¹⁶ one can see that although the usual second-order weak-ferromagnetic invariants of the type

 $M_i L_{2y}$ are forbidden in LiCoPO₄, the *Pnma* symmetry of the crystal allows fourth-order invariants containing the product $M_y L_{2y}$.

These invariants are the following: $M_{\nu}L_{2\nu}L_{1\nu}L_{3\nu}$, $M_{\nu}L_{2\nu}L_{1x}L_{3x}$, $M_{y}L_{2y}L_{1z}L_{3z}$, $M_{v}L_{2v}L_{1x}L_{2z}$, $M_{y}M_{z}L_{2y}L_{2z},$ $M_{\rm v}L_{2\rm v}L_{1z}L_{2x}$, $M_{\nu}M_{z}L_{2\nu}L_{3x}$, $M_y M_x L_{2y} L_{2x}$, and $M_y M_z L_{2y} L_{3z}$. In addition, "gradient" invariants are allowed, which can lead to the formation of a modulated magnetic structure. Among them we mention the second-order invariant $(M_v dL_{2v}/dx - L_{2v} dM_v/dx)$ ⁴ Since the projection of the antiferromagnetic vector $L_{2\nu}$ transforms in the same way as the projection of the toroidal moment T_z (Ref. 4), the corresponding homogeneous and inhomogeneous invariants with a toroidal moment are also possible. At the present time it is not possible to answer the question of which mechanism gives rise to the weak ferromagnetism in $LiCoPO_4$. We can only say that the nonmonotonic behavior of the spontaneous magnetic moment on heating of the sample, which is attested to by the behavior of the magnetization of the crystal in a field of 0.05 T, indicates the presence of competing mechanisms. A similar dependence of the weak-ferromagnetic moment has been observed in crystals of antiferromagnetic vanadates, in particular, yttrium vanadate.¹⁷ It must also be noted that the features of the behavior of the magnetic linear birefringence in a cyclically varying magnetic field¹² implies that LiCoPO₄ must have an incommensurate modulated structure, if not spontaneous then magnetic-field induced. Depending on the mechanism giving rise to the weak ferromagnetism, the magnetic point group of the crystal may be one of the following noncentroantisymmetric groups: $m(\perp y)$ (this group admits a "longitudinal" weak-ferromagnetic structure $M_{\nu}L_{2\nu}L_{1\nu}L_{3\nu}$; 2'(||x) (which admits the structures $M_y L_{2y} L_{1x} L_{2z}$, $M_y L_{2y} L_{1x} L_{3x}$, $M_y M_z L_{2y} L_{2z}$, and $M_y M_z L_{2y} L_{3x}$), $m'(\perp z)$ (which admits the structures $M_{\nu}L_{2\nu}L_{1z}L_{3z}$, $M_{\nu}L_{2\nu}L_{1z}L_{2x}$, $M_{y}M_{x}L_{2y}L_{2x}$, and $M_{y}M_{z}L_{2y}L_{3z}$).

The presence of a quadratic magnetization effect in the $LiCoPO_4$ crystal for H||b remains open question. Although

an approximation of the M(H) curves by third-order polynomials does give corrections quadratic in H which have different signs for the two antiferromagnetic states, they are too small. Their small value and substantial difference leaves uncertainty as to whether they correspond to a physical effect or are the result of a small systematic error and scattering in the experimental data.

The authors thank V. I. Fomin and V. I. Kut'ko for a helpful discussion of the results.

*E-mail: kharchenko@ilt.kharkov.ua

³H. Wiegelmann, *Magnetoelectric Effects in Strong Magnetic Fields*, PhD Thesis, University of Konstanz, Konstanzer Dissertationen, Vol. 461, Hartung-Gorre, Konstanz (1995).

- ⁵R. E. Newham and M. J. Redman, J. Am. Ceram. Soc. 48, 547 (1965).
- ⁶F. Kubel, Z. Kristallogr. 209, 755 (1994).
- ⁷ R. P. Santoro, D. J. Segal, and R. E. Newnham, J. Phys. Chem. Solids 27, 1192 (1966).
- ⁸A. Goni, L. Lezama, G. E. Barberis, J. L. Pizzarro, M. I. Arriortua, and T. Rojo, J. Magn. Magn. Mater. **164**, 251 (1996).
- ⁹J.-P. Rivera and J. Korean, Phys. Soc. 32, S1855 (1998).
- ¹⁰G. Gorodetsky and D. Treves, Phys. Rev. A **135**, 97 (1964); G. Gorodetsky, B. Sharon, and S. Shtrikman, Solid State Commun. **5**, 739 (1967).
- ¹¹ A. V. Bibik, N. F. Kharchenko, and S. V. Petrov, Fiz. Nizk. Temp. **15**, 1280 (1989) [Sov. Phys. JETP **15**, 707 (1989)]; N. F. Kharchenko, R. Szymczak, and M. Baran, J. Magn. Magn. Mater. **140**, 161 (1995).
- ¹² M. F. Kharchenko, O. V. Miloslavska, Yu. M. Kharchenko, H. Schmid, and J.-P. Rivera, Ukr. J. Phys. Opt. 1, 16 (2000).
- ¹³M. F. Sykes and M. E. Fisher, Physica 28, 919 (1962).
- ¹⁴ V. L. Ginzburg, A. A. Gorbatsevich, Yu. V. Kopayev, and B. A. Volkov, Solid State Commun. **50**, 339 (1984).
- ¹⁵A. A. Gorbatsevich and Yu. V. Kopayev, Ferroelectrics 161, 321 (1994).
- ¹⁶E. A. Turov, Physical Properties of Magnetically Ordered Crystals [in Russian], Izd. Akad. Nauk SSSR, Moscow (1963).
- ¹⁷ Y. Ren, T. T. M. Palstra, D. I. Khomskii, and G. A. Sawatsky, Phys. Rev. B 62, 6577 (2000).

Translated by Steve Torstveit

¹M. Marcier, J. Gareyte, and E. F. Bertaut, C. R. Acad. Sci. Paris B 264, 979 (1967).

²J.-P. Rivera, Ferroelectrics 161, 147 (1994).

⁴I. Kornev, M. Bichurin, J.-P. Rivera, S. Gentil, H. Schmid, A. G. Janse and P. Wyder, Phys. Rev. B 62, 12247 (2000).