Magnetic anisotropy in Li-phosphates and origin of magnetoelectricity in LiNiPO$_4$

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Li-based phosphates are paradigmatic materials for magnetoelectricity. By means of first-principles calculations, we elucidate the microscopic origin of spin anisotropy and of magnetoelectric effects in LiNiPO$_4$. The comparison with LiCoPO$_4$ reveals that Co-$d^7$ and Ni-$d^8$ electronic clouds show distinct orbital shapes, which in turn result in an opposite trend of the local spin anisotropy with respect to the surrounding O$_6$ cages. Due to magnetic anisotropy, the Ni-based phosphate shows a peculiar “angled-cross” spin ground-state, which is responsible for magnetoelectricity. In this respect, we show that, under a magnetic field $H_z$, an electronic polarization $P_z$ arises, with an estimated linear magneto-electric coefficient in good agreement with experiments.

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Olivine phosphates LiCoPO$_4$ and LiNiPO$_4$ are attracting large interests, due to their peculiar magnetoelectric (ME) effect \( [i.e. \, \text{the control of ferroelectric (magnetic) properties via a magnetic (electric) field}] \) as well as their application for electrodes in rechargeable Li batteries$^1,2$. Recently, ferrotoroidal domains and antiferromagnetic domains have been independently observed in LiCoPO$_4$ by using second harmonic generation$^3$. The toroidal moment, generated by a vortex of magnetic moments, is considered as source of a novel \textit{ferroic order}, closely related to ME effects$^4,5$ as well as to multiferroicity$^6$ (\textit{i.e.} coexistence of long-range magnetic and dipolar orders). In fact, LiCoPO$_4$ shows a nonzero linear ME coefficient, $\alpha_{xy}$ and $\alpha_{yx}$, at low temperature, consistent with the toroidal moment $T$ nearly parallel to $z$ axis$^5$, whereas LiNiPO$_4$ shows $\alpha_{xz}$ and $\alpha_{xz}$$^2$. Although magnetoelectricity has been macroscopically investigated by means of Landau theory$^5,3$, its microscopic origin has not been clarified yet nor first principles calculations aimed at investigating ME effects in phosphates exist in the literature. In LiCoPO$_4$, antiferromagnetic (AFM) spins were found to be along the $b$ axis$^10$ or uniformly rotated from this axis by 4.6°$^8$. In LiNiPO$_4$, it was proposed the collinear AFM spins to lie along the $c$ axis$^11$, but recently a non-collinear structure in a “spin-cross” style$^8,12$ was suggested, in order to explain the butterfly shape of the ME hysteresis curve$^13$.

In this letter, within Density-functional theory (DFT) we investigate the magnetic anisotropy for Li-phosphates LiTMPO$_4$ (TM = Ni, Co) and we are able to correlate the orbital degree of freedom with the calculated anisotropy and spin-configuration. The discussion on magnetic anisotropy is particularly important for LiNiPO$_4$, where we find, as magnetic ground-state, a peculiar spin-cross configuration that leads to magnetoelectricity; finally, we clarify the microscopic origin of ME effects, our calculated ME coefficient being in quantitative agreement with experiments.

\textbf{Methodology and structural details.} DFT simulations were performed using the VASP code$^14$ and the PAW pseudopotentials$^15$ within the GGA+$U$ formalism$^16$ (\( U=5 \) eV and \( J=0 \) eV for Ni $d$-states). Other values of $U=2$ and 8 eV were also tested. The cut-off energy for the plane-wave expansion of the wave-functions was set to 400 eV and a $k$-point shell of (2, 4, 4) was used for the Brillouin zone integration. Lattice parameters were fixed as experimentally observed$^{17,18}$. The internal atomic coordinates were fully optimized in a (fully-compensated) AFM configuration, keeping $S_1 = S_2 = -S_3 = -S_4$ configuration. In the orthorhombic $Pnma$ ($D_{2h}^5$) paramagnetic space group, these four Co/Ni sites are related by eight symmetry operations; all the rotations and mirror reflections accompany translations, so that the Co/Ni sites are slightly deviated from high-symmetry positions. Optimized coordinates of the four Co/Ni ions are: Co1/Ni1(1/4+, 1/4, -δ), Co2/Ni2(3/4+ε, 1/4, 1/2+δ), Co3/Ni3(3/4−ε, 3/4, δ), Co4/Ni4(1/4−ε, 3/4, 1/2−δ), where $\epsilon=0.0268$ and $\delta=0.0207$ for Co, $\epsilon=0.0249$ and $\delta=0.0152$ for Ni. The spin-orbit coupling (SOC) term was computed self-consistently inside each atomic sphere, with a radius of 1 Å. The electronic polarization $P$ was calculated using the Berry phase method$^{19}$.

\textbf{Magnetic anisotropy: LiCoPO$_4$ vs LiNiPO$_4$.} As shown in Fig$^1$ each Co ion is surrounded by highly distorted oxygen octahedra, so that the partially filled $t_{2g}$ shell shows a dumbbell-shaped charge distribution, axially elongated along the $n_d$ direction (along m1-m2 O-Co-O bonds). This peculiar shape is expected to induce a strong local magnetic anisotropy via the SOC term. On the other hand, in LiNiPO$_4$, the Ni-$d^8$ orbital shows a more isotropic sphere–like shape.

Both the global and local magnetic anisotropy were investigated by rotating four spins simultaneously, keeping a collinear AFM coupling. The \textit{global} magnetic anisotropic energy (MAE) was calculated by differ-

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enances in the total energy with different spin-orientations, whereas the local anisotropic energy was evaluated as proportional to the expectation value of the SOC energy: 

$$E_{SOC} = \langle \frac{1}{2} \sum_{i} \Sigma \cdot \alpha^i \rangle \langle \Sigma \cdot \alpha^i \rangle \text{meV/cell}$$

(integrated in each atomic sphere). Here the electronic cloud.

Fig. 2 (a) and (b) shows the MAE of Co spins in the ac and ab planes, respectively. The global easy axis is the b direction, in agreement with the experimental suggestion that spins should be aligned along the b axis (possibly with a slight rotation). The MAE is rather high (more than 10 times larger than the orbitally-ordered Mn spins in TbMnO$_3$ [21]). As shown by the spin angle dependence of $E_{SOC}$ (cfr Fig. 2 (a)), the easy/hard axial direction depends on each Co site. $E_{tot}$ can be fitted by a conventional quadratic anisotropic term for $S_i$ spins:

$$D(S_i/|S_i| \cdot n_l)^2$$

where $n_l$ is the site-dependent hard axis, described as $n_1 = n_3 = (\cos \alpha, 0, \sin \alpha)$, $n_2 = n_4 = (\cos \alpha, 0, -\sin \alpha)$ (see, Fig. 1). According to the fitting, $D =$ 7.39 meV and $\alpha =$ 35.48°: this implies the hard axis $n_l$ to be nearly along the m1 bond, so that Co spins are aligned in an easy plane perpendicular to $n_l$. In terms of site-dependent anisotropy, we note that the stable AFM spin ordering $S_1 = S_2 = -S_3 = -S_4$ is different from the orbital ordering $L_1 = L_3$, $L_2 = L_4$ which causes a local anisotropy. In such a configuration, all four spins are allowed to lie in the easy plane only when collinear AFM spins are pointing along the b axis. Therefore the b axis is the easy axis in the collinear AFM configurations for Co spins.

Our calculations show for Ni spins an opposite trend of $E_{SOC}$, with respect to the Co spin, both in the ac and ab planes (cfr Fig. 2); moreover, the MAE is almost two orders of magnitude smaller, consistent with the spherical $d^8$ electronic cloud. Here the b axis is the global hard axis. Assuming the easy axis to lie in the ac plane and by fitting $E_{tot}$ to the anisotropic term, we estimate $D =$ -0.50 meV and $\alpha =$ 46.7°. Here $\alpha$ is close to $\pi/4$.
so that two opposite contributions from local anisotropy nearly cancel out (Fig. 2(c)) and induce a small in-plane anisotropy. The negative value of $D$ implies the existence of an easy axis $\mathbf{n}_1$ of Ni spins in the ac plane (see. Fig. 3), $\mathbf{n}_1 = \mathbf{n}_3 = (\sin \alpha, 0, \cos \alpha)$, $\mathbf{n}_2 = \mathbf{n}_4 = (\sin \alpha, 0, \cos \alpha)$ which is close to the $\mathbf{n}_1$ direction at Co spins. Therefore, the $c$ axis is the global easy axis for Ni spins if a collinear AFM configuration is assumed. However, in order to stabilize the local anisotropic term, the spins are expected to slightly tilt with respect to the $c$ axis. This deviation, denoted as “angled cross” spin configuration, has been already discussed by Chupis [2] in terms of Landau theory and suggested to play an important role for magnetoelectricity. This issue has been carefully investigated here by tilting the spins by an angle $\theta$ from the $c$ axis. Indeed, as shown in Fig. 3, the non-collinear spin structure in the ac plane with $\theta \sim 1^\circ$ gives the lowest energy. We considered a generic Hamiltonian for $\mathbf{S}_i$ ($i = 1$ to 4) spins, including a Heisenberg term, an relativistic anisotropy term and a Zeeman–like term (see next paragraph, where a finite external H-field will be introduced):

$$\mathcal{H} = \sum_{(i,j)} J_{ij} \frac{\mathbf{S}_i \cdot \mathbf{S}_j}{|\mathbf{S}_i| |\mathbf{S}_j|} + \sum_i D(\frac{\mathbf{S}_i}{|\mathbf{S}_i|} \cdot \mathbf{n}_i)^2 + \sum_i \mathbf{S}_i \cdot \mathbf{H} \quad (1)$$

In this H=0 case, a delicate balance of the first two terms occurs: As the spin is tilted towards the local easy axis, the SOC-term is stabilized, whereas the $J_{ij}$ coupling becomes unstable. As a result, the equilibrium occurs in a non-collinear “angled-cross” spin-configuration.

Magnetoelectricity in LiNiPO$_4$. The existence of a local magnetic anisotropy is particularly important in the context of magnetoelectricity. In order to investigate ME effects in LiNiPO$_4$, hereafter we focus on the change in the spin configuration under a magnetic field with respect to the “angled cross” ground-state. The exchange coupling constants $J_{ij}$ were evaluated by total energy differences fitted to Eq. (1), considering several AFM configurations. Our calculated values are $J_{12} = J_{34} = -0.118$ meV, $J_{13} = J_{24} = 1.46$ meV, $J_{14} = J_{23} = 3.92$ meV (the positive sign means AFM coupling). The dominant $J_{14}$ keeps the spins in the AFM configuration, whereas $J_{12}$ and $J_{13}$ are responsible for removing the degeneracy of some AFM configurations, i.e. the AFM spin configuration $\mathbf{S}_1 = \mathbf{S}_2 = -\mathbf{S}_3 = -\mathbf{S}_4$ gives the most stable energy. The $J$ values are consistent with the fact that four Ni sites are separated into two pairs (Ni1, Ni4) and (Ni2, Ni3) by a Li intercalated layer, so that different pairs are expected to be weakly coupled. The anisotropy coefficient $D$ is also obtained from DFT, as reported above. A nonzero applied magnetic field, $H_x$, is expected to tilt the Ni spins from the angle-crossed spin configuration, with angles from the $c$ axis, denoted as $\theta_1$ and $\theta_2$ [2] (here we assume the relation $\theta_1 = \theta_4$ and $\theta_2 = \theta_3$ by considering the symmetry under the magnetic field.) By using DFT parameters, Eq.(1) is easily minimized by Newton method with $\theta_1$ and $\theta_2$ angles varying by few degrees in a way proportional to $H_x$ (cfr Fig. 3(b), inset).

Constraining the spin angles as obtained from the Newton minimization for each H-field, we evaluate the electronic polarization. A small but finite $P_z$ is obtained, confirming magnetoelectricity. As shown in Fig. 4 all spins have positive $x$ components for $H_x > 5 T$; however, the sign of the moment doesn’t affect the induced $P_z$. 

FIG. 3: Total energy $\Delta E_{\text{total}}$ (black solid line) and $\Delta E_{\text{SOC}}$ (dashed red line) at each Ni site vs the direction of non-collinear Ni spins in the “spin-cross” configuration (shown in the inset). The minimum is marked by a vertical blue arrow. The dashed line is a function proportional to $1 - \cos \theta$, as a guide to the eye, to outline the “asymmetrical” behaviour of the DFT data.

FIG. 4: (a) Spin configuration in the ac plane under an applied field $H_x$. (b) Magnetic-field induced electric polarization along $z$ (with and without SOC, as well as considering D=0 in Eq.(1), see text) in LiNiPO$_4$. The magnetization $M_x$ is also shown (left-triangles, referred to the right y-axis) Inset: spin angle $\theta_1$ and $\theta_2$ (in degrees) vs $H_x$ (T)
which is rather linearly proportional to $H_z$, consistent with the experimentally observed behaviour at low temperature. From the slope of the P-H curve from H=0 to 10 T, the linear ME coefficient $\alpha_{xx}$ is estimated as $0.59 \mu C/m^2T = 0.74ps/m$, comparable with the low-temperature experimental value $\alpha_{xx}^{exp} = 1.5ps/m$.\footnote{12}

Let us now investigate the microscopic origin of magnetoelectricity. Electric dipoles are found to be mainly induced by symmetric exchange\footnote{22}, often referred to as “inverse” Goodenough-Kanamori (iGK) interaction \footnote{24} in Ni1-O-Ni4 (or Ni2-O-Ni3) bonds. For small $H$, the other conventional mechanism for magnetically-induced polarization - related to antisymmetric exchange and often labeled as “inverse Dzyaloshinskii-Moriya (iDM)” - is negligible. However, for high magnetic fields, the iDM becomes sizeable (cfr Fig.4 b), where the comparison between $P_z$ values including - or not - the SOC term is reported. In this context, we note that the existence of a local anisotropic term is important to induce $P$: Assuming $D = 0$ in Eq.(1), so that $\theta_1 = \theta_2$, we find that the induced $P_z$ is less than half with respect to the nonzero $D$ case (cfr Fig[4]b).

Finally, we estimate toroidal moments based on Ref.\footnote{3}. The collinear AFM spin configuration in LiCoPO$_4$ induces $(0, 0, -1.52)\mu_B\AA$, whereas the noncollinear spin configuration (at $H=0T$) in LiNiPO$_4$ induces $(0.19, 0.94, 0)\mu_B\AA$ per unit cell. We observe that the spin crossed state causes a small $T_{2g}$-component; however the $T_{3g}$ component, coming from the compensated AFM spin configuration, is relevant to the ME effect with finite $P_z$ and $H_z$.

In conclusion, we have presented a careful investigation of the spin-anisotropy in Li-based transition-metal phosphates. We found that LiNiPO$_4$ shows a peculiar ground-state spin configuration: due to a site-dependent magnetic anisotropy, it shows non-collinear spins arranged as “angled-cross”-like. This is relevant in the context of magnetoelectricity: due to the ground-state noncollinearity, the spin configuration induced by an applied magnetic field leads to a net electric polarization, as shown by a realistic first-principles estimate of the magnetoelectric coefficient in agreement with experiments. Our results suggest a possible avenue for elucidating the origin of the ME effects in other compounds.

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