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Reference


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Magnetoelectric properties of LiCoPO$_4$: microscopic theory

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Abstract

The microscopic description of the magnetoelectric effect in LiCoPO$_4$ is given. The “one-ion” approximation in which the magnetic order is presented by a Weiss molecular field approximation is taken as the basis of the model. Using the lowest possible order of perturbation theory the mechanism analogous to that of the changes due to an electric field of $g$-factor rather than a mechanism which involves changes of the quadratic axial term (“D term”) in the spin-Hamiltonian is considered. Within the framework of the model it is shown that the odd part of the crystalline electric field and operator of the electric dipole transition can be represented by an effective operator with even parity that allows us a priori to take into account a parity selection rule. The expressions for the magnetoelectric tensor have been obtained. The theory may be applicable not only to the description of the static ME response but also to the description of the response of the system at optical frequencies. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

LiCoPO$_4$ belongs to the well-known family of orthorhombic antiferromagnets with general formula LiMPO$_4$ (where, M = Ni$^{++}$, Co$^{++}$, Mn$^{++}$, Fe$^{++}$) which are known to be magnetoelectrics [1]. In Ref. [2], where a detailed experimental investigation of the linear magnetoelectric (ME) effect was performed, the value of coefficient $\alpha_{yx}$ was found to be 30 ps/m, quite large even for crystals with rare-earth elements. The microscopic theory of the magnetoelectric effect which involves changes of some parameter in a spin Hamiltonian was considered in [3–6]. The purpose of this paper is to demonstrate that the magnetoelectric effect in LiCoPO$_4$ is very nearly of the “one-ion” type. We shall consider the mechanism of the magnetoelectric effect which is based on the lowest possible order of perturbation theory and analogous to the change of the $g$-factor due to $E$. The reason for such an approach is that the width in energy of the ground state spin multiplet is about 20% of the energy separation between the orbital ground state and the first excited orbital state [7].
2. Model description

As the unperturbed single-ion Hamiltonian \( H_0 \), let us take the Hamiltonian of the crystal in the magnetically ordered phase, i.e. the unperturbed single-ion Hamiltonian \( H_0 \) contains contributions describing free ion \( \text{Co}^{2+} \) \( H_t \), the even part of the crystalline electric field \( H_C \), the spin–orbit \( H_{LS} \) and exchange interactions \( H_{ex} \):

\[
H = H_t + H_C + H_{LS} + H_{ex} + H^u + H_h + H_E
= H_0 + H^u + H_h + H_E.
\]

We need to be concerned only with monochromatic fields. Thus in dipole approximation we take

\[
H_{\text{E}}(t) = \left(-\frac{|e|}{2}\right) \cdot E e^{-i\omega t} + \left(-\frac{|e|}{2}\right) \cdot E \cdot E e^{i\omega t}
= E e^{-i\omega t} + E e^{i\omega t},
\]

\[
H_{\text{B}}(t) = \mu_B/2(L + 2S) \cdot H e^{-i\omega t} + \mu_B/2(L + 2S) \cdot H e^{i\omega t}
= H e^{-i\omega t} + H e^{i\omega t},
\]

\[
\delta\langle P(t) \rangle = \langle \Psi \rangle - \langle \sum_j r_j \rangle \Psi.
\]

\[
\delta\langle P^0(t) \rangle = \sum_p \chi_{sp}(-\omega) \cdot h^p e^{-i\omega t} + \sum_p \chi_{sp}(\omega) \cdot h^{p*} e^{i\omega t}.
\]

Replacing \( |\Psi\rangle \) by the perturbed wave function at large positive times \( |\Psi^\oplus\rangle \) and following the approach of formal scattering theory, we obtain

\[
|\Psi^\oplus\rangle = (1 + G H' + G H' G' + \cdots) |g\rangle,
\]

where \( G \) is the appropriate Greens operator.

It is easy to see that the lowest terms which are proportional to the first power of \( h^0 \) and \( H_C^0 \) contain \( H' \) twice and we have terms like

\[
\langle H_C^0 \rangle_{uu} \langle P \rangle_{nn} \langle L + 2S \rangle_{n'g'}.\]

3. Effective even operator

Since the odd part of the crystalline potential and the electric dipole moment occur together only, the total effect of them can be represented by means of an even operator [8]

\[
\langle g_j | P_{\text{EFF}} | g_i \rangle = \frac{1}{E_{ug}} \sum_u \langle g_j | H_C^0 | u \rangle \langle u | P | g_i \rangle + \langle g_j | P | u \rangle \langle u | H_C^0 | g_i \rangle,
\]

where \( E_{ug} = 126.3 \times 10^3 \text{ cm}^{-1} \) is approximate mean energy separation between the ground state 3d\(^7\) and the nearest opposite-parity manifold 3d\(^4\)p for free Co\(^{2+}\). The first term in Eq. (7) is the matrix element of the electric dipole moment between the small odd-parity component in state \( g_j \) and the even-parity state \( g_i \), the second term being that between the even-parity state \( g_j \) and the small odd-parity component in state \( g_i \).

In terms of spherical harmonics the electric dipole moment is expressed as

\[
P^t_q = -|e| \sum_j r_j C^t_q(\theta_j, \phi_j),
\]

where \( q = 0, \pm 1 \).

Now, the effective even operator may be expressed as a series of spherical harmonics of the form

\[
P_{\text{EFF}} = \sum_{k', q'} q'_k e^{ik'q'} C^k_q(\theta_j, \phi_j) = \sum_{k', q'} b_{k'} C^k_q(\theta_j, \phi_j),
\]
where

\[ b_{k}^{\xi} = \sum_{K,Q} b_{K}^{\xi}(K,Q) = \frac{2}{E_{2uK,Q}} \sum_{l,l'} (-1)^{l'} B_{K}^{l}(e|e|\cdot r^k) \times \left( \begin{array}{c} K \\ Q \end{array} \right) g_{Q,k} \cdot \mathcal{Z}, \]

\[ \mathcal{Z} = (2k + 1) \frac{\{ k, k', K \} \{ l, l' \} \{ q, q' \}}{(l||C^{(k)}||l')(l'||C^{(K)}||l').} \]

To calculate the equivalent even operator we consider \( A_{1}^{+1}, A_{3}^{+1} \) odd harmonics only, other odd harmonics will be ignored. By using the radial integrals

\[ \langle r \rangle = 1.18 \text{ a.u.}, \quad \langle r^3 \rangle = 5.91 \text{ a.u.} \]

the crystal field parameters are

\[ B_{1}^{\pm 1} = A_{1}^{+1} \langle r \rangle = \mp 29143.81 + i37757.651 \left( \text{cm}^{-1} \right), \]

\[ B_{3}^{\pm 1} = A_{3}^{+1} \langle r^3 \rangle = \mp 5252.59 + i10042.87 \left( \text{cm}^{-1} \right), \]

\[ B_{3}^{\pm 3} = A_{3}^{+3} \langle r^3 \rangle = \mp 5762.61 - i3602.01 \left( \text{cm}^{-1} \right). \]

(12)

After some calculation we get (see Table 1):

1. \( b_{2}^{+1}(K = 1, Q = \mp 1) = \pm c_1 + id_1 \)
   \[ = \pm 0.222519 - i0.288288 \left( \text{a.u.} \right), \]

2. \( b_{2}^{+1}(K = 3, Q = \mp 1) = \pm c_2 + id_2 \)
   \[ = \mp 0.00801926 - i0.01533327 \left( \text{a.u.} \right), \]

3. \( b_{2}^{0}(K = 1, Q = \mp 1) = c_3 + id_3 \)
   \[ = 0.128472 - i0.166443 \left( \text{a.u.} \right), \]

4. \( b_{2}^{0}(K = 1, Q = -1) = c_4 + id_4 \)
   \[ = -0.128472 - i0.166443 \left( \text{a.u.} \right), \]

5. \( b_{2}^{0}(K = 3, Q = +1) = c_5 + id_5 \)
   \[ = 0.00694489 + i0.0132785 \left( \text{a.u.} \right), \]

6. \( b_{2}^{0}(K = 3, Q = +1) = c_6 + id_6 \)
   \[ = -0.00694489 + i0.0132785 \left( \text{a.u.} \right), \]

7. \( b_{2}^{0}(K = 1, Q = \mp 1) = \pm c_7 + id_7 \)
   \[ = \mp 0.31469 - i0.407701 \left( \text{a.u.} \right), \]

8. \( b_{2}^{0}(K = 3, Q = \mp 1) = \pm c_8 + id_8 \)
   \[ = \pm 0.00283524 + i0.00542093 \left( \text{a.u.} \right), \]

9. \( b_{2}^{0}(K = 3, Q = \mp 3) = \pm c_9 + id_9 \)
   \[ = \mp 0.120471 - i0.0075302 \left( \text{a.u.} \right). \]

And for effective even operator we obtain (in Eq. (13) and (14) \( 1 \text{ a.u.} = 2.52 \times 10^{-18} \text{ esu cm} \))

\[ b_{2}^{0} = - i0.3063 \left( \text{a.u.} \right), \]

\[ b_{2}^{+1} = \pm 0.2145 - i0.3036 \left( \text{a.u.} \right), \]

\[ b_{2}^{+2} = \pm 0.3055 - i0.4098 \left( \text{a.u.} \right). \]

Further we shall restrict our consideration to the same coordinate system as in Ref. [7] (\( \alpha = 90^{\circ}, \beta = 90^{\circ}, \gamma \approx -90^{\circ} -33^{\circ} \)). The ME tensor for such a case has the following form:

\[ \chi_{\text{ME}} = \begin{pmatrix} 0 & 0 & 0.83876x_{12} \\ 0 & 0 & 0.5445x_{21} \\ 0.83876x_{21} & 0.5445x_{21} & 0 \end{pmatrix}. \]

(15)

Let us now consider three cases separately.

**Case 1:** We are interested in the form of the effective even operator for \( \delta\langle P \rangle \). Using Eq. (14) and the fact that \( P_{x} = P_{1}^{0} \) we get the following expression for the effective even operator:

\[ P_{\text{EFF}} = b_{2}^{-1}C_{1}^{z} + b_{2}C_{1}^{z}. \]

**Case 2:** The component of the polarization along \( x \) direction \( \delta\langle P \rangle \) is given by

\[ P_{x} = \frac{1}{\sqrt{2}}(P_{1}^{-1} - P_{1}^{+1}). \]

(17)
Consequently, using Eq. (13) and Table 1 for the effective even operator we have
\[
P_{\text{EFF}} = \frac{1}{\sqrt{2}} \{ i \cdot (d_y - d_8 - d_7) \cdot (C_2^2 - C^2_z) + (c_6 - c_8 - c_7) \cdot (C^2_2 + C^2_z) + 2 \cdot (c_4 + c_6)C_0^2 \}.
\tag{18}
\]

Case 3: The component of the polarization along \( y \) direction \( \delta \langle P'(t) \rangle \) is given by
\[
P^y = \frac{i}{\sqrt{2}}(P_1^{-1} + P_1^1).
\tag{19}
\]

Using Eq. (13) and Table 1 for the effective even operator we get
\[
P_{\text{EFF}} = \frac{1}{\sqrt{2}} \{ \text{Re}[b^2_g] \cdot (C_2^2 - C^2_z) + i \text{Im}[b^2_g] \times (C_2^2 + C^2_z) + 2i(d_4 + d_6)C_0^2 \}.
\tag{20}
\]

4. Magnetoelastic susceptibility

Following Ward [9] the diagrams may now be constructed and evaluated. It is easy to see that we do not have any restrictions due to the parity selection rule and the first non-vanishing contribution is of the second order. In general, we have to include the possibility of the resonance magnetic transitions. If we do so the propagator \( G \) is not a Hermitian one, but for the exited state \( |n \rangle \) has an additional complex term in the denominator \(+ i \Gamma_n/2\), where \( \Gamma_n \) is the width of the state \( |n \rangle \).

After some calculations we obtain
\[
\chi^{\text{ME}} = \frac{N \mu_B}{\hbar} \sum_n \omega_n \left( \frac{\omega_{ng}^2 - \omega^2 + \Gamma_n^2/4 \cdot A - (\Gamma_n/2) \left( \omega_{ng}^2 + \omega^2 + \Gamma_n^2/4 \right) \cdot B}{(\omega_{ng}^2 - \omega^2 + \Gamma_n^2/4)^2 + \omega^2 \Gamma_n^2} \right),
\tag{22}
\]

where \( A + iB = \langle P_{\text{EFF}} \rangle_{gn} \langle (L + 2S) \rangle_{ng} \) and \( N \) is the number of magnetic ions per unit volume.

For the static ME susceptibility we obtain
\[
\chi^{\text{ME}}(0) = \frac{N \mu_B}{\hbar} \sum_n \frac{A \cdot \omega_{ng} - B \cdot \Gamma_n/2}{(\omega_{ng}^2 + \Gamma_n^2/4)}.
\tag{23}
\]

Using Eqs. (22) and (23) and calculated wave functions we can find the magnetoelastic susceptibility. The wave functions can be found by the same procedure as it was done in Ref. [7] including exchange field in molecular-field approximation. Undoubtedly the arithmetic will be complex and we estimate the order of magnitude of \( |\chi^{\text{ME}}| \).

\[N = 1.4 \times 10^{22} \text{ cm}^{-3} = 0.21 \times 10^{-2} \text{ a.u.}; \quad \mu_B = 3.642 \times 10^{-3} \text{ a.u.}; \quad b^2_g \sim 0.5 \text{ a.u.} \]

The matrix element \( \langle C_0^2 \rangle_{gn} \langle (L + 2S) \rangle_{ng} \) has an order of magnitude \( \sim 1; \omega_{ng} \sim 170 \text{ cm}^{-1} = 0.77 \times 10^{-3} \text{ a.u.} \) is the energy separation between the lowest-lying Kramers doublet and the nearest exited level [7]. The final result of our estimate is

\[
\delta \langle P(t) \rangle = \frac{\mu_B}{2} \sum_n \left( \frac{\langle P_{\text{EFF}} \rangle_{gn} \langle h \cdot (L + 2S) \rangle_{ng}}{\omega_{ng} - \omega - i \Gamma_n/2} + \frac{\langle h \cdot (L + 2S) \rangle_{gn} \langle P_{\text{EFF}} \rangle_{ng}}{\omega_{ng} - \omega - i \Gamma_n/2} \right) e^{+i\omega t} + \left( \frac{\langle P_{\text{EFF}} \rangle_{gn} \langle h \cdot (L + 2S) \rangle_{ng}}{\omega_{ng} - \omega + i \Gamma_n/2} + \frac{\langle h \cdot (L + 2S) \rangle_{gn} \langle P_{\text{EFF}} \rangle_{ng}}{\omega_{ng} + \omega + i \Gamma_n/2} \right) e^{-i\omega t}.
\tag{21}
\]
\(|\chi^{\text{ME}}| \sim 2.5 \times 10^{-3}[\text{cm}] = 8.2 \text{ (ps/m)}\). It is necessary to note that the model we have considered accounts for the electronic component of the ME effect only. The numerical estimate based on this mechanism explains the observed value \([2]\) to be within an order of magnitude. Another type of effect which can contribute to \(\chi^{\text{ME}}\) are the microscopic strains. This effect was proposed by Rado \([3\text{–}5]\). Measuring \(\chi^{\text{ME}}\) at optical frequencies could distinguish between these two possibilities.

Another possible interaction which we did not take into consideration is due to an additional term in a spin–orbit operator. We can write the spin–orbit interaction in the following form:

\[
H_{\text{LS}} = \lambda (LS) - \frac{\mu_B}{mc} (S \cdot [E \times p]) = V_1 + V_2. \tag{24}
\]

The first term in Eq. (24) is the operator of spin–orbit interaction with nuclear field, the second term with an electric field \(E = E^{\text{int}} + E^{\text{ext}}\), \(E^{\text{ext}}\) is the external electric field and \(E^{\text{int}}\) is the electric field due to the fields generated by surrounding charges. For instance, for \(\text{LiCoPO}_4\) internal electric fields according to Eq. (12) \(E_x\) and \(E_y\) are not equal to zero but \(E_z = 0 (z \parallel \mathbf{b})\).

We are interested in the second term in Eq. (24). Taking the derivative with respect to \(E^{\text{ext}}\) we obtain for the polarisation operator

\[
P = e\mathbf{r} + \mu_B \left[ \frac{p}{mc} S \right] = P_1 + P_2. \tag{25}
\]

Thus the additional term arises in the polarisation operator which is proportional to the magnetic moment and electron momentum. This term is stipulated by the fact that the moving particle with a magnetic moment creates an electrical field which is proportional to the velocity of the particle. The contribution of such a term to the magnetoelectric effect was considered in Ref. \([10]\).

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