Unusual spin fluctuations and magnetic frustration in olivine and non-olivine LiCoPO₄ detected by ³¹P and ⁷Li nuclear magnetic resonance

S.-H. Baek,¹ R. Klingeler,² C. Neef,² C. Koo,² B. Büchner,¹,³ and H.-J. Grafe¹
¹IFW-Dresden, Institute for Solid State Research, PF 270116, 01171 Dresden, Germany
²Kirchhoff Institute for Physics, University of Heidelberg, 69120 Heidelberg, Germany
³Institut für Festkörperphysik, Technische Universität Dresden, 01062 Dresden, Germany
(Dated: February 14, 2014)

We report ³¹P and ⁷Li nuclear magnetic resonance (NMR) studies in new non-olivine LiZnPO₄-type LiCoPO₄tetra microcrystals, where the Co²⁺ ions are tetrahedrally coordinated. Olivine LiCoPO₄, which was directly transformed from LiCoPO₄tetra by an annealing process, was also studied and compared. The uniform bulk magnetic susceptibility and the ³¹P Knight shift obey the Curie-Weiss law for both materials with a high spin Co²⁺ (3d⁷, S = 3/2), but the Weiss temperature Θ and the effective magnetic moment μeff are considerably smaller in LiCoPO₄tetra. The spin-lattice relaxation rate T¹⁻¹ reveals a quite different nature of the spin dynamics in the paramagnetic state of both materials. Our NMR results imply that strong geometrical spin frustration occurs in tetrahedrally coordinated LiCoPO₄, which may lead to the incommensurate magnetic ordering.

I. INTRODUCTION

The olivine structured lithium transition metal phosphates LiMPO₄ (M = Fe, Mn, Co, and Ni) have attracted interest from both fundamental and technical points of view. They reveal a variety of unusual magnetic, magnetoelectric, and ferrotoroidic properties associated with high spin (HS) M²⁺ ions.¹⁻³ Also, their low cost, low toxicity, high stability, and high energy density made them promising candidates of high-voltage cathode materials for Li-ion batteries.⁶⁻¹¹ Among the olivine LiMPO₄ family, LiCoPO₄ features a very large linear magnetoelectric effect¹²⁻¹³ and a high theoretical energy density up to 801 Wh/kg based on its high discharge plateau 4.8 V versus Li/Li⁺.¹⁴⁻¹⁵

Olivine LiCoPO₄ crystallizes in the orthorhombic Pnma space group.¹⁶ The Co²⁺ (S = 3/2) ions sit in the center of the distorted CoO₆ octahedra which share corners and edges with PO₄ tetrahedra, as illustrated in Fig. 1 (a). Below Tₐ ≈ 21 K, the moments order antiferromagnetically, with a tilt of 4.6° away from the crystallographic b-axis within bc plane, and the crystal structure changes to the P12₁₁ symmetry.¹⁷⁻¹⁹ In this low symmetry, a nonzero toroidal moment is allowed and confirmed experimentally.²⁰⁻²²

For optimal performance of electrode materials for Li-ion batteries, it is crucial to get insight into the fundamental structural, electronic, and magnetic properties of the materials and their limits and trends for applications.²³⁻²⁰ Therefore, recently discovered non-olivine structured LiCoPO₄ is interesting and may provide an important step forward in the understanding of the impact of structure and magnetism on the performance of a battery material. LiCoPO₄tetra possesses Pn₂₁₀ symmetry and consist of CoO₆ octahedra, instead of CoO₆ octahedra in the olivine structure, sharing only corners with PO₄ tetrahedra.²²⁻²⁴ [see Fig. 1 (b)]. The non-olivine structure becomes unstable at high temperatures towards the olivine one.

Initial studies indicate that tetrahedral LiCoPO₄ exhibits poor performance in terms of cycling stability and discharge capacity compared to the olivine phosphate.²³⁻²⁴ In an attempt to elucidate the detailed magnetic properties of both compounds associated with their structural aspects, we carried out an NMR study on tetrahedral LiCoPO₄tetra as well as on the annealed olivine compound. Our results of the Knight shift and the spin-lattice relaxation rates show that the tetrahedrally coordinated Co²⁺ spins in LiCoPO₄tetra are strongly frustrated, resulting in quite different magnetic properties, compared to olivine LiCoPO₄. The magnetic structure in the ordered state

FIG. 1: Crystal structure of (a) olivine (Pnma symmetry) (b) tetrahedral (Pn₂₁₀ symmetry) LiCoPO₄, projected along the crystallographic c axis. Li atoms are omitted for clarity. Their unit cells are drawn as dotted lines.
II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

Non-olivine LiCoPO$_4^{\text{tetra}}$ microcrystals with $Pn2_1a$ symmetry were synthesized by the microwave-assisted hydrothermal synthesis technique, as described in detail in Refs. 23, 24. Olivine LiCoPO$_4$ with $Pnma$ symmetry was obtained by annealing the non-olivine compound at 700°C for 24 hours under an argon atmosphere.

The temperature dependence of the static uniform magnetic susceptibility $\chi(0,0)$ of LiCoPO$_4^{\text{tetra}}$ and LiCoPO$_4^{\text{olivine}}$ was measured using a SQUID magnetometer in the field of 1 kOe after cooling in zero magnetic field.

$^7$Li and $^{31}$P NMR measurements have been carried out using a spin-echo method in a fixed field of 7.0494 T in the temperature range of 5–400 K. Since $^{31}$P (nuclear spin $I = 1/2$) does not involve electric quadrupole effects, it is an ideal probe to study magnetism and spin fluctuations in these materials. $^{31}$P NMR spectra over most of the measured temperature range are relatively narrow and quite symmetric, in comparison with the large linewidth and strong anisotropy observed in other Li phosphates, which allowed us to determine the Knight shift and the linewidth reliably. The spin-lattice relaxation rates $T_1^{-1}$ were measured using the saturation recovery method and $T_1$ was obtained by fitting the relaxation of the nuclear magnetization $M(t)$ to a single exponential function, $1 - M(t)/M(\infty) = A \exp(-t/T_1)$ where $A$ is a fitting parameter.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Magnetic susceptibility $\chi$ and $^{31}$P Knight shift $K$

Fig. 2 shows the molar static susceptibility $\chi_{\text{mol}} = M/H$ as a function of temperature for both olivine and tetrahedral LiCoPO$_4$. The drop of the $\chi$ data at low temperatures indicates that in both systems long range antiferromagnetic order evolves at low temperature. The transition can be clearly observed in the magnetic specific heat $c_{\text{mag}} \sim \partial(\chi_{\text{mol}}T)/\partial T$ (see inset) as both compounds show an anomaly at $T_N = 21$ K and 7 K, respectively.

At high temperatures, in both compounds follow a Curie-Weiss law, $\chi_{\text{mol}} = C/(T+\Theta) + \chi_0$, where $\chi_0$ is a $T$-independent susceptibility (see inset of Fig. 2(b)). Fitting the data with the CW law yields the Weiss temperatures $\Theta = 52(5)$ K (olivine) and $\Theta = 7(1)$ K (tetra), and the effective magnetic moments $5.1 \mu_B$ (olivine) and $4.4 \mu_B$ (tetra). Both values of $\mu_{\text{eff}}$ exceed the spin-only value of 3.87 $\mu_B$ expected for the HS $3d^7$-configuration for full quenching of the orbital moment. In LiCoPO$_4^{\text{tetra}}$, the orbital admixture to the measured effective $g = 2.27$ is governed by the reduced spin-orbit coupling $\lambda$ and the tetrahedral crystal field (CF) splitting $\Delta_t$ of the Co$^{2+}$ orbital states of $e_g$ and $t_{2g}$ symmetry. It can be approximated by

$$g = 2 - \frac{8 \cdot \lambda}{\Delta_t}. \quad (1)$$

With $\lambda \approx -143$ cm$^{-1}$, the data are consistent with $\Delta_t \approx 4250$ cm$^{-1}$. In contrast, the electronic configuration of HS Co$^{2+}$ in the octahedral configuration $t_{2g}^2e_g^2$ realized in LiCoPO$_4^{\text{tetra}}$ exhibits a stronger orbital contribution since it involves only partially filled low-lying orbital triplet states with pseudo angular momentum $\ell = 1$. The observed effective moment agrees well with the findings in Ref. 18.

In this paper, we mainly concentrate on the NMR data obtained on both materials. Hence, we note that the broadening of the NMR line is essentially determined by the uniform bulk susceptibility as can be deduced from Fig. 2(b) where the full width at half maximum (FWHM) of the $^{31}$P NMR spectra is plotted against $T$ as an implicit parameter. Further information on the static magnetic properties is obtained from measurements of the $^{31}$P Knight shift, $^3K$. Its temperature dependence confirms CW-behaviour in both materials. The data in Fig. 3 are well described by $K = C'(T+\Theta) + K_0$, where $K_0$ is the T-independent non-spin shift. For both materials, $K_0$ appears negligibly small, indicating that $K$ probes almost entirely the spin part of the magnetic susceptibility.

Focusing on the evolution of antiferromagnetic order, the static susceptibility data imply deviations from the mean-field Curie-Weiss-like behaviour already at relatively high temperatures. In the olivine sample, small deviations from the experimental data are observed below $\sim 250$ K as visible in Figs. 2(a) and (b, inset). The experimentally observed susceptibility is smaller than predicted by the Curie-Weiss law which is in agreement to the evolution of antiferromagnetic fluctuations well above $T_N$.

In the tetragonal polymorph, such behavior is present below $\sim 50$ K which is best seen if the magnetic specific heat in Fig. 2(a) (inset) is considered.

In order to compare the static susceptibility measured by bulk and local techniques, the inset of Fig. 3 shows a plot of $^3K$ versus $\chi$. $^3K$ is proportional to $\chi$ over a wide temperature range. The small deviation from linearity occurring below $\sim 60$ K for LiCoPO$_4^{\text{tetra}}$ is attributed to a small amount of paramagnetic (PM) impurities to which $K$ is insensitive. This account is indeed corroborated by the good agreement between the linewidth and $\chi$ in the $T$ region where $K$ deviates $\chi$, as shown in the inset of Fig. 2 since a random distribution of PM moments would broaden the NMR line without affecting its shift.

The linear slope of $dK/d\chi$ corresponds to the hyperfine (hf) coupling constants, $A_{\text{hf}} = 1.96$ kOe/$\mu_B$ (tetra) and 1.71 kOe/$\mu_B$ (olivine). Note that $^3K$ in both compounds
FIG. 2: (a) Temperature dependence of static susceptibility and magnetic specific heat (inset) of both olivine and tetragonal LiCoPO$_4$. Solid curves are Curie-Weiss fits. (b) NMR linewidth (FWHM) of $^{31}$P spectrum tracks $\chi$ in the whole temperature range investigated. Inset: Inverse static susceptibility.

almost vanishes at $\chi = \chi_0 \sim 0$, confirming the non-spin susceptibility contribution $K_0 \sim 0$.

B. Spin-lattice relaxation rate $T_1^{-1}$ and dynamical susceptibility

The $^{31}$P spin-lattice relaxation rate $^{31}T_1^{-1}$ as a function of temperature is presented in Fig. 3. For the olivine compound, $^{31}T_1^{-1}$ increases steadily with decreasing $T$ and is rapidly enhanced below 40 K, exhibiting a sharp anomaly followed by a rapid drop. The sharp peak (vertical solid line) indicates the onset of magnetic order at $T_N = 21$ K, which agrees with literature values. In our case, the relatively sharp transition width which is comparable to $T_N$ indicates the quasi-3D nature of the magnetic order rather than 2D. For LiCoPO$_4^{\text{tetra}}$, the $^{31}T_1^{-1}$ data are an order of magnitude larger than those of LiCoPO$_4^{\text{olivine}}$, displaying a similar temperature dependence. $T_N$ could not be identified since $^{31}T_1$ becomes too short to be measured near the transition, but the temperature at which $^{31}T_1^{-1}$ diverges appears to be consistent with $T_N = 7$ K (vertical dashed line).

For olivine LiCoPO$_4$, inelastic neutron scattering yields moderate magnetic exchange coupling constants. In the $bc$-plane, the dominating nearest neighbor coupling amounts to $J_{nn}^{\text{olivine}} = 9$ K while smaller next nearest neighbor and interlayer couplings of $\sim 1 - 2$ K imply a tendency to weak frustration and 2D behavior. In the case of LiCoPO$_4^{\text{tetra}}$, where $T_N$ as well as $\Theta$ are significantly smaller than in the olivine material, magnetic coupling is presumably weaker and/or the tendency towards 2D and frustration stronger.

In the paramagnetic limit, $T_1^{-1}$ could be approximated by the relation

$$ T_1^{-1} \propto \frac{A_{hf}^2 \sqrt{S(S+1)}}{\hbar J_{ex}}. $$

Using this equation, one can estimate the ratio, $T_1^{-1}(\text{tetra})/T_1^{-1}(\text{olivine}) = 6.5$, using the relation $J_{ex} = \frac{3k_B\Theta}{zS(S+1)}$ where $z$ is the number of nearest-neighbors. This value satisfactorily accounts for the difference of $^{31}T_1^{-1}$ between the two compounds at high temperatures, proving that the system indeed lies in the localized limit at high temperatures.
In general, while the Knight shift is proportional to the static spin susceptibility at $q = 0$, i.e., $K = A_{hf} \chi(0, 0)$, $T_1^{-1}$ reflects the $q$-average of the imaginary part of the dynamical susceptibility $\chi''$ at low energy:

$$T_1^{-1} \propto T \gamma_n^2 A_{hf}^2 \sum_q \chi''(q, \omega_L)/\omega_L,$$

where $\gamma_n$ is the nuclear gyromagnetic ratio and $\omega_L$ the Larmor frequency. Since there is no difference of the Knight shift at high temperatures far above $T_N$ between the two compounds, we conclude that spin fluctuations are of dominantly antiferromagnetic nature for both olivine and tetrahedral LiCoPO$_4$.

The most striking feature is that $3^1T_1^{-1}$ for both compounds increases with decreasing temperature, as shown in Fig. 4. Such a $1/T$-dependence of $T_1^{-1}$ is very rare in the paramagnetic limit. Fig. 4 clearly shows the linear variation of $T_1$ in terms of $T$, particularly, in LiCoPO$_4^{\text{olivine}}$. This in turn implies that the $q$-average of the dynamical susceptibility $\sum_q \chi''(q, \omega_L)$ from Eq. (3) varies in proportion to $1/T^2$, in contrast to the uniform static susceptibility $\chi(0, 0)$ that obeys the CW law. A plot of $1/\sum_q \chi''(q, \omega_L)$ versus $T^2$ is given in the inset of Fig. 4, which provides evidence of the quadratic temperature dependence of the inverse dynamical susceptibility. Note that this plot eliminates the effect of the hf coupling constants, allowing the direct comparison of the two systems.

To ensure that the unusual $T$-dependence of $3^1T_1^{-1}$ is not site-dependent, but represents the intrinsic dynamical susceptibility of the system, we also measured the $^7$Li spin-lattice relaxation rate, $7^1T_1^{-1}$, as a function of temperature. The results are presented in Fig. 5, revealing a similar $T$-dependence as $3^1T_1^{-1}$. In fact, Fig. 5 proves that $3^1T_1$ and $7^1T_1$ as a function of temperature are accurately scaled to each other for both compounds.

From Figs. 4 and 5, the different behaviors of $T_1^{-1}$ in the two compounds are noticeable. Namely, for LiCoPO$_4^{\text{olivine}}$, the $T_1$ data follow a linear $T$ behavior in the whole temperature range investigated except the region near $T_N^{\text{olivine}}$. In contrast, for LiCoPO$_4^{\text{tetra}}$, the $T_1$ data deviate from the $T$-linear behavior at $\sim 150$ K, suggesting that an additional relaxation mechanism is developed. Another noticeable feature is that the $T$-linearity of $T_1$ is considerably smaller in LiCoPO$_4^{\text{tetra}}$, seemingly approaching the normal CW behavior (i.e., $T_1(T) \rightarrow$ constant at high $T$) which is observed in other olivine lithium phosphates, LiMnPO$_4$ and LiFePO$_4$.

The different magnetic properties of LiCoPO$_4^{\text{tetra}}$ and LiCoPO$_4^{\text{olivine}}$ could be understood by considering their inherent spin networks. There are five exchange pathways between the Co$^{3+}$ spins in olivine LiCoPO$_4$, $29,32$ in the $bc$ plane, one can identify the nearest-neighbor coupling $J_1$ mediated through Co-O-Co superexchange path and the next-nearest neighbor coupling $J_2$ and $J_3$ along the $b$ and $c$ axis, respectively, through PO$_4$ tetrahedra (Fig. 1a depicts only $J_1$ coupled Co atoms). The interplane couplings $J_4$ and $J_5$ are also mediated by PO$_4$ tetrahedra and are known to be ferromagnetic, while the intraplane couplings $J_1$, $J_2$, and $J_3$ are all antiferromagnetic. This spin network involves weak geometrical...
frustration since $J_1$ is much larger than other exchange couplings.

This situation is dramatically altered in LiCoPO$_4^{\text{tetra}}$. As clearly shown in Fig. 1(b), there is no longer Co-O-Co superexchange path and all the exchange interactions are mediated by corner-shared PO$_4$ tetrahedra and might be comparable to each other in strength. Naturally, this spin network likely results in strong frustration. The frustration may be consistent with the strong reduction of the effective exchange interaction and ordering temperature $T_N$. Note that in the case of competing FM and AFM interactions the ratio $T_N/\Theta$ does not provide reliable information on magnetic frustration. Since Co$^{2+}$ ions behave more like paramagnets in LiCoPO$_4^{\text{tetra}}$, one may argue that the frustration effect modifies the spin dynamics which causes the peculiar upturn of $T_1^{-1}$. At low temperatures, the frustration can induce the incommensurate or spin-glass-like magnetic ordering. In this case, magnetic short-range fluctuations may extend far above $T_N$, being responsible for the additional enhancement of $T_1^{-1}$ which was observed below $\sim$ 150 K.

Now we discuss the puzzling feature of the $1/T$-dependence of $T_1^{-1}$, which implies the inverse quadratic temperature dependence of the dynamical susceptibility. To begin with, one may conjecture that Li diffusion motion causes the increase of $T_1^{-1}$ with decreasing $T$. However, we rule out this possibility because both mobile $^7$Li and immobile $^{31}$P nuclei detect the identical $T$-dependence of $T_1^{-1}$, as demonstrated in Fig. 6. In principle, $A_{hf}$ may increase with decreasing $T$, causing the $T$-dependence of $T_1^{-1}$. Again, this is clearly not the case from the uniquely defined $A_{hf}$ from the $K$ vs. $\chi$ plot over a wide temperature range (see the inset of Fig. 3). Therefore, we conclude that unusual spin dynamics is present and persists even in the high $T$ region ($T \gg 10J_{ex}$), causing the inverse quadratic $T$-dependence of $\sum \chi''(q,\omega_L)$. One plausible explanation could be given if $J_{ex}$ in Eq. (2) decreases with decreasing temperature. Although this scenario may be incompatible with the well-defined $\Theta \propto J_{ex}$, if spin fluctuations at small $q < Q$ are developed with decreasing temperature, the resultant effective exchange coupling could be reduced.

IV. CONCLUSIONS

We present $^7$Li and $^{31}$P NMR studies in both non-olivine and olivine structured LiCoPO$_4$ microcrystals. It turns out that the exchange interactions among the Co$^{2+}$ spins are greatly reduced in LiCoPO$_4^{\text{tetra}}$, which accounts for the difference of the spin-lattice relaxation rates $T_1^{-1}$ between the two compounds. In contrast to the Curie-Weiss behavior of the static susceptibility found at high temperatures, the dynamical spin susceptibility deduced from the spin-lattice relaxation rates is inversely quadratic in temperature, which is particularly strong and robust in LiCoPO$_4^{\text{oliv}}$. For LiCoPO$_4^{\text{tetra}}$, the unusual temperature dependence is considerably weakened and breaks down at low temperatures. Together with the reduced effective exchange coupling and ordering temperature, this different spin dynamics is attributed to strong frustration effect inherent in the corner-shared CoO$_2$PO$_4$ geometry of this metastable material. The additional enhancement $T_1^{-1}$ at low temperatures in LiCoPO$_4^{\text{tetra}}$ suggests that the frustration may lead to complex incommensurate magnetic order.

Acknowledgement

We thank Andrei Malyuk for annealing the LiCoPO$_4^{\text{tetra}}$ sample. This work was supported by the DFG (Grant Nos. GR3330/3-1 and KL1824/2-2) and by the BMBF (Project 03SF0397).
From the scaling, one can deduce the hf coupling constants of the $^7\text{Li}$ directly from those of the $^{31}\text{P}$: 0.79 kOe/µ$_B$ (tetra) and 0.69 kOe/µ$_B$ (olivine).