NMR study of magnetic structure and hyperfine interactions in binary helimagnet FeP

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We performed a $^{31}$P NMR study of the metallic iron phosphide FeP in zero external magnetic field, as well as by sweeping the externally applied magnetic field $H$ both on powder and single crystalline samples at several fixed frequencies. It was the main goal of our work to determine and explore the field dependent transformation of the magnetically ordered helical structure in FeP: the zero-field NMR spectrum for the polycrystalline sample can be easily explained assuming an incommensurate spiral ordering of Fe magnetic moments with a dominating contribution to the local field at the phosphorus nucleus from the Fe – $^{31}$P transferred hyperfine interactions. The components of the transferred hyperfine-interaction tensor were evaluated within a straightforward model approach.

The NMR lineshape of the powdered FeP sample gradually changes with increasing field from the trapezoidal-like shape at low fields to a pronounced asymmetric double-horn shape at highest field. The former is typically obtained for powdered samples in applied magnetic fields while the latter is characteristic for the NMR spectra of non-magnetic atoms in single-crystalline helimagnets. The observed transformation of our $^{31}$P NMR spectra of FeP provides strong evidence of the spin-reorientation of the spin-flop type in FeP which occurs in the range of strong external fields $4 \, \mu_0 H < 5$ T confirmed also by specific-heat measurements.

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The line pattern of the single-crystal $^{31}$P NMR spectra for external magnetic fields directed within the (ac)-plane exhibit a pronounced four-peak structure characteristic of an incommensurate helimagnetic ground state with two pairs of magnetically inequivalent phosphorus positions. These spectra were successfully simulated assuming a simple planar helix of Fe magnetic moments in the (ab)-plane with a phase shift of 36 degrees between Fe1-Fe3 and Fe2-Fe4 sites according to data from neutron scattering. Rotational single crystal field-sweep NMR experiments were performed both below and above the spin-reorientation transition field at fixed frequencies of $\nu_{\text{Larmor}}$ ($^{31}$P) = 33 MHz and 140 MHz, respectively. Theoretical estimations of the transferred hyperfine coupling provide an excellent quantitative description of the observed angular dependences for the experimentally determined field separations between the resonance fields of $^{31}$P in magnetically ordered FeP and the resonance field of free Larmor precession, which serves as the diamagnetic reference field. Rotational single-crystal NMR experiments in high fields reveal an effect of varying phosphorous local fields distribution caused by an iron spin-reorientation transition in high magnetic field.

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I. INTRODUCTION

The scientific interest into iron phosphide FeP is largely associated with intrinsic complexity of its unusual helical magnetic structure, details and generation mechanisms of which are still a matter of discussions.

FeP system has a complicated electronic structure. It has been controversial whether the Fe 3d states dominating magnetic properties are localized or itinerant. The nature of the magnetism in the simplest iron phosphide
is of fundamental importance in understanding the interplay between localized and itinerant magnetism.

The FeP phosphide has an orthorhombic structure with the Pnma space group at room temperature. The structure consists of iron ions that occupy equivalent crystal sites equivalent crystal sites surrounded by distorted octahedra of phosphorous atoms (FeP₆) and with distorted octahedral phosphorous atoms surrounding them (FeP₆), and bears four formula units per unit cell (Fig. 1a).

Distorted FeP₆ octahedra are superexchange coupled via three intermediate phosphorus atoms with acute Fe-P-Fe superexchange bonding angles ~ 70-75°.

According to magnetic data for FeP, this compound exhibits a magnetic transition at \( T_N \approx 120 \text{K} \) to the double antiferromagnetic helix with the iron moments lying in the (ab)-plane. Following the helicoidal structure proposed in Ref. the magnetic moments are parallel within the planes 1, 2, 3, 4 normal to the c axis (Fig. 1b).

As the plane changes 1–3 or 4–2, the direction of the spin rotates by \( \sim 36° \) (the difference of the angles between the spin directions of two Fe atoms separated by 0.4 c) with the relative angle \( \sim 176° \) between adjacent planes separated by 0.1 c (Fig. 1b).

Such a complex helicoidal magnetic structure is explained as a result of a competition of different isotropic (super)exchange interactions and/or anisotropic antisymmetric Dzyaloshinskii-Moriya coupling (see, e.g., recent review article Ref. ). It is worth noting that the use of circular polarized x-rays reveals a right-handed chirality in isostructural FeAs that points to the antisymmetric Dzyaloshinskii-Moriya coupling to be main candidate to explain both a small canting for magnetic moments of Fe1, Fe2 (Fe3, Fe4) ions and spiral spin rotation in FeP.

The helical magnetic ordering wave vector is found to change with temperature and this could imply that the system is sensitive to small perturbations. In fact, there are several frustrated nonequivalent Fe-P bonds in the material, which are likely to be responsible for the sensitivity of the ground state.

Taking into account that the propagation vector, \( k \approx (2\pi/c) \times 0.20 \) (the spins rotate in the (ab)-plane with a period of propagation along the c-axis of \( \sim 5c \)), is only approximately commensurate with the c axis, such rotation between adjacent moments along the c axis implies the presence of a quasi-continuum of possible orientations of iron moments \( \mu_{Fe} \) lying in the (ab)-plane. According to the results obtained in Ref., the magnetic structure of FeP may be described assuming two nonequivalent iron positions with different magnetic moments, \( \mu_1 \approx 0.37 \mu_B \) and \( \mu_2 \approx 0.46 \mu_B \). At the same time, in the case of isostructural arsenide FeAs with nearly the same magnetic structure, polarized neutron scattering showed that magnetic helicoid has elliptic deformation within the (ab)-plane with the longest axis of the ellipse being aligned with the b-axis. It should be noted that namely b-axis was attributed by Westerstrandh et al. to be the easy axis of magnetization in FeP.

The powder neutron diffraction applied to study the magnetic properties of the iron pnictides FeP and FeAs cannot distinguish between a simple double spiral model with two discrete iron positions and a quasi-continuous elliptically polarized distribution of iron moments, thus suggesting that other techniques should be employed. Early ⁵⁷Fe Mössbauer works performed for FeP in the paramagnetic temperature region \( (T > T_N) \) showed that all iron cations occupy unique crystallographic positions, being in accordance with the crystal data. However, identification and selfconsistent analysis of the very complex magnetic hyperfine spectra at \( T > T_N \) caused serious difficulties and left a number of questions. One of the most comprehensive Mössbauer studies of FeP single crystals in an external magnetic field was performed by Håggström et al. A reasonable fit was obtained by using a superposition of several Zeeman patterns with different values of magnetic hyperfine fields on the ⁵⁷Fe nuclei and partial contributions. According to each discrete Zeeman pattern arises from different orientations of the magnetic hyperfine field in the (ab)-plane. It was shown that in order to get a good fit, a bunching of spins along a-axis direction in the (ab)-plane is necessary. Unfortunately, the authors did not discuss the origin of such bunching in context of the electronic structure of iron ions in FeP. Moreover, there is no information on the temperature evolution of the hyperfine Zeeman structure of Mössbauer spectra, in particular, near the critical point \( (T \sim T_N) \) that would be very useful to clarify the nature of the magnetic phase transition.

The Mössbauer measurements for powdered samples of FeP performed at 4.2 K in strong magnetic fields up to \( 7.4 \text{T} \) were reasonably fitted under assumption that the grains turned in the field giving only two orientations for the grains in the field corresponding to the a- and b-axes parallel to \( B_{ext} \) with a preference to b-axis to be an easy axis in FeP. Unfortunately, the authors do not provide field dependences.
Recently, a detailed Mössbauer study of isostructural monoarsenide FeAs was published by Blachowski et al.\textsuperscript{12} where the quasi-continuous variation of the hyperfine magnetic field amplitude with the iron spin orientation varying in the \((ab)\)-plane was taken into account. However, despite good fitting of all experimental spectra measured in a wide temperature range below \(T_N\), this model still leaves some unanswered questions. In particular, it is assumed the existence of two nonequivalent Fe1 and Fe2 positions, which disagrees with the high temperature spectra \((T > T_N)\) and structural data for FeAs\textsuperscript{13}. Moreover, the authors\textsuperscript{13} did not explain a rather unusual profile of the spatial anisotropy of Fe1 and Fe2 magnetic moments that points at a lack of proportionality between the hyperfine field and the magnetic moments on the iron atoms. We can not exclude that the above conclusions are the result of constraints made by the authors in their model fitting of experimental spectra. In particular, one could assume that the angle defining the relative orientation of the spins for a given propagation wave vector \((\mathbf{k})\) of helicoid is constant upon moving along the \(c\)-axis. This statement requires independent experimental confirmation.

A.V. Sobolev et al.\textsuperscript{14} have reported results of the combined \(^{57}\text{Fe}\) Mössbauer and \(^{31}\text{P}\) NMR studies of the iron phosphide FeP powder sample performed in a wide temperature range including the point \((T_N \approx 120\,\text{K})\) of magnetic phase transitions. The \(^{57}\text{Fe}\) Mössbauer spectra at low temperatures \(T < T_N\) present a very complex Zeeman pattern with line broadenings and sizeable spectral asymmetry. It was shown that the change of the observed spectral shape is consistent with the transition into a space-modulated helicoidal magnetic structure. Analysis of the experimental spectra was carried out assuming an anisotropy of the magnetic hyperfine field \(H_{hf}\) at the \(^{57}\text{Fe}\) nuclei when the Fe magnetic moment rotates with respect to the principal axis of the electric field gradient (EFG) tensor. The results did show that a good fitting of the experimental spectra can be achieved without assumptions of formation of two nonequivalent crystallographic positions of the Fe cations, as was suggested earlier. The main reason for the observed asymmetry of hyperfine structure is the spatial modulation of the rotation angles between adjacent moments \(\mu_{Fe}\) along the \(c\)-axis, which induces the modulation of the hyperfine Hamiltonian eigenvalues. The obtained large temperature independent anharmonicity parameter \(m \approx 0.96\) of the helicoidal spin structure results from easy-axis anisotropy in the plane of the iron spin rotation. It was assumed that a very low maximal value of \(H_{hf}(11\,\text{K}) \approx 36\,\text{kOe}\) and its high anisotropy can be attributed to the stabilization of iron cations in the low-spin state \((S_Fe = 1/2)\). It should be noted that recent XPS data\textsuperscript{15} indicate, rather, the intermediate spin-3/2 value of the presumably \(\text{Fe}^{3+}\) valence state of the iron ion. However, FeP exhibits metallic behaviour with complex narrow-band structure\textsuperscript{12,16,17}, it has been controversial whether the Fe 3d states dominating magnetic properties are localized or itinerant.

The underlying mechanisms of the evolution of magnetism is also a significant issue and still in debate. In this regard, we expect that NMR studies of local fields on nuclei can shed light on the nature of magnetism in FeP and provide some clues for further investigations.

The crystal structure of the binary helimagnet FeP contains very suitable NMR nuclei \(^{31}\text{P}\) \((I = 1/2, \gamma/2\pi = 17.235\,\text{MHz/T})\). Due to its high NMR sensitivity, lack of quadrupole broadening and 100\% natural abundance this provides an unique opportunity to probe the Fe-based magnetic structure and hyperfine interactions in FeP using \(^{31}\text{P}\) NMR spectroscopy. The field-sweep \(^{31}\text{P}\) NMR spectrum of the FeP powder sample was first measured at fixed frequency of 80 MHz in the paramagnetic state at 155 K and in magnetically ordered state at 1.55 K\textsuperscript{14}. The high-temperature NMR line was very narrow (FWHM \(\approx 6 \cdot 10^{-2}\,\text{kOe}\)) with the peak situated almost at the diamagnetic Larmor field \(H_{L_{\text{Larmor}}} = 46.42\,\text{kOe}\). With decreasing temperature below \(T_N\) the \(^{31}\text{P}\) spectra changed dramatically. The spectrum measured at lowest temperature of 1.55 K was extremely broad with FWHM \(\approx 11.6(4)\,\text{kOe}\) and the width at the line basement \(\approx 16.4(4)\,\text{kOe}\) which is more than two orders of magnitude higher than the FWHM in the paramagnetic state. This result unambiguously indicated that in the magnetically ordered state the effective magnetic field on \(^{31}\text{P}\) nuclei is strongly affected by the hyperfine field transferred from Fe cations. The spatial distribution of these transferred fields with respect to external magnetic field was reflected in a specific trapezoidal \(^{31}\text{P}\) line shape which is typical for powder samples.

In present paper we continued these \(^{31}\text{P}\) NMR study of the phosphide FeP. At variance with previous preliminary NMR measurements the \(^{31}\text{P}\) NMR spectra were measured both at zero external field and by sweeping the magnetic field at several fixed frequencies in the wide range of \(18 \div 120\,\text{MHz}\). Field-sweep measurements were carried out both on powder and single crystal samples. Our main goal is to examine the \(\text{Fe}^{3+}\) hyperfine interactions and observe the transformation of the FeP magnetic helical structure under applied external magnetic field. The paper is organized as follows: in Sec.II we address the preparation of the FeP samples, its characterization, and some issues of the NMR measurements. Sec.III represents results of the zero-field \(^{31}\text{P}\) NMR measurement, its simulation, and some results of the calculation of the magnetic dipole contribution to the transferred \(\text{Fe}^{3+}\) hyperfine interaction. Results of the field-sweep \(^{31}\text{P}\) NMR measurements and simulations for the FeP powder sample are presented in Sec.IV. Results of the field-sweep \(^{31}\text{P}\) NMR measurements and simulations for the FeP single-crystalline sample are presented in Sec.V. A brief summary is presented in Sec.VI.
II. EXPERIMENTAL

Polycrystalline sample of FeP was prepared according to [14] by heating of stoichiometric mixture of iron powder (Alfa Aesar, 99.995%) and pieces of red phosphorus (Alfa Aesar, 99.999%) in evacuated quartz ampoule at the temperature 850 °C for 48 h. To prevent surface oxidation in a moist air all operations were carried out in a glovebox (O₂ and H₂O volume fraction < 1 ppm).

Powder X-ray diffraction analysis was performed utilizing Bruker D8 Advance diffractometer (Cu-Kα1 radiation, Ge-111 monochromator, reflection geometry) equipped with a LynxEye silicon strip detector. XRD spectra confirmed that the obtained sample is the FeP single phase powder with the orthorhombic unit cell: a = 5.203(1) Å, b = 3.108(1) Å, and c = 5.802(1) Å, space group Pnma, in agreement with the literature data [31].

Iron monophosphide FeP single crystals were grown by chemical vapor transport with iodine [21]. The composition of the obtained crystals was confirmed by the EDX and XRD methods. For the 31P NMR investigation the bulky single crystal with linear dimensions of 3 - 4 mm (volume of about 48 mm³) and weight of 296 mg was selected (Fig. 2). Its single crystallinity and directions of the crystallographic axes depicted in Fig. 2 were determined by the Laue method. During the NMR experiment the crystal was rotated around the (010) axis aligned parallel to the RF coil.

![Image of a single-crystal FeP. Faces perpendicular to the crystallographic axes are indicated.](image)

The 31P NMR measurements were performed in the magnetically ordered state at 1.55 K and 4.2 K using a conventional phase coherent pulsed NMR spectrometer. NMR spectra were measured by sweeping the magnetic field at several fixed frequencies in the wide range of 18 ÷ 120 MHz, the signal was obtained by integrating the spin-echo envelope in the time domain and averaging over scan accumulation number which depends on frequency. For comparison at 80 MHz the 31P NMR spectrum was measured also in the paramagnetic phase at 155 K. The fine powder sample was fixed in paraffin in order to avoid skin-depth effects and the reduction of the resonance circuit quality factor due to high metallic conductivity. This also prevents the sample grains from re-orienting in the applied field. In addition, 31P zero-field NMR spectrum was measured at 4.2 K using a frequency step point-by-point spin-echo technique.

III. ZERO FIELD 31P NMR

NMR spectrum of 31P nuclei in FeP measured at zero external magnetic field (zero-field NMR) at 4.2 K is presented in Fig. 3. It demonstrates a very broad intensity distribution in the range approximately from 10 to 15.3 MHz with asymmetric two-horn shape with the edge peaks situated at ν< = 10.90 and ν> = 14.75 MHz. The main advantage of the zero-field NMR technique in magnetic materials is that the observed NMR spectrum directly probes the local magnetic field profile at the crystallographic site of the NMR nuclei. Dividing the frequency values of the peaks by γ(31P)/2π = 17.235 MHz/T one immediately obtains the edge local field values on phosphorus site: μ0H< (31P) = 0.63 T and μ0H> (31P) = 0.86 T for the left and right peaks, respectively. Moreover, in contrast to typical collinear antiferromagnets, where singlet zero-field NMR lines at non-magnetic atoms are usually observed, the 31P asymmetric two-horn line profile in FeP (Fig. 3) unambiguously points to anisotropic and anharmonic helical local magnetic field distribution at P site (e.g. compare with BiFeO₃ [17,18]). Typically helical structure anisotropy can be described as follows

\[
H_{loc} = [H_z^2 \sin^2 \theta + H_x^2 \cos^2 \theta]^{1/2},
\]

where \(\theta\) is the 31P local field orientation angle, \(H_>, H_<\) are the smallest and largest values of the transferred hyperfine field.

The shape of the spectrum \(P(\nu)\) can be analyzed according to the model used in Refs. [17,18]

\[
P(\nu) = \int_0^\pi I(\theta) F(\nu - \nu(\theta)) d\theta,
\]

\(I(\theta)\) is the signal intensity in the part of cycloid where the helix magnetic moment makes an angle \(\theta\) with the b-axis, \(F(\nu - \nu(\theta))\) is the local line shape function. Since the \(I(\theta)\) is proportional to density of angle distribution for the helix magnetic vectors, it can be derived from the \(\theta(z)\) dependence as follows:

\[
I(\theta) \propto \frac{1}{\partial \theta(z)/\partial z},
\]

where \(z\) is the coordinate along the cycloid propagation c-axis.

According to the 57Fe Mössbauer data analysis in FeP discussed in detail in [13], the \(\theta(z)\) dependence for anharmonic magnetic helix on Fe sites can be described by the
elliptic Jacobi function as follows
\[ \sin \theta(z) = sn \left[ \frac{4K(m)}{\lambda} z, m \right], \]
where \( K(m) \) is an elliptic integral of the first kind, \( \lambda \) is the helical period, and \( m \) is the anharmonicity parameter.

Interestingly, almost indistinguishable dependence \( \sin \theta(z) \) can be obtained if we use a simplest model of the anharmonic spiral:
\[ \theta(z) = qz + k \sin 2qz, \]
where \( q \) is the helix wave vector, \( k \) the helix anisotropy (anharmonicity) parameter, or the bunching parameter. So, at \( m = 0.95 \) it is enough to take \( k = 0.35 \), at \( m = 0.5 \), \( k = 0.1 \). However, unlike this simple helix, for the complex "Jacobian" helix we arrive at a rather simple \( \theta \)-dependence for \( I(\theta) \):
\[ I(\theta) \propto \left(1 + \cos^2 \theta \right)^{-\frac{1}{2}}. \]
For simple helix (5), one can use a relatively good approximation
\[ I(\theta) \propto (1 + 2k \cos \theta)^{-1}. \]
Finally, the line shape of the zero-field \( ^{31}\text{P} \) NMR spectrum can be calculated as it was suggested in Refs. 17-18
\[ F(\nu) \propto \int_0^\pi \left[ (m^{-1} - 1 + \sin^2 \theta)^{-\frac{1}{2}} \times \right. \]
\[ \left. \left[ \delta^2 + (\nu - [\nu_x^2 \sin^2 \theta + \nu_z^2 \cos^2 \theta] \frac{1}{2})^2 \right]^{-1} d\theta \right. \]
where we made use of Lorentzian individual line shapes with a constant line-width, \( \nu_x, \nu_z \) are the edge frequencies. The best fit of theoretical NMR spectra calculated using Eq. (5) to the experimental \( ^{31}\text{P} \) NMR spectrum gives the anharmonicity parameter \( m = 0.19 \) and is depicted in Fig. 3. As seen from the figure we arrive at a rather nice agreement with experimental data. Moreover, a visually indistinguishable theoretical curve can be obtained with simple helix (5) and approximate expression (7) for \( I(\theta) \) given \( k = 0.03 \). It should be noted that the value \( m = 0.19 \) is much less than the value \( m = 0.96 \) obtained from the fitting of the \( ^{57}\text{Fe} \) Mössbauer spectra in FeP. It seems, the \( ^{31}\text{P} \) nuclei "see" a less anharmonic magnetic spiral than the \( ^{57}\text{Fe} \) nuclei. However, one needs to keep in mind that in a sense, the \( ^{31}\text{P} \) NMR provides a more direct way to estimate the Fe spiral anharmonicity than that of the \( ^{57}\text{Fe} \) M"ossbauer spectroscopy due to its complicating factors like the existence of the electric field gradient and the \( ^{57}\text{Fe} \) – \( ^{31}\text{P} \) – Fe supertransferred hyperfine coupling. In addition, instead of Eq. (1) the authors14 used the expression for hyperfine field
\[ H_{loc} = H_a \cos^2 \theta + H_b \sin^2 \theta, \]
which is valid only if the local field has a low anisotropy.
Local dipole field components (T)

-0.2 -0.1 0 0.1 0.2

0 40 80 120 160 200 240 280 320 360

Angle (deg.)

Local dipole field components (T)

0 0.1 0.2 0.3 0.4

0 40 80 120 160 200 240 280 320 360

Angle (deg.)

V. FIELD-SWEEP $^{31}$P NMR OF THE FeP POWDER SAMPLE

The field-sweep $^{31}$P NMR spectrum of the FeP powder sample measured at fixed frequency of F = 80 MHz in the paramagnetic state at 155 K is presented in Fig. 5 (left bottom panel). The line is very narrow (FWHM ≈ 6 mT; line width at the basement 15 mT).
with the peak situated almost at the calculated Larmor field of \( B_L = 2\pi F/\gamma = 4.642 \text{T} \) at 80 MHz. With decreasing the temperature below \( T_N \) the \(^{31}\text{P} \) spectra change dramatically. The spectrum measured at lowest temperature of 1.55 K is presented in the same panel. The spectrum is now extremely broad with the width at the line basement of about \( \approx 1.76 \text{T} \) which is more than two orders of magnitude higher than the FWHM in the paramagnetic state. This result indicates that in the magnetically ordered state the effective magnetic field on \(^{31}\text{P} \) nuclei is strongly affected by the hyperfine field with the magnitude about 1 T transferred from Fe atoms. Moreover, as seen from Fig. 5 (left bottom panel) the \(^{31}\text{P} \) NMR line shape measured at 80 MHz (\( B_L = 4.642 \text{T} \)) is much more complicated than that measured at 60 MHz (\( B_L = 3.48 \text{T} \); right top panel) with characteristic trapezoidal shape discussed in our previous paper.\(^{13}\) In order to study in more detail the observed field dependence of the \(^{31}\text{P} \) NMR line shape we performed a series of field-sweep \(^{31}\text{P} \) NMR spectra measurements on the FeP powder sample in the magnetically ordered state at 1.55 K at eight various fixed frequencies in the range of 11 \( \div \) 140 MHz. The resulting spectra are presented in Fig. 5. At the lowest frequency of 11 MHz (\( B_L = 0.638 \text{T} \); right bottom panel) the strongest echo intensity was observed already at external magnetic field \( B = 0 \). Namely this enabled us to perform zero field NMR measurement on \(^{31}\text{P} \) nuclei in FeP which was discussed in Sec.II. With increasing external field the echo intensity rapidly decreases with two distinct steps at around \( B - B_L = -0.4 \text{T} \) and \( B - B_L = 0.6 \text{T} \). At next frequency, 18 MHz (\( B_L = 1.044 \text{T} \); right next to bottom panel), the \(^{31}\text{P} \) NMR signal at zero field is already absent and an echo intensity is distributed very broadly between symmetric limits \( B - B_L = -0.9 \text{T} \) and \( B - B_L = 0.9 \text{T} \) indicating minimal and maximal local induced magnetic field at P site. There are also almost symmetrically placed characteristic features: the left horn at \( B - B_L = -0.564 \text{T} \) and right step at \( B - B_L = 0.596 \text{T} \). At two next frequencies, 33 MHz (\( B_L = 1.915 \text{T} \)) and 60 MHz (\( B_L = 3.48 \text{T} \)) the characteristic trapezoidal-like \(^{31}\text{P} \) NMR line profile is formed (Fig. 5, two upper right panels) which was discussed in detail in\(^{13}\). The intensity distribution limits and both left and right features stay at the same positions as at 18 MHz indicating that the absolute value of the induced field on P site does not change with external magnetic field. Further increase of frequency and corresponding external field range leads to dramatic transformation of the trapezoidal-like \(^{31}\text{P} \) NMR spectrum of FeP as shown in Fig. 5 (left column). At \( F = 80 \text{MHz} \) (\( B_L = 4.642 \text{T} \)) a pronounced peak arises instead of the right shoulder of former trapezoid (Fig. 5, left bottom panel). Also, the broad maximum is forming at \( B - B_L = -0.2 \text{T} \). This tendency is continued at \( F = 100 \text{MHz} \) (\( B_L = 5.802 \text{T} \)) where the right and central peaks grow up significantly. Moreover, additional peak instead of the left singularity of the former trapezoid appears. At two highest measured frequencies, 120 MHz (\( B_L = 6.963 \text{T} \)) and 140 MHz (\( B_L = 8.123 \text{T} \)) two side peaks are transforming into characteristic asymmetric edge horns while the broad central decreases and almost vanishes at 140 MHz (Fig. 5, two upper left panels). Two important points should be mentioned. First, at all frequencies in the range of 11 \( \div \) 140 MHz and corresponding Larmor fields range of 0.638 \( \div \) 8.123 T the \(^{31}\text{P} \) NMR spectral intensity is distributed in the very same symmetrical limits from \( B - B_L = -0.9 \text{T} \) and \( B - B_L = 0.9 \text{T} \) which indicates that the maximum absolute value of local induced magnetic field at P site is 0.9 T that is in good agreement with our ZF NMR experiment. Second, the asymmetry in intensity of the singularities is changing with increasing field: at low fields (up to 3.5 T, right column in Fig. 5) the left singularity of the spectrum is more intensive while at high fields (above 4.5 T, left column in Fig. 5) the right peak is more intensive.

The observed transformation of \(^{31}\text{P} \) NMR spectra of FeP from trapezoidal-like shape at low external fields (up to 3.5 T, right column in Fig. 5) typical for powder
samples to asymmetric double-horn shape at high fields (above 4.5 T, left column in Fig. 5) typical for NMR on non-magnetic atoms like Li in single-crystalline helimagnets LiCu$_2$O$_2$\cite{23,24} or Na in NaCu$_2$O$_2$\cite{25} seemingly indicates a spin-reorientation transition in the FeP grains which occur in the range of external fields $3.5 \div 4.5$ T.

In strong fields, one could expect the spins in the powder sample to turn so as to be collinear with the external field. For example, in helimagnetic MnP when applying the field in the $b$-direction, the helical spin structure transforms to a saturated ferromagnetic structure when the external field exceeds $B_{ext} = 0.3$ T, whereas for $B_{ext}$ parallel to the $a$-axis the helical structure transforms to a fan structure at $B_{ext} = 0.8$ T which then transforms to a saturated ferromagnetic structure at $B_{ext} = 4.5$ T\cite{26}. Assuming that a similar situation is valid for FeP Häggström et al.\cite{7} believe it is not surprising that a large magnetic anisotropy can turn the crystallites in the powder sample to turn so as to be collinear with the external field.

In a recent publication\cite{27}, a phenomenological model has been proposed which implies a "phase separation" of the system to the field-dependent volume fractions with powder-like and single-crystalline responses. Indeed, for rather small external fields $\mu_0 H_{ext} \leq 3.5$ T the trapezoidal shape of the $^{31}$P NMR signal for powder FeP sample (right column in Fig. 5) can be quite satisfactorily described in the framework of a simple theory of the NMR line shape in a powder sample under the assumption of a single value of the local field for all nuclei\cite{11,12}.

$$F(H) \propto \int \frac{H^2 - H_{loc}^2 + H_{res}^2}{H_{loc}h^2} \frac{1}{\delta} \exp \left[ -\frac{(h - H)^2}{2\delta^2} \right] dh,$$

(11)

where $H = H_{ext} + H_{int} \cos \theta$, $\theta$ is the angle between external and local fields, $\delta$ is the half-width of a single NMR line. But already in the Ref.\cite{13} approximation one can see a systematic discrepancy between the theory and experiment due to the steeper slope of the experimental spectrum. In order to explain it we suggest additional canting of the local fields distribution related to their preferable aligning along the external field direction described by excessive magnetic energy $h H_{loc} \cos \psi / E$. Here $\psi$ is the angle between external and local fields, $E$ is the energy constant. Following Boltzmann-like distribution one obtains\cite{27}:

$$F(H) \propto \int \frac{H^2 - H_{loc}^2 + H_{res}^2}{H_{loc}h^2} \exp \left[ -\frac{h^2 + H_{loc}^2 - H_{res}^2}{2E} \right] \times$$

$$\frac{1}{\delta} \exp \left[ -\frac{(h - H)^2}{2\delta^2} \right] dh,$$

(12)

As one can see from the right column of Fig. 5 theoretical curves corresponding to (12) are in good agreement with experiment. The best approximation value of $\mu_0 H_{loc}$ gradually decreases from 0.72 T to 0.69 T from 18 MHz to 60 MHz spectrum, so the zero frequency limit seems to be equal to estimation of mean $^{31}$P local field by ZF NMR ($\sim 0.74$ T).

However, for strong external fields $\mu_0 H_{ext} \geq 4.6$ T the NMR line-shape resembles a superposition of the powder spectrum and that of the single-crystalline helimagnetic one. The former we will describe as above in the case of rather weak external fields, while for the latter we will use the most simplified phenomenological description that can be applied to one-dimensional helimagnet.

Suppose the field on the phosphorus nuclei can be represented as follows

$$H = H_{ext} + H_{int} \cos \theta,$$

(13)

where for $\theta$ instead of Eq. (5), we will use the generalization expression

$$\theta(z) = qz + k_1 \sin qz + k_2 \sin 2qz,$$

(14)

which allows us to take into account both effects of anisotropy (symmetrical bunching) and external field (asymmetrical bunching).

The shape of the NMR line is determined by the density distribution of the field values $H$: $g(z) \propto |dH(z)/dz|^{-1}$ and the individual line shape. After simple algebra we get

$$F(H) \propto \int \frac{H_{loc}^2 (H_{loc}^2 - (H_{res} - h)^2)^{1/2}}{H_{int}^2 + k_1 (H_{res} - h) + 2k_2 (2(H_{res} - h)^2 - H_{int}^2)} \frac{1}{\delta} \exp \left[ -\frac{(h - H)^2}{2\delta^2} \right] dh,$$

(15)

where we, model assumption (cf. Eq. 7), used a simple model assumption

$$I(\theta) \propto \left[ (1 + k_1 \cos \theta + 2k_2 \cos 2\theta) \right]^{-1},$$

(16)
and \( H_\parallel = H_{res} + H_{int} \), \( H_\perp = H_{res} - H_{int} \). Left column in Fig. 6 clearly demonstrates the applicability of the model approach. For instance, the experimental NMR spectrum \( ^{31}\text{P} \) at a frequency of 120 MHz is described by the superposition of the main contribution of the single-crystalline helimagnetic phase with \( \mu_0 H_{int} = 0.7 T \), \( k_1 = 0.05 \), \( k_2 = -0.40 \) and a relatively small contribution with a "powder” response \( ^{12}\text{P} \) with \( \mu_0 H_{int} = 0.35 T \).

Thus the shape of the NMR lines gradually changes with an increase in the field from the trapezoidal shape in low fields to a pronounced asymmetric shape with two "horns” in strong fields, characteristic of single-crystal helimagnets. In principle, this is in agreement with the results of Ref. 2, which indicate the orientation of crystal grains in a strong magnetic field. To obtain additional information on the effect of an external magnetic field on the magnetic structure of powder samples, we investigated the effect of the field on the specific heat.

Temperature dependence of specific heat (see Fig. 6) reveals the pronounced peak at \( T_N \approx 120 K \), related to the magnetic ordering, in good agreement with susceptibility data and Mössbauer spectroscopy. We approximated the lattice contribution using the Debye model in the temperature range of 150 – 300 K that point to the value of Debye temperature of 499 K with the high temperature asymptote is 5.94 R, which is very close to 6 R, as assumed from the simple idea of 2 atoms per mole. Calculating the lattice contribution for the whole temperature range one can extract the magnetic part of specific heat (left inset in Fig. 6). It demonstrates only ordering peak at \( T_N \) and equals almost zero at all other temperatures. At the ordered state (\( T = 2K \)) we also measured magnetic field dependence of specific heat (right inset in Fig. 6). For both directions of field variation, increasing and decreasing, the pronounced bending feature of \( C(B) \) was observed at fields of 3–6 T indicating some kind of continuous field-induced spin-orientation transition in agreement with the experimental \( ^{31}\text{P} \) NMR results for FeP powder sample.

Our phenomenological model gives a soundly description of the evolution of the NMR spectra of a polycrystalline sample with increasing external field, however, more specific information can be obtained only with a NMR study of single-crystalline samples.

VI. FIELD-SWEEP \( ^{31}\text{P} \) NMR OF THE FeP SINGLE-CRYSTALLINE SAMPLE

Typical \( ^{31}\text{P} \) NMR spectrum of the FeP single crystal measured in ZFC mode at 120 MHz is shown in Fig. 7 together with the powder NMR spectrum at the same frequency. The shape of the single-crystalline NMR spectrum is expectedly changed as compared with the powder one, indicating the presence of preferred orientations of the local fields on \( ^{31}\text{P} \) nuclei.

A pair of distinct doublets is clearly observed in all spectra. These doublets can be obviously attributed to the contribution of phosphorus nuclei at nonequivalent positions, P5,6 and P7,8, respectively. As can be seen from Fig. 7, the external pair of peaks is situated exactly at the edges of the powder spectrum and is almost symmetrical with respect to the Larmor field with the separation of \( \sim 0.85 \text{T} \) that corresponds to a frequency of 14.75 MHz, which is very close to the frequency of the right "horn" in the zero-field NMR spectrum of phosphorus (see Fig. 5).
A. External magnetic field rotated in the (ac)-plane: low fields

For a quantitative analysis of the four-peak structure of the spectrum, we considered the behavior of the single-crystal NMR spectrum during sample rotation in the coil aligned along the b-axis of the sample, which corresponds to the field rotation in the (ac)-plane. It was reasonable to start with measurements in low fields below the spin-orientation transition established by the powder NMR measurements and the specific heat data. Therefore the first rotational $^{31}$P field-sweep NMR measurements series was performed at fixed frequency of 33 MHz at 4.2 K. Respective values of Larmor field (1.915 T) and the maximum field of NMR signal observation ($\approx 2.8$ T) are substantially lower than the field that causes the beginning of the orientation transition ($\sim 4$ T). Thus, with good accuracy, one can assume that the crystal rotation is equivalent to the rotation of its magnetic structure. As far as the rotation was performed around (010) axis, perpendicular to the external field, we could observe any possible angle between the field and (ab)-plane.

Rotational single crystal NMR experiments were performed in the NMR probe equipped with the goniometer using the following protocol:
1. After measurement of previous $^{31}$P NMR spectrum the magnetic field was not reduced to zero since the maximum magnetic field of 2.8 T in these measurements is considerably less than the field of spin-reorientation transition of 4-5 T, according to powder NMR data.

2. The FeP crystal inside goniometer of the NMR probe was all the time immersed in liquid helium bath of the cryostat, without removing and heating up in-between measurements.

3. The $^{31}$P spectrum measurement was started with sweeping magnetic field in an arbitrary direction for the same reason as mentioned in No.1.

Some typical experimental spectra are presented in Fig.9. Observed spectra usually possessed four asymmetric peaks at the edges (Fig.9p). Intensity distribution between them is very similar to planar cycloid spectra. Indeed, according to discussion in Section IV, $^{31}$P local fields may form up to four planar cycloids with any possible local field direction within them. Rotation gradually varies the spacing between pairs of peaks with a periodicity of $2\pi$. When two inner peaks are getting closer they turn into certain complex structure (Fig.9k). Sometimes these two pairs of peaks merge into one pair (Fig.9c) or a single complicated structure (Fig.9d). For clarity we performed typical gauss-broadened simulations of the spectra for two simple cases (red solid curves in Fig.9b,c) by two-cycloid model with $B_L$ fixed at 1.915 T, using the following formula for field-dependent intensity $F(B_{ext})$:

$$
F(B_{ext}) \propto \frac{\pi}{2} \int_{0}^{\pi} \exp \left[ -\frac{(B_{loc} \cos \theta \cos \alpha + \sqrt{B_{L}^2 - B_{loc}^2 \sin^2 \theta \cos^2 (\alpha + \gamma) - B_{ext}^2})}{2\delta} - \frac{B_{loc} \cos \theta \cos (\alpha + \gamma) + \sqrt{B_{L}^2 - B_{loc}^2 \sin^2 (\alpha + \gamma) - B_{ext}^2})}{2\delta} \right] d\theta \frac{d\alpha}{\delta} + \frac{\pi}{2} \int_{0}^{\pi} \exp \left[ -\frac{(B_{loc} \cos \theta \cos \alpha + \sqrt{B_{L}^2 - B_{loc}^2 \sin^2 \theta \cos^2 \alpha - B_{ext}^2})}{2\delta} - \frac{B_{loc} \cos \theta \cos \alpha + \sqrt{B_{L}^2 - B_{loc}^2 \sin^2 \theta \cos^2 \alpha - B_{ext}^2})}{2\delta} \right] d\theta \frac{d\alpha}{\delta} \tag{17}
$$

Here $\alpha$ and $\alpha + \gamma$ are the angles between $B_{ext}$ and local fields planes, the details will be discussed below.

For convenience of the observed spectra analysis, we plot the angular dependences of the above mentioned peaks positions (Fig.9). Based on continuity considerations, when a part of the spectrum turns into complex structure (Fig.9k,d) the borders of this structure are plotted. The correspondence between the peaks or borders of neighboring orientations was determined by minimizing the derivatives (smoothness) of the angular dependences $B(\alpha)$ curves for each of them, where $\alpha$ is the angle between $B_{ext}$ and local fields plane.

Fig.9 demonstrates that peaks may be combined in pairs $B_1$ and $B_2$, $B_3$ and $B_4$ (according to given notations). Inside each pair the peaks positions change with the angle in antiphase, and between these pairs there is a constant angle shift $\gamma$. Then these pairs can be associated with planes, containing $^{31}$P local fields, and the angle shift $\gamma$ – with the spatial angle between these planes. It is easy to show that observed $B(\alpha)$ dependences are in good agreement with the proposed interpretation. One can make a logical assumption about the symmetry of the local fields distribution with respect to the inversion procedure. In this case the minimum and maximum angles between $B_{ext}$ and $B_{loc}$ would be $\alpha$ and $\pi - \alpha$. Then, equating the effective field $|\vec{B}_{loc} + \vec{B}_{ext}|$ to the Larmor field $B_L$ for different $\vec{B}_{loc}$ intra-plane orientations it is easy to derive from the cosine theorem the peaks/borders positions dependence on angle $\alpha$:

$$
B_{ext} = \sqrt{B_{L}^2 - B_{loc}^2 \sin^2 (\alpha)} \pm B_{loc} \cos (\alpha) \tag{18}
$$
The Larmor field value (1.915 T), the dotted line indicates the field value of \( \sqrt{B_L^2 - B_{loc}^2} \) at which the borders of cycloid subspectra merge (see text). Solid lines are \( B(\alpha) \) approximations by Eq. (18), for details see text.

The resulting approximation curves are plotted in Fig. 8 as the solid lines. \( B_L \) was fixed at 1.915 T and the variable angle shift \( \alpha_0 \) was added to \( \alpha \). This shift corresponds to previously unknown orientation of the local fields plane relative to the crystallographic axes and therefore to the external field. Although no local fields anisotropy is considered here, it should not significantly affect the curves described by Eq. (18) except for the cases when local fields planes are oriented close to perpendicular to the external field (e.g. Fig. 8). Approximation functions parameters \( B_{loc} \) and \( \alpha_0 \) (Table 2) are consistent with each other and reveal the local field value of 0.85(2) T for both planes and the angle 47(2)\(^\circ\) between them. It is worth mention that this local field estimation is very close to the maximum value according to ZF NMR although we did not introduce any anisotropy to our model. It means that direction of the maximum 31P local field is almost perpendicular to the \( b \)-axis, so we could orient it along the external field.

In the framework of the proposed concept spectra from Fig. 5 can be associated with the following particular cases (schematically drawn in the right panel of Fig. 8):

a) One of the planes is almost perpendicular to the external field (\( \alpha = \pi/2 + \pi n \)) and gives narrow distribution around \( B = \sqrt{B_L^2 - B_{loc}^2} \approx 1.72 \text{T} \), and another one forms a typical cycloid spectrum.

b) One of the planes is oriented along the external field (\( \alpha = \pi n \)) and forms the spectrum with the maximum span and peaks symmetrical with respect to \( B_L \), another one forms spectrum with smaller span.

c) Two planes are oriented symmetrically with respect to the external field (\( \alpha_{1,2} = \pm \gamma/2 + \pi n \)) and give rise to identical merging spectra.

d) Two planes are also oriented symmetrically with respect to the external field but at larger angle to it (\( \alpha_{1,2} = \pi/2 \pm \gamma/2 + \pi n \)) and give rise to similar merging spectra.

It’s worth mention that it was not possible to achieve such an orientation that the perpendicular to the external field plane would give the single line at \( B = \sqrt{B_L^2 - B_{loc}^2} \). The minimum observed span of one of the components is presented in Fig. 8. Apparently this is due to more complicated local fields distribution structure compared to equal fields uniformly distributed in the plane. For example, ZF NMR experiment revealed the anisotropy of phosphorus local fields that may give rise to spectrum distribution between \( \sqrt{B_L^2 - B_{loc}^2} \) and \( \sqrt{B_L^2 - 2B_{loc}^2} \) that is already about \( \sim 0.1 \text{T} \). Moreover, possible non-uniformity of the in-plane distribution, canting of the local fields distribution planes to \( b \)-axis or non-complanarity of the local fields vectors exclude the possibility to observe a narrow single line from one of the planes at any orientation. These complications also may cause the relatively sophisticated spectrum for other orientations like depicted in Fig. 8.

To conclude this Section we note that simple model of magnetic iron structure according to neutron data without introducing any magnetic moment anisotropy and anharmonism is enough to describe 31P local fields distribution and perform comprehensive 31P NMR spec-

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**TABLE II:** Parameters of approximation function (18) for single crystal in low fields.

| \( \alpha_0 (\degree) \) | \( B_{loc} (T) \) |
|------------------------|-----------------|
| B1 | 73.8(7) | 0.842(12) |
| B2 | 73.8(7) | 0.854(9)  |
| B3 | 25.5(4)  | 0.846(7)  |
| B4 | 27.6(5)  | 0.848(5)  |
tra analysis and simulation in magnetically unperturbed state of FeP.

**B. External magnetic field rotated in the \((ac)\)-plane: high fields**

Rotational single crystal NMR experiments in high fields (above the spin-reorientation transition field) at \(F_L(31P) = 140\) MHz were performed at 5.5 K. In contrast to low fields experiment the following protocol was used for high fields:

1. After measurement of previous \(31P\) NMR spectrum the NMR probe with the sample was removed from the VTI and heated up to room temperature.
2. After rotation the sample on the fixed angle of 15\(^\circ\) the NMR probe was installed back in the cryostat and cooled down to 5.5 K in zero field.
3. Maximum magnetic field of 9.2 T was introduced.
4. The next \(31P\) spectrum measurement was started always with decreasing magnetic field.

The typical \(31P\) NMR spectra of the FeP single crystalline sample measured at 140 MHz are presented in Fig. 10. As seen from this picture the main features of spectra are similar to the low field case (Fig. 8), thus one can try to simulate them using approach of Eq. (17). Unexpectedly, applying original Eq. (17) leads to systematic deviation of spectral intensity between peaks as well as widening the edge peaks compared to the experiment (see blue curve on 30 deg spectrum in Fig. 10). This evidences for varying of phosphorous local fields distribution caused by iron spin-reorientation transition. To account for this effect we introduce in Eq. (17) an additional weighting factor. Assuming that the density of the distribution of local fields increases with orientation along the field and against the field and decreases with orientation perpendicular to the field we used the weighting factor in the simplest reasonable form: 

\[
\exp[\cos^2(\theta) \cos^2(\alpha_i)/E_b].
\]

The square is taken from considerations of symmetry of the distribution over the field and against the field. Here \(\theta\) is the angle of the local field in the plane, \(\alpha_i\) is the orientation angle of the plane of the local fields distribution relative to the external field (\(i = 1, 2\), \(E_b\) is some energy constant characterizing the degree of condensation (bunching) of the vectors of the local field (the less \(E_b\), the greater the concentration). Such an approach gives narrower peaks for spectra with a large span and wider horns with a noticeable intensity between them for spectra with a small span. It is worth noting that the integral of such weighting factors will depend on \(\alpha_i\), thus the contributions from the two planes were additionally normalized so that their integral intensities were equal. The resulting simulations are presented as red solid curves in Fig. 10.

In Fig. 11 we present the angular dependencies of the peak-to-Larmor field separations for all the four peaks, similar to Fig. 9. The position of all the peaks gradually changes, forming two pairs of symmetric sinuosoids. These rotation curves can be easily described by the same Eq. (18) as in the low fields case. One can see that curves intersect in the vicinity of \(B_L\) (zero on the \(B - B_L\) scale) that is related to very small difference between \(B_L\) and \(\sqrt{B_L^2 - B_{loc}^2}\) when \(B_L >> B_{loc}\). Indeed the approximation of the rotation curves (solid lines in Fig. 11) is in good agreement with experiment and gives reasonable values of approximating parameters (see (Table 3)), resulting in mean values of \(B_{loc} = 0.85(2)\) T and \(\gamma = 45(1)\). These values almost coincide with those for low fields within errors.

![Fig. 10: The \(31P\) NMR spectra of the FeP single crystalline sample measured at 140 MHz (maximum possible), \(T = 5\) K, when it was rotated around the axis of the coil (\(6\)-axis).](image-url)

| \(\alpha_i(\circ)\) | \(B_{loc}(T)\) |
|-------------------|----------------|
| B1                | -15.5(6) 0.851(9) |
| B2                | -14.5(4) 0.848(8)  |
| B3                | -59.9(5) 0.841(8)  |
| B4                | -60.0(4) 0.844(5)  |

**TABLE III: Parameters of approximation function (18) for single crystal in low fields.**
The transformation of the magnetic helical structure of metallic iron phosphide FeP in external magnetic field was investigated by the NMR spectroscopy on $^{31}$P nuclei both in zero magnetic field and by a field-sweeping at several fixed frequencies. Zero field NMR spectrum for polycrystalline sample can be easily explained assuming an incommensurate spiral ordering of Fe magnetic moments with a leading contribution to the local field on the phosphorus nucleus from the Fe–$^{31}$P transferred hyperfine interactions, isotropic and anisotropic. All the components of the tensor of transferred hyperfine interactions were evaluated within a simple physically based model approach. The shape of the powder $^{31}$P field-sweep NMR spectra measured at several fixed frequencies gradually changes with an increase in the field strength from trapezoidal in low fields to clearly asymmetric double-horn (characteristic for single crystalline helimagnetics) in strong fields. The shapes of the spectra were described within the proposed phenomenological model which suggests a superposition of the powder contribution and contribution from the spin-flop-like phase, whose specific weights depend on the external field strength.

The shape of the single-crystalline $^{31}$P NMR spectrum at external magnetic field directed within the $(ac)$-plane exhibit a distinct four-peak structure (inner and outer doublets) characteristic of incommensurate helimagnetic ground state with two pairs of inequivalent phosphorus positions. The spectra were successfully simulated assuming a simple planar helix of Fe magnetic moments in the $(ab)$-plane with the phase shifts of $\approx 36^\circ$ between Fe1-Fe3 and Fe2-Fe4 sites according to neutron data from[3].

Spectral position of each of the four peaks of the single-crystal $^{31}$P NMR spectrum during crystal rotation in a coil around the $b$-axis, which corresponds to the field rotation in the $(ac)$-plane, obeys a simple sinusoidal-like angular dependence. The position of all the peaks gradually changed, forming two pairs of antiphase rotational curves shifted relative to each other by $\gamma \approx 45^\circ$. These pairs can be associated with planes, containing local fields on $^{31}$P, and the angle shift $\gamma$ – with the spatial angle between these planes related with two pairs of phosphorus atoms P5,6 and P7,8. Theoretical estimations of the transferred hyperfine coupling provide a quantitative description of the angular dependencies for the peak-to-Larmor field separations.

Rotational single crystal NMR experiments in high fields (above the spin-reorientation transition field) performed at $F_L (^{31}P)=140$ MHz revealed a considerable change in $^{31}$P NMR spectral shape: spectra demonstrate narrower peaks and decreased spectral intensity between them as compared with low-field rotational experiment. This effect is more pronounced for spectra with a large span, i.e. crystal orientations with phosphorus local fields planes aligned close to the external field direction. This effect evidences for varying of phosphorous local fields distribution caused by iron spin-reorientation transition in high magnetic field registered also by specific heat measurements. It was successfully accounted by introducing a special weighting factor in the spectra simulation procedure resulting in a good agreement with experimental high-field NMR spectra.

Concluding, the ligand $^{31}$P NMR spectroscopy is demonstrated to provide both quantitative information about the transferred hyperfine Fe–$^{31}$P coupling and novel information about the incommensurate Fe spin structure and its transformation in external fields.

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