Федеральное государственное бюджетное учреждение науки
Физический институт имени П.Н. Лебедева
Российской академии наук

Joint Institute for Nuclear Research

JINR Association of Young Scientists and Specialists

The XXVII International Scientific Conference of Young Scientists and Specialists

Devoted to the 110th anniversary of Bruno Pontecorvo

Faculty of Physics Lomonosov Moscow State University

«Evolution of the helimagnetic structure upon arsenic substitution for phosphorus in the Fe(P,As) system: NMR spectroscopy study»

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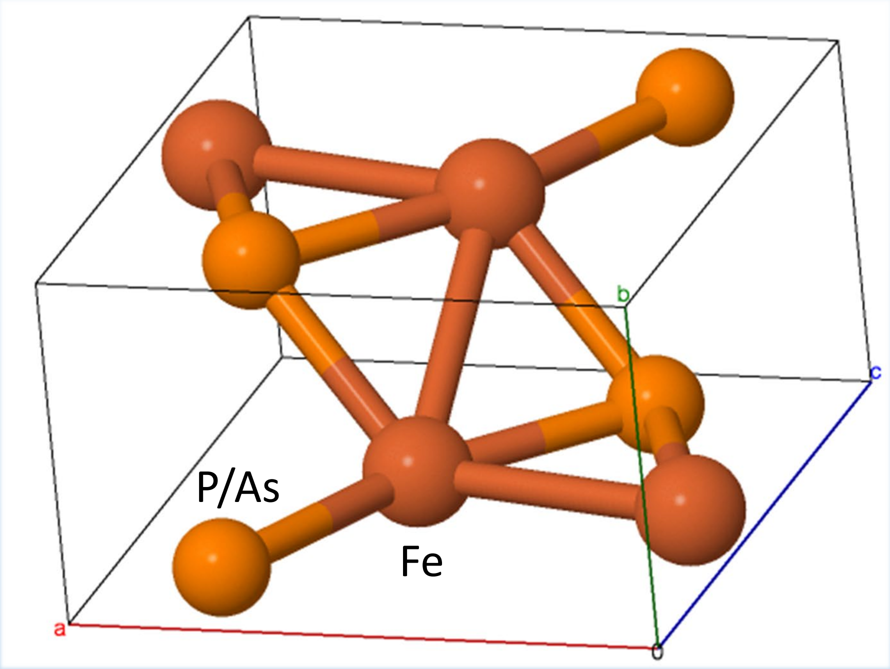
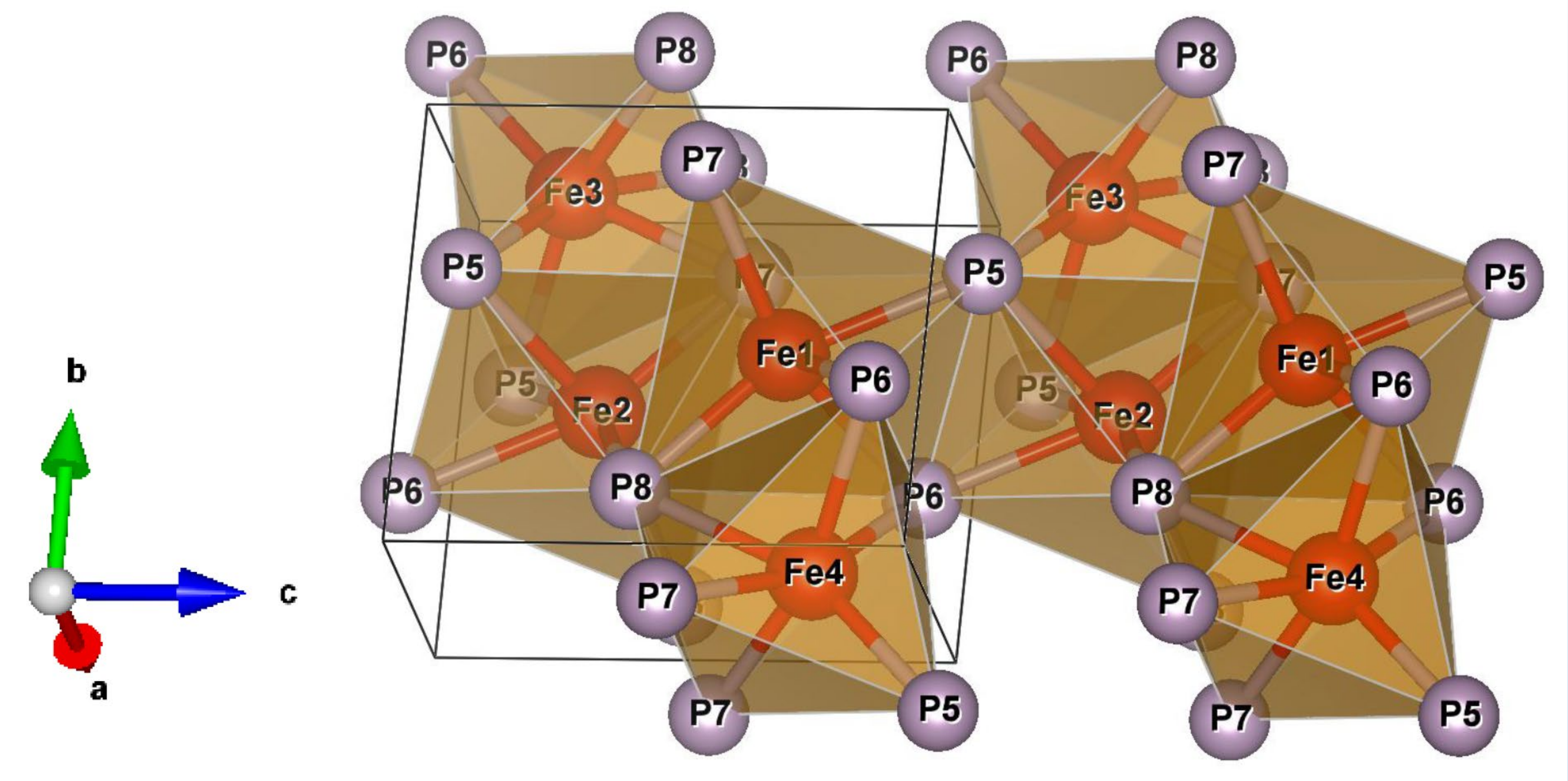
Cristal structure of FeP





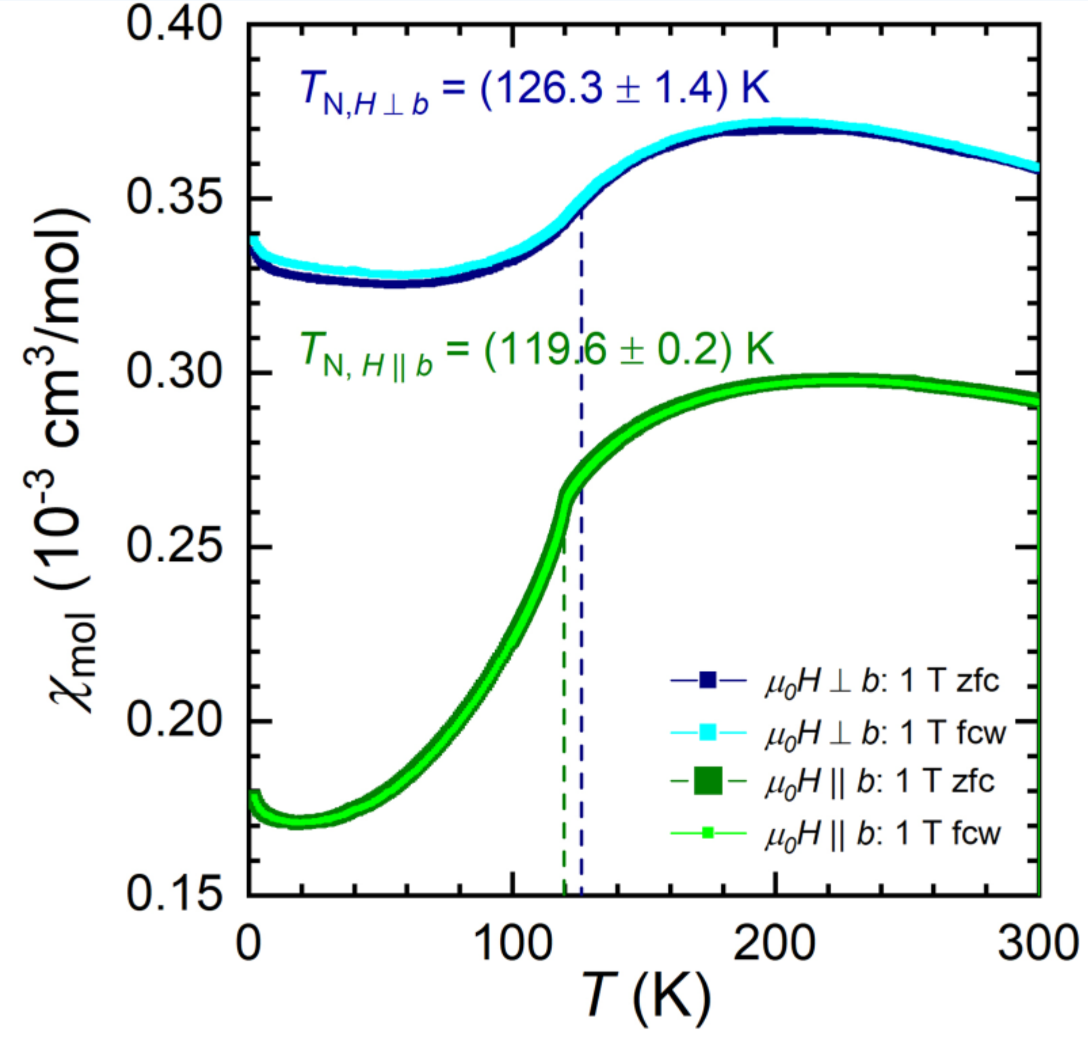
	FeP	**FeAs**
a (Å)	3.05	3.32
b (Å)	5.15	5.40
c (Å)	5.76	6.00
α, β, γ(°)	90	90
V ($Å^3$)	90.50	107.31

FeP has an orthorhombic structure with the *Pnma* space. The structure consists of iron ions that occupy equivalent crystal sites (*4c* Wyckoff position, same as P sites) surrounded by distorted octahedra of phosphorous atoms (FeP_6), and bears four formula units per unit cell.

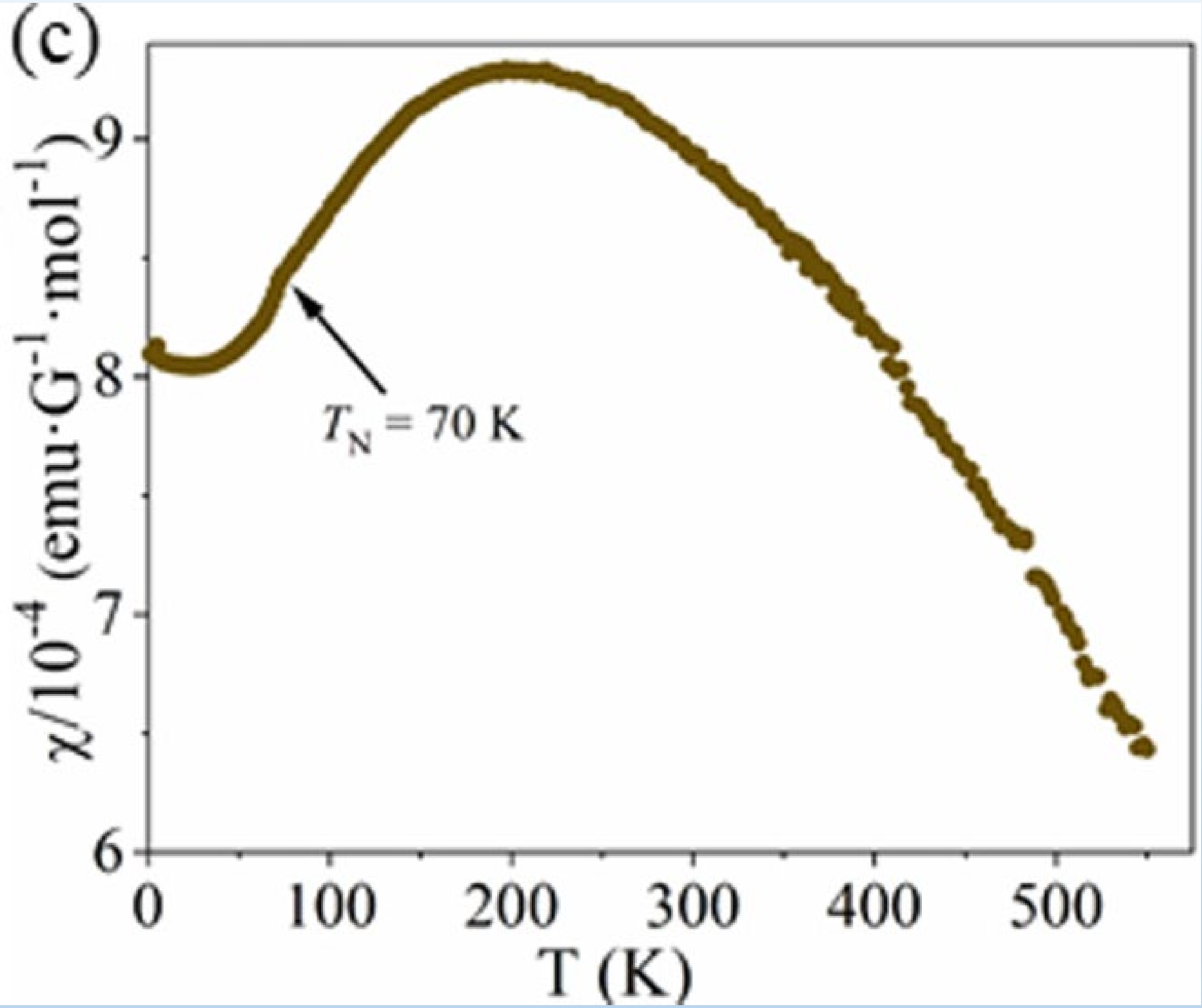
Teterin, Y.A., Sobolev, A.V., Presnyakov, I.A. et al. J.Exp.Theor.Phys. 124, 251–260 (2017).

Magnetic properties of

FeP



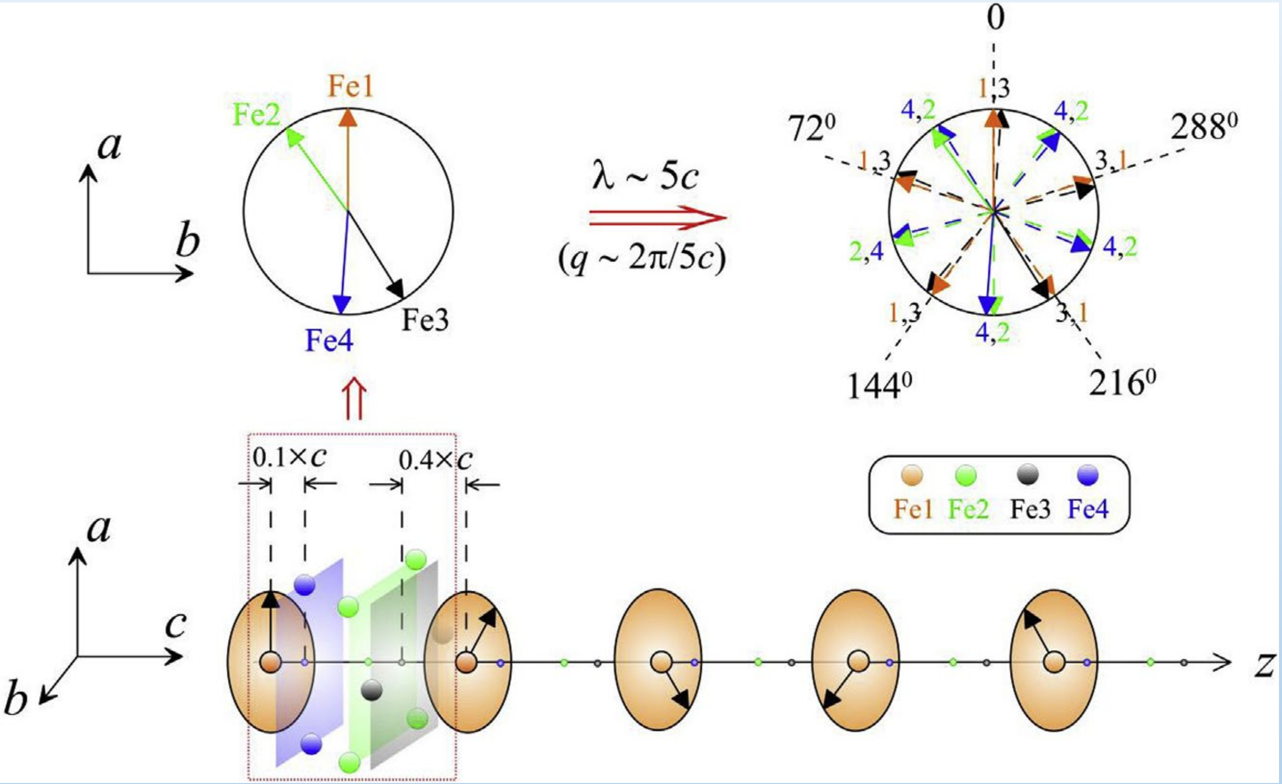
FeAs



Chernyavskii, I. O. et al. Physical Review Materials, 4(8) (2020). doi:10.1103/physrevmaterials.4.083403
E. E. Rodriguez et al, Phys. Rev. B 83, 134438 (2011). doi:10.1103/PhysRevB.83.134438

Magnetic structure of FeP. Two models of helical structure.

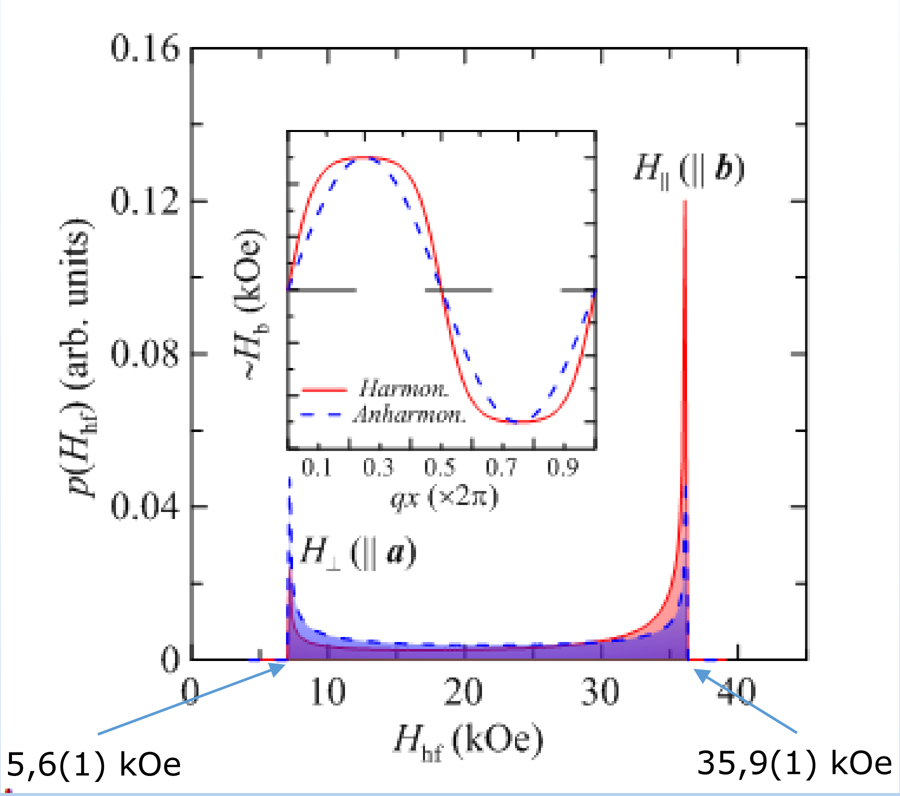
Double helical spin structure from neutron diffraction study



$\lambda \approx 29{,}2$ Å $\mu_{Fe1} = 0{,}46\mu_B$ и $\mu_{Fe1} = 0{,}37\mu_B$

G.P. Felcher, F.A. Smith, D. Bellavance, A. Wold, Phys. Rev. B 3 (1971) 3046.

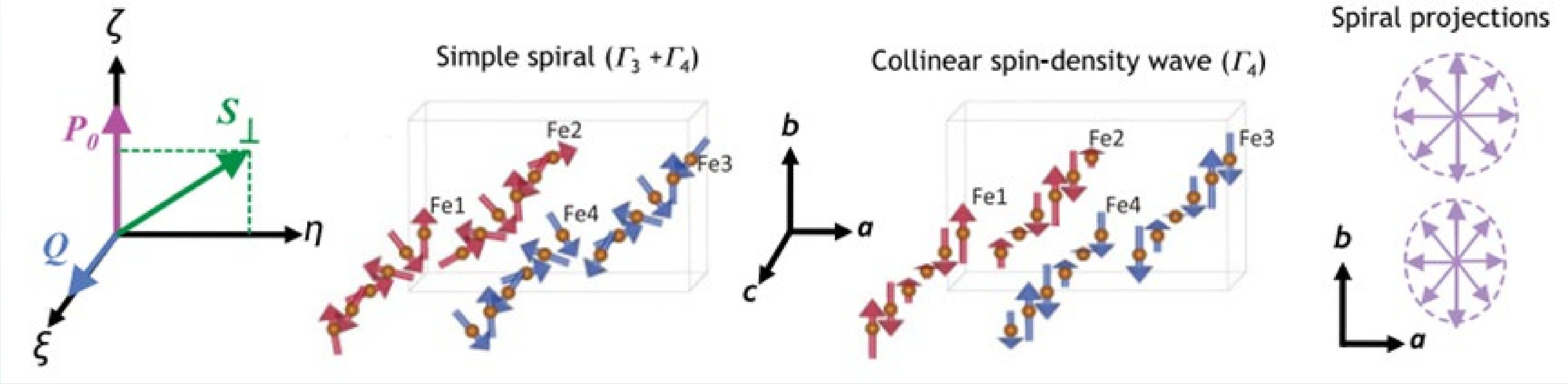
Helical spin structure from Mössbauer spectroscopy

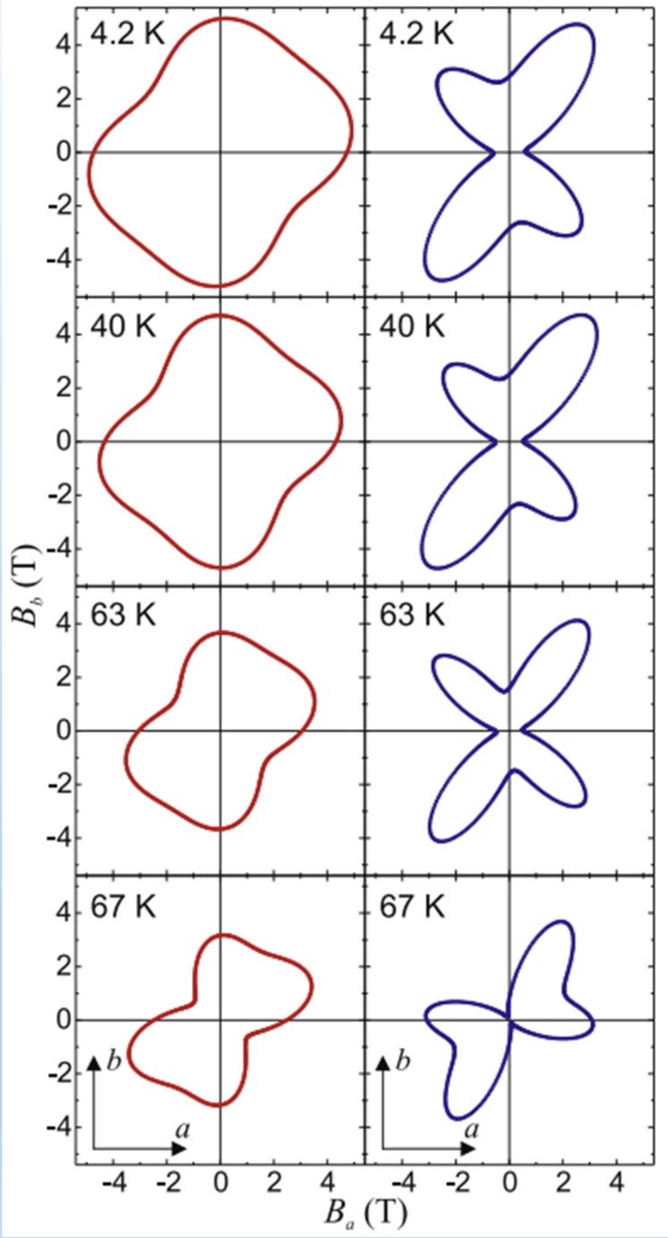


$S_{Fe} = ½$ (low spin), one helical spin structure, easy-axis anisotropy, large temperature independent anharmonicity parameterm $m \approx 0{,}9$

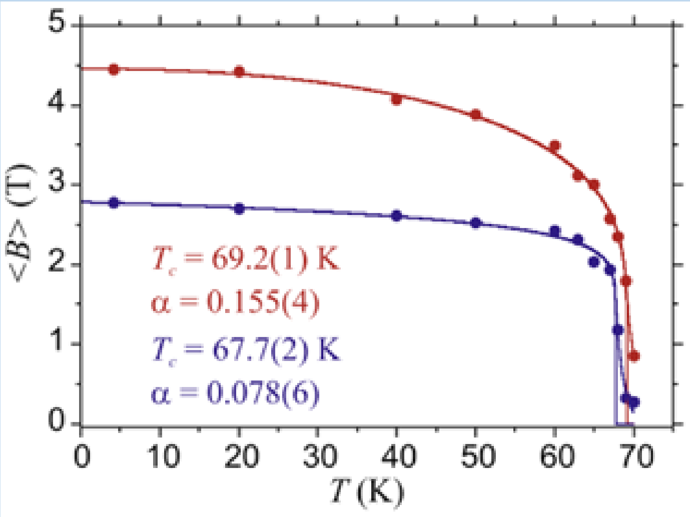
Sobolev Alexey V., Presniakov Igor A., Gippius Andrey A. et al., Journal of Alloys and Compounds, v. 675,p. 277-285 (2016).

Magnetic structure of FeAs.





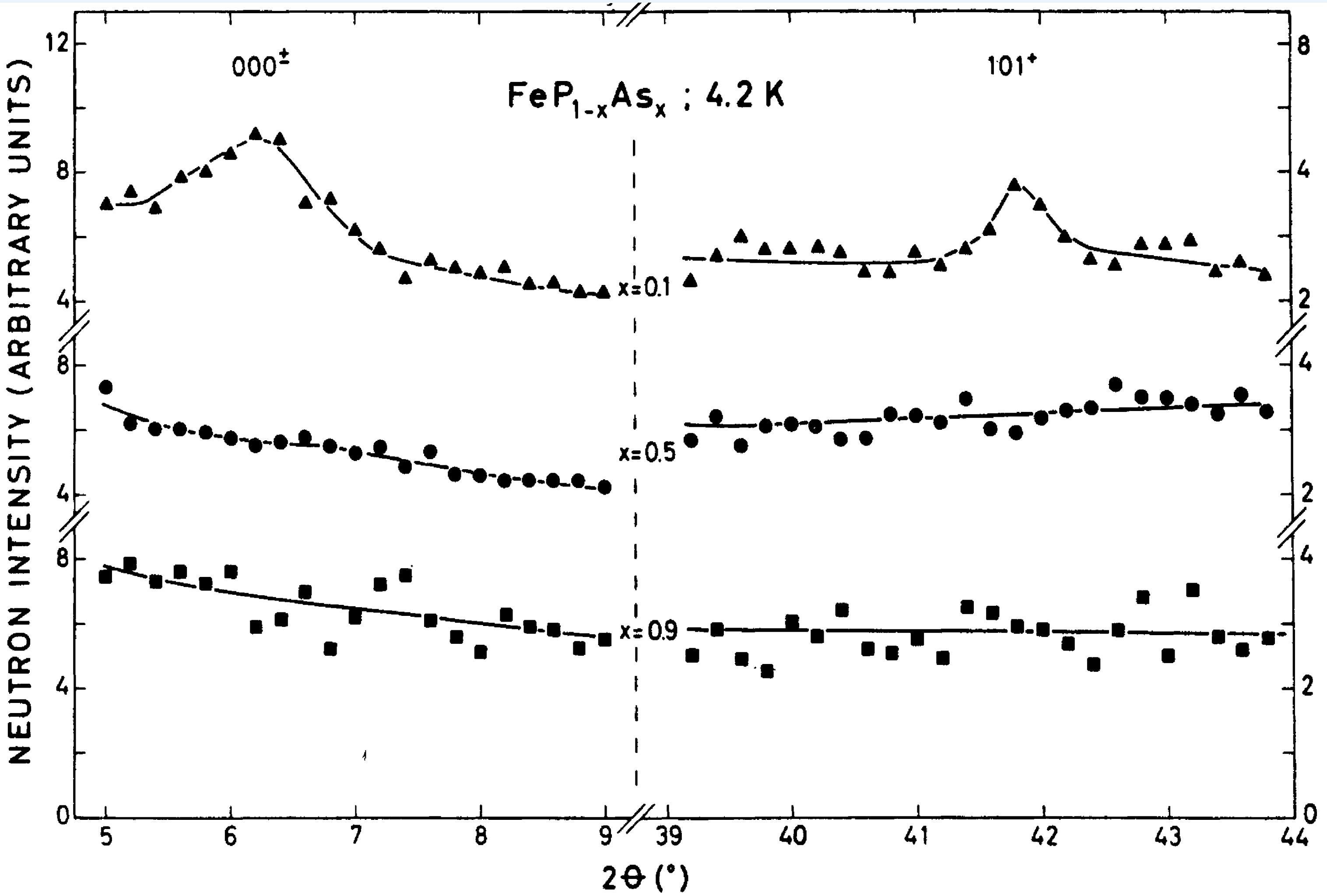
	$\alpha^{1`2}=\alpha^{3`4}$	$\alpha^{2`3}=\alpha^{4`1}$	$\mu(\mu_B)$	$1/\tau$(c lengths)	T_N
FeP	176^{o}	-140^{o}	0.46; 0.37	5.0	125±1
FeAs	154^{o}	-86^{o}	≈0.5	2.67	77±1



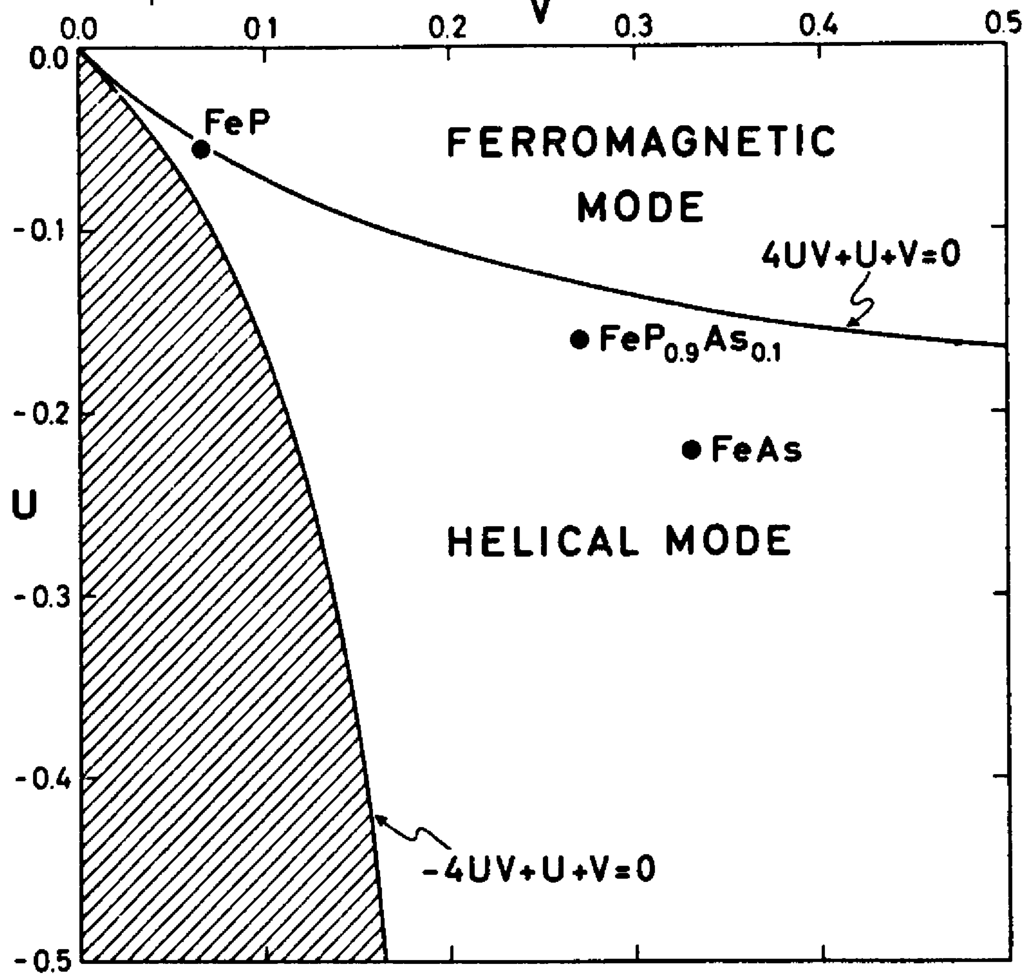
E. E. Rodriguez et al, Phys. Rev. B 83, 134438 (2011). doi:10.1103/PhysRevB.83.134438
Błachowski et al. Journal of Alloys and Compounds, 582, 167–176 (2014). doi:10.1016/j.jallcom.2013.08.049

Magnetic structure of $FeP_{1-x}As_x$.

Partial neutron diffraction diagrams for $FeP_{1-x}As_x$ (x=0.1, 0.5 and 0.9)



Relevant quadrant of U,V stability diagram for helimagnetic and ferromagnetic modes in MnP type compounds according to isotropic model.



However, due to the very small magnetic moment of iron and the poor signal-to-noise ratio, the authors of this article report that they cannot assess the helicoids' destruction. It is possible that there is broadening of this reflex.

Selte K. et al., Acta Chemica Scandinavica v. 28a p. 957-962 (1974) DOI: 10.3891acta.chem.scand.28a-0957

MSU & LPI Solid-State NMR Lab

Cryogenic High Homogeneity Cryogen Free Measurement System (CFMS) **12 T**, VTI 1.6 – 400 K + Digital NMR spectrometer

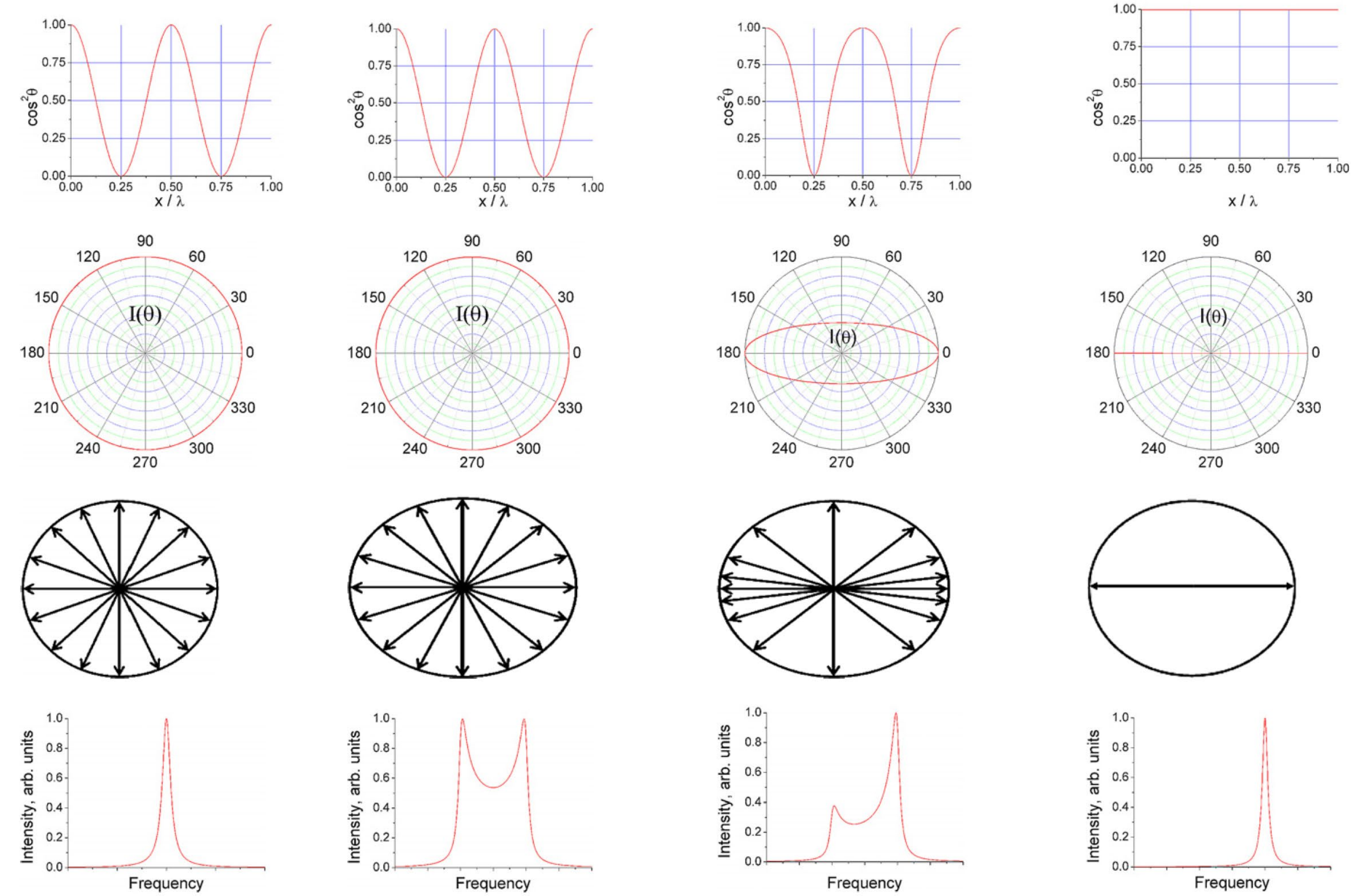
RTI High Homogeneity Liquid Helium magnetic Systems 7.3 T

Bruker MSL-300 NMR Spectrometer + CIA helium cryostat 1.4-325 K

Influence of anisotropy and parameter m on magnetic properties and zero field NMR line shape.

Influence of anisotropy and parameter m on magnetic properties and zero field NMR line shape. From top to bottom: anisotropy type and $\theta(x)$ dependence, $\cos^2\theta(x)$ dependence, $I(\theta)$ dependence (in polar coordinates), magnetic vectors schematic representation, zero field NMR line shape.

$\nu(\theta) = \text{const};$ $\theta(x) = 2\pi^* x/\lambda$	$\nu(\theta) = \nu_\perp + (\nu_\parallel - \nu_\perp)^* \cos^2\theta;$ $\theta(x) = 2\pi^* x/\lambda$	$\nu(\theta) = \nu_\perp + (\nu_\parallel - \nu_\perp)^* \cos^2\theta;$ $\sin\theta(x) = sn(x/\lambda, m)$	$\nu(\theta) = \nu_\perp + (\nu_\parallel - \nu_\perp)^* \cos^2\theta;$ $\sin\theta(x) = sn(x/\lambda, m) = 0$



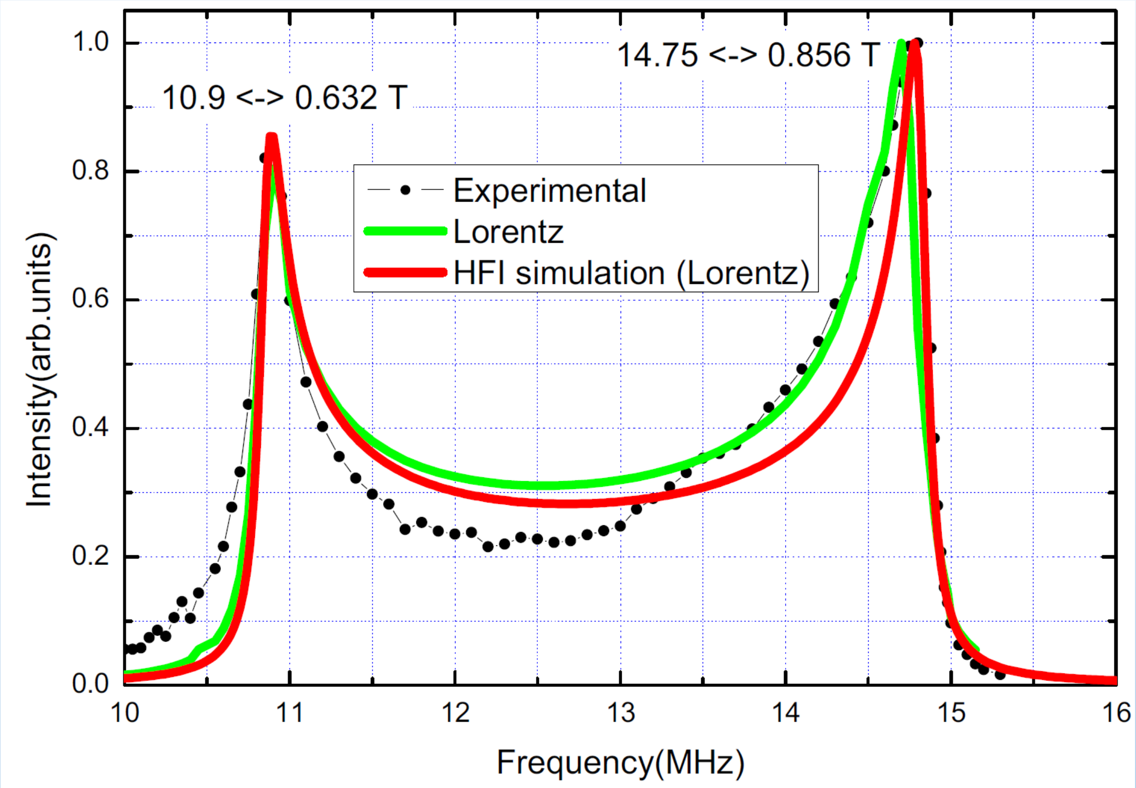
Simulation results of the ^{31}P ZF-NMR spectrum of FeP at various *m*

$$\cos\vartheta(z) = sn\left[\pm\frac{4K(m)}{\lambda}z, m\right]$$

Gippius, A. A. et al., Solid State Communications, 152(6), 552–556 (2012). doi:10.1016/j.ssc.2011.12.028

NMR study of magnetic structure and hyperfine interactions in FeP

zero-field NMR

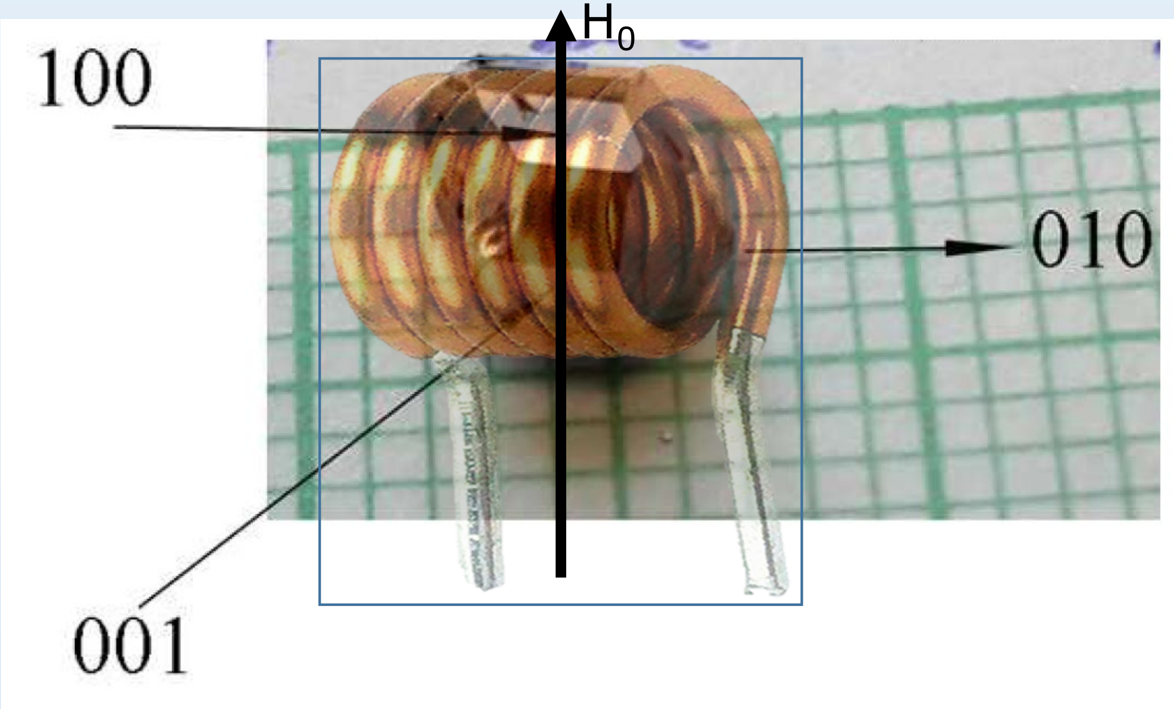


^{31}P zero-field NMR spectrum measured in FeP at 4.2 K.

anharmonicity parameter m = 0.19 (“Jacobian” helix) or k = 0.03 (simple helix)

Lorentzian individual line shape (δ = 0.06 MHz).

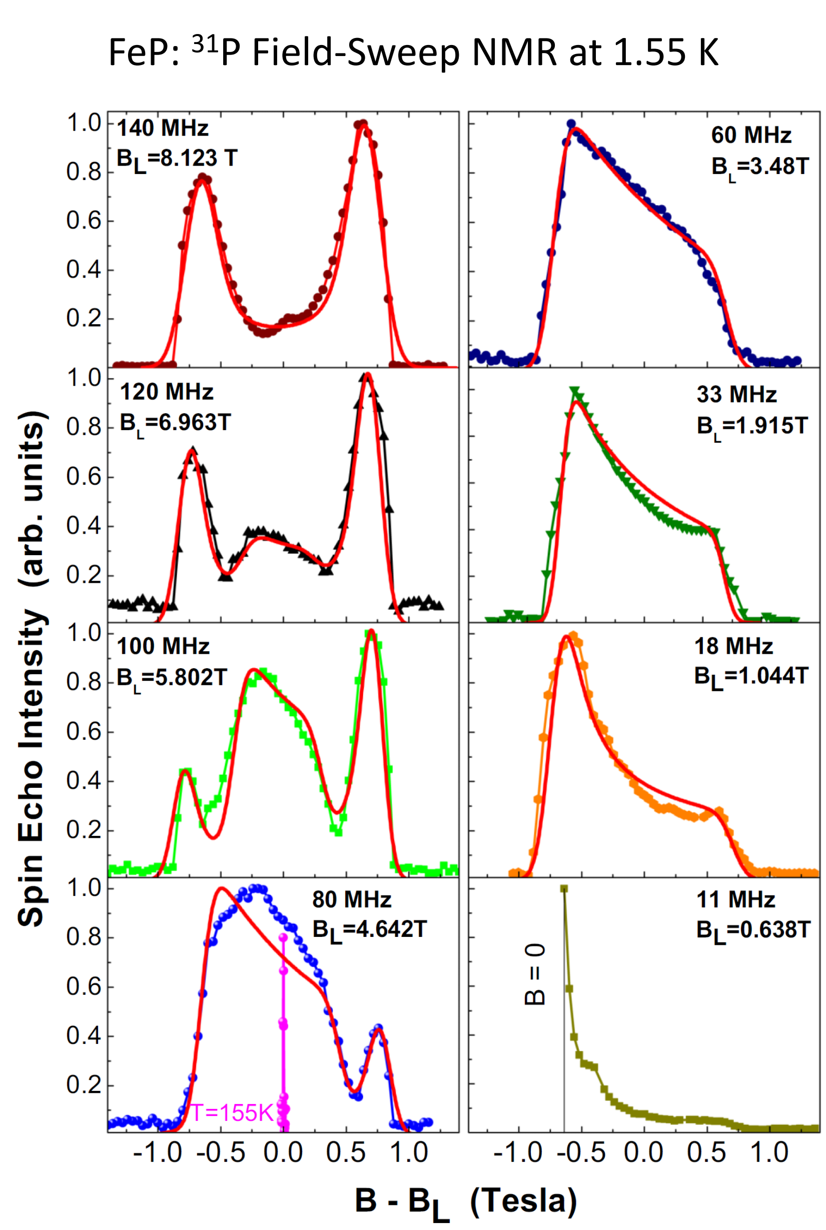
^{31}P Field-Sweep NMR spectra of the FeP single crystalline sample



Large single crystals of FeP were first obtained by the scientific group headed by Prof. Morozov I.V. at the Department of Chemistry of MSU

A. A. Gippius, et al. NMR study of magnetic structure and hyperfine interactions in the binary helimagnet FeP. Phys.Rev.B 102 (2020) 214416

NMR study of magnetic structure and hyperfine interactions in $FeP_{1-x}As_x$ (x=0, 0.1)



FeP

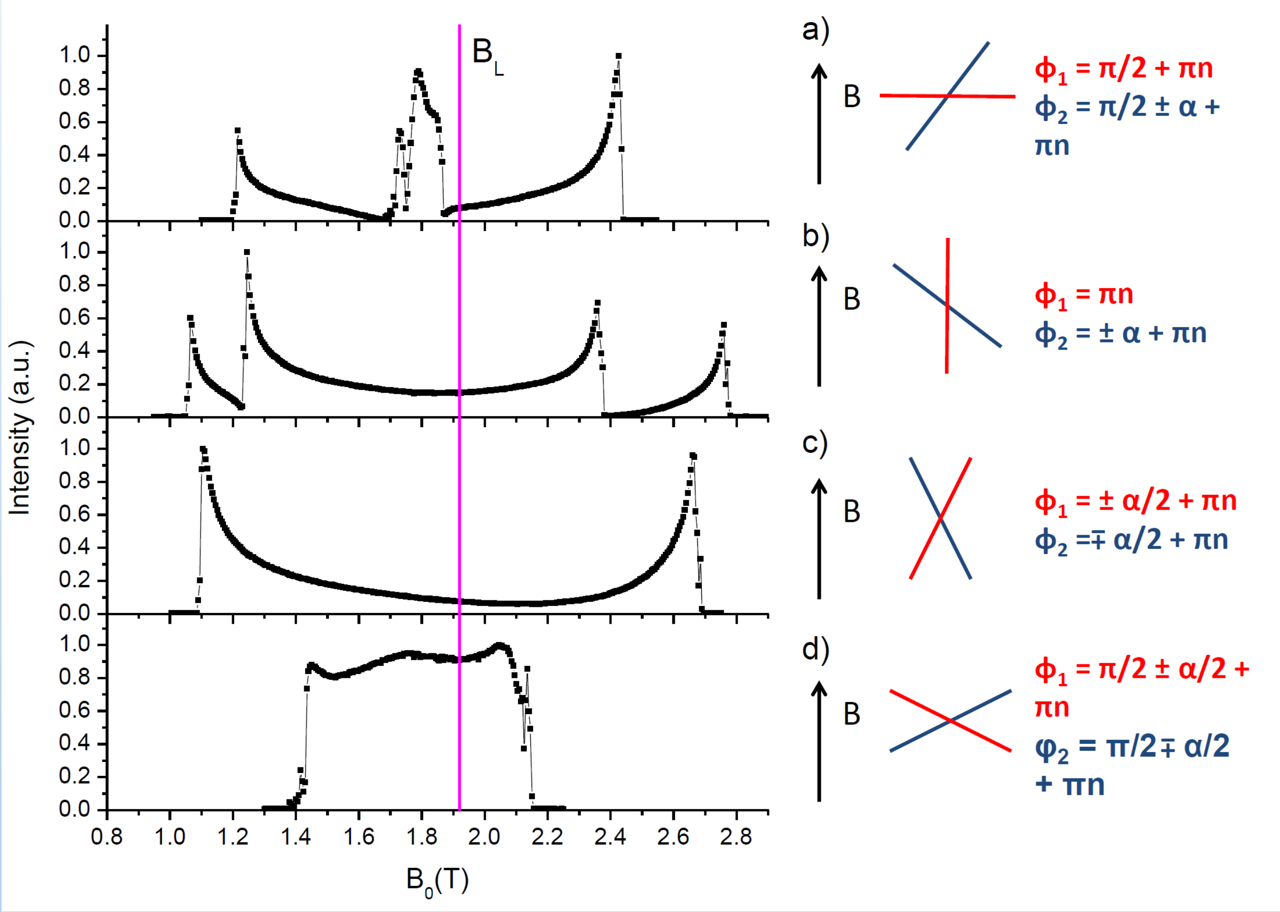
- From field-sweep ^{31}P NMR spectra on powder sample FeP we conclude that a continuous spin-reorientation transition occurs in an external magnetic field range of 4–7 T, which is also confirmed by specific-heat measurements.

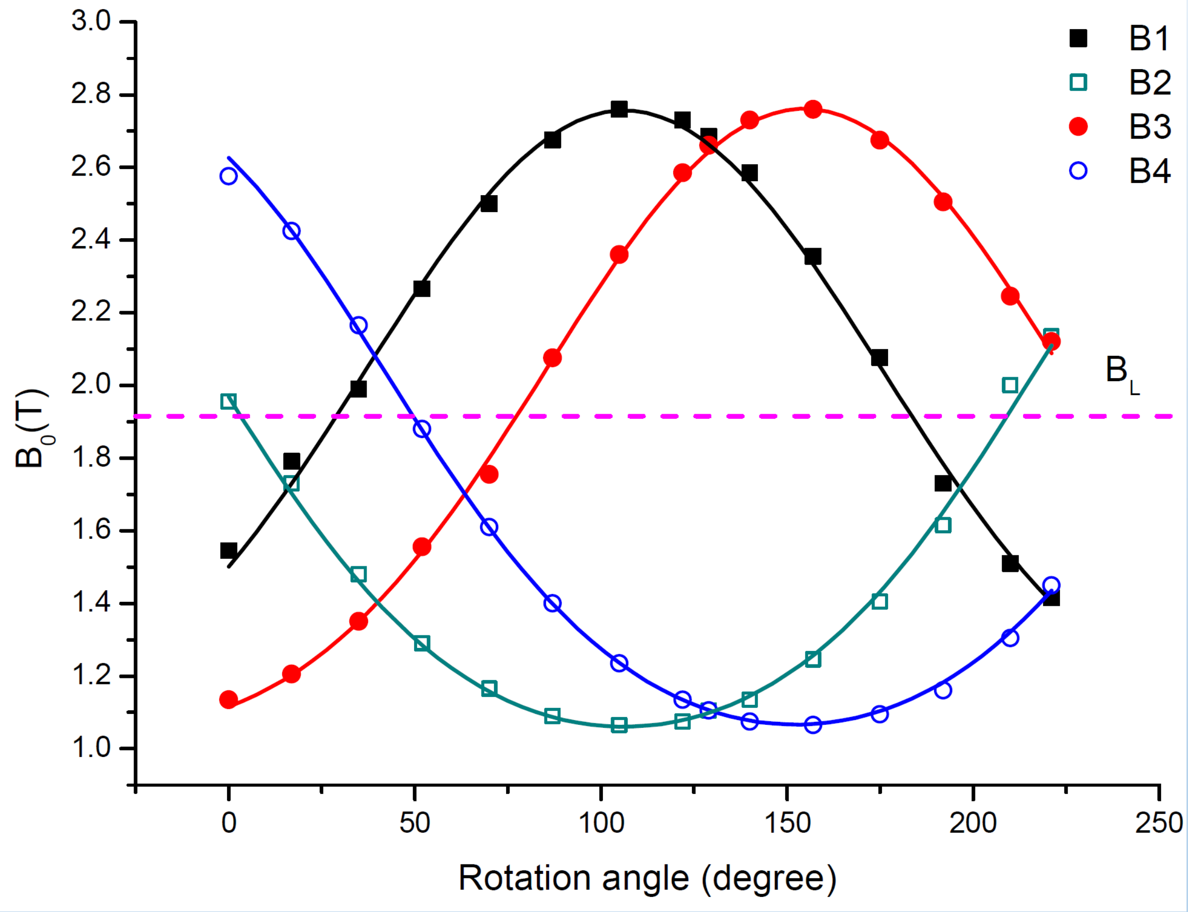
$FeP_{0.9}As_{0.1}$

- Spin-reorientation transition is not observed up to 9 Tesla
- At frequencies above 50 MHz, a significant peak is observed in the 31P field-sweep NMR spectra at the Larmor field.

NMR study of magnetic structure and hyperfine interactions in FeP (*single crystal*).

Field-Sweep NMR at low magnetic field (33 MHz)



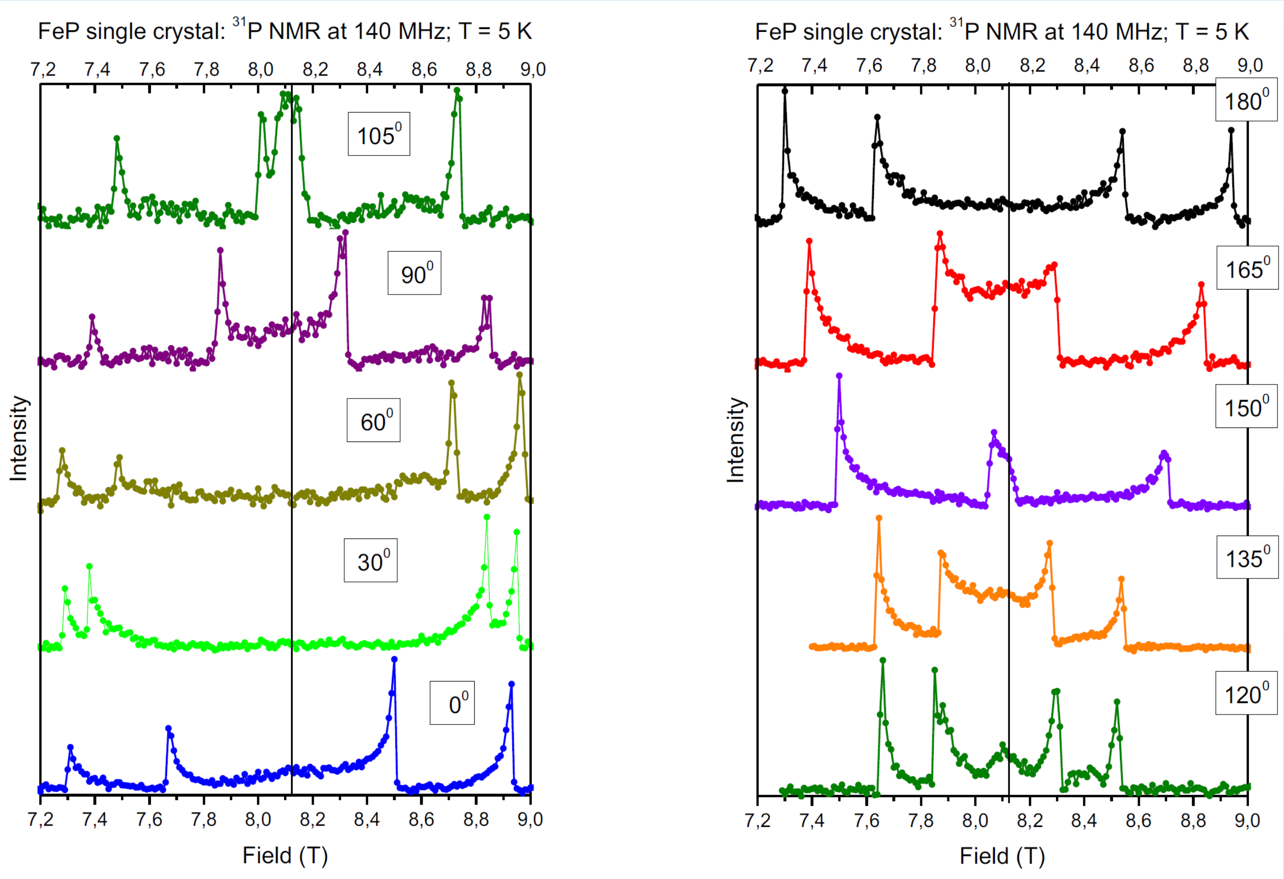


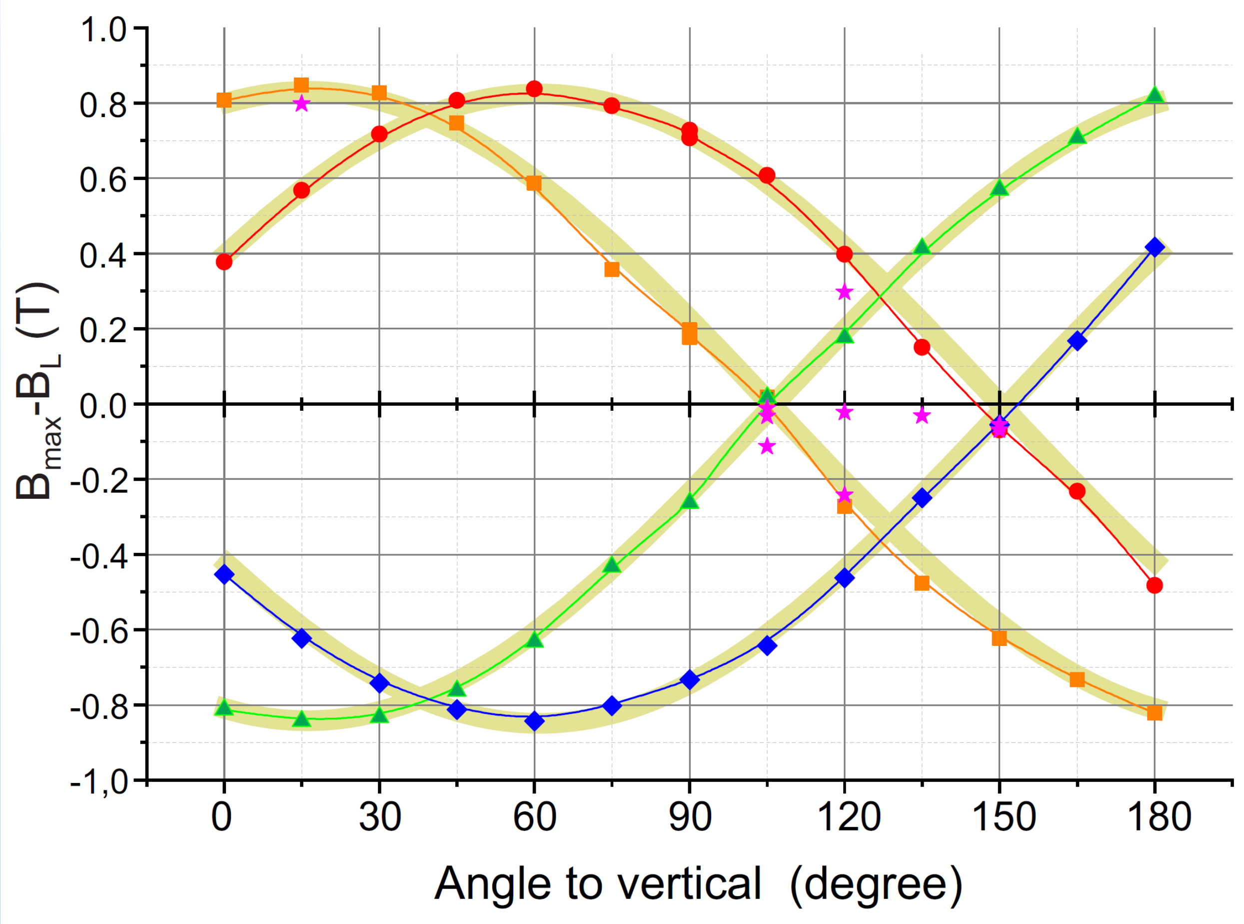
$$B_{ext} = \sqrt{B_L^2 - B_{loc}^2 sin^2(\varphi)} \pm B_{loc}\cos(\varphi)$$

A. A. Gippius, et al. NMR study of magnetic structure and hyperfine interactions in the binary helimagnet FeP. Phys.Rev.B 102 (2020) 214416

NMR study of magnetic structure and hyperfine interactions in FeP (*single crystal*).

Field-Sweep NMR at high magnetic field (140 MHz)





$$B_{ext} = \sqrt{B_L^2 - B_{loc}^2 sin^2(\varphi)} \pm B_{loc}\cos(\varphi) \longrightarrow B_{ext} = B_L \pm B_{loc}\cos(\varphi)$$

A. A. Gippius, et al. NMR study of magnetic structure and hyperfine interactions in the binary helimagnet FeP. Phys.Rev.B 102 (2020) 214416

Magnetic structure and hyperfine interactions in $FeP_{1-x}As_x$ (x=0.5) from Mössbauer spectroscopy

According to Mössabauer spectroscopy, the magnetic structure of $FeP_{1-x}As_x$ practically does not change up x = 0.5:

- are well described by the model of a magnetic helicoid on Fe atoms with strong anharmonicity (m = 0.90).
- $H_{||} \approx 37$ kOe in FeP
  $H_{||} \approx 30$ kOe in $FeP_{0.5}As_{0.5}$
  $H_{||} \approx 47$ kOe in FeAs

- anisotropic field $\Delta H_{anis} = H_{||} - H_{\perp}$
  $\Delta H_{anis} = 30$ kOe in FeP
  $\Delta H_{anis} = 24$ kOe in $FeP_{0.5}As_{0.5}$
  $\Delta H_{anis} = 35$ kOe in FeAs

^{57}Fe Mössbauer spectra of the $FeP_{1-x}As_x$ (x=0, 0.33, 0.5)compounds measured in the magnetically ordered state at T = 11 K (upper panels) and the magnetic field profiles reconstructed from them on Fe (lower panels).

NMR study of magnetic structure and hyperfine interactions in $FeP_{1-x}As_x$ (x=0.33, 0.5)

In contrast to the Mössbaur data, the NMR spectra do not show the line shape characteristic of a helicoidal magnetic structure.

- NMR spectrum is a Gaussian lines perfectly symmetric relative to the B_L
- Exhibited gradual transition into spin-glass like state in the temperature range of 20-30 K.

^{31}P NMR spectra $FeP_{1-x}As_x$ (x=0.33, 0.5) measured at a fixed frequency of 100 MHz at various temperatures in the range 2 - 150 K. The solid black vertical line shows the position of the Larmor field of ^{31}P nuclei at this frequency.

NMR study of magnetic structure and hyperfine interactions in $FeP_{1-x}As_x$ (x=0.33, 0.5)

The Gaussian shape of the ^{31}P NMR line is likely due to the difference of more than 4 orders of duration between the time of Mössbauer and NMR experiments.

The interaction time of a *γ*-quanta with a ^{57}Fe nucleus in Mössbauer spectroscopy experimentsis is a fraction of nanoseconds, whereas the duration of NMR experiments ranges from several tens of microseconds to several milliseconds.

FWHM of the Gaussian fit of the ^{31}P NMR spectra in $FeP_{0.5}As_{0.5}$ and $FeP_{0.67}As_{0.33}$ as a function of temperature.

Conclusions:

1. **FeP**

- Anharmonicity at the P site m ≈ 0.19 to be substantially lower than that found at the Fe site by Mössbauer spectroscopy (m ≈ 0.96).
- Observed the spin-reorientation transition of the FeP helical spin structure in the external magnetic field range of 4 – 7 T.
- Established the phenomenological model, which implies phase separation into field-dependent volume fractions with random and oriented responses.
- Demonstrated that all observed ^{31}P NMR spectra can be treated within a model of an isotropic helix of Fe magnetic moments in the (ab)-plane with a phase shift of 36° and 176° between Fe1-Fe3 (Fe2-Fe4) and Fe1-Fe2 (Fe3-Fe4) sites, respectively, in accordance with the neutron scattering data.

2. **$FeP_{1-x}As_x$ (x=0.1)**

- The values of local magnetic fields on ^{31}P have not changed compared to unmodified FeP.
- Spin-reorientation transition is not observed up to 9 Tesla

3. **$FeP_{1-x}As_x$ (x=0.33, 0.5)**

- Helical magnetic structure in the $FeP_{1-x}As_x$ (x=0.33, 0.5) compounds is completely vanished.
- At all temperatures the spectrum can be satisfactory approximated by single Gaussian line. The observed behavior indicates that instead of sharp transition from paramagnetic state into ordered magnetic helical state at 120 K in the undoped binary FeP the 33% and 50% As substituted compounds $FeP_{1-x}As_x$ (x=0.33, 0.5) exhibited gradual transition into spin-glass like state in the temperature range of 20-30 K.

Thank you for your attention!

We welcome suggestions for collaborative research.