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

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FeP has an orthorhombic structure with the \textit{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\textsubscript{6}), and bears four formula units per unit cell.

<table>
<thead>
<tr>
<th></th>
<th>FeP</th>
<th>FeAs</th>
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</thead>
<tbody>
<tr>
<td>(a) (Å)</td>
<td>3.05</td>
<td>3.32</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>5.15</td>
<td>5.40</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>5.76</td>
<td>6.00</td>
</tr>
<tr>
<td>(\alpha, \beta, \gamma) (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(V) (Å(^3))</td>
<td>90.50</td>
<td>107.31</td>
</tr>
</tbody>
</table>
Magnetic properties of FeP

![Graph showing magnetic properties of FeP](image)

- $T_{N,H \perp b} = (126.3 \pm 1.4) \text{ K}$
- $T_{N,H \parallel b} = (119.6 \pm 0.2) \text{ K}$

Magnetic properties of FeAs

![Graph showing magnetic properties of FeAs](image)

- $T_N = 70 \text{ K}$


Magnetic structure of FeP. Two models of helical structure.

Double helical spin structure from neutron diffraction study

Helical spin structure from Mössbauer spectroscopy

$\lambda \approx 29,2 \text{ Å} \quad \mu_{\text{Fe}1} = 0,46\mu_\text{B} \quad \text{и} \quad \mu_{\text{Fe}1} = 0,37\mu_\text{B}$

$S_{\text{Fe}} = \frac{1}{2}$ (low spin), one helical spin structure, easy-axis anisotropy, large temperature independent anharmonicity parameter $m \approx 0,9$


Magnetic structure of FeAs.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha^{12} = \alpha^{34}$</th>
<th>$\alpha^{23} = \alpha^{41}$</th>
<th>$\mu (\mu_B)$</th>
<th>$1/\tau (\text{c lengths})$</th>
<th>$T_N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeP</td>
<td>176°</td>
<td>-140°</td>
<td>0.46; 0.37</td>
<td>5.0</td>
<td>125±1</td>
</tr>
<tr>
<td>FeAs</td>
<td>154°</td>
<td>-86°</td>
<td>$\approx 0.5$</td>
<td>2.67</td>
<td>77±1</td>
</tr>
</tbody>
</table>

Magnetic structure of $\text{FeP}_{1-x}\text{As}_x$.

Partial neutron diffraction diagrams for $\text{FeP}_{1-x}\text{As}_x$ ($x=0.1$, 0.5 and 0.9)

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.

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. 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.

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

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

NMR study of magnetic structure and hyperfine interactions in FeP

$^{31}$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 ($\delta = 0.06$ 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.

FeP: $^{31}$P Field-Sweep NMR at 1.55 K

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 $^{31}$P 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)

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

NMR study of magnetic structure and hyperfine interactions in FeP (*single crystal*).
Field-Sweep NMR at high magnetic field (140 MHz)

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

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).
- $H_{||} \approx 37 \text{ kOe}$ in FeP
  $H_{||} \approx 30 \text{ kOe}$ in FeP_{0.5}As_{0.5}
  $H_{||} \approx 47 \text{ kOe}$ in FeAs
- anisotropic field $\Delta H_{\text{anis}} = H_{||} - H_{\perp}$
  $\Delta H_{\text{anis}} = 30 \text{ kOe}$ in FeP
  $\Delta H_{\text{anis}} = 24 \text{ kOe}$ in FeP_{0.5}As_{0.5}
  $\Delta H_{\text{anis}} = 35 \text{ kOe}$ 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 $T = 11 \text{ K}$ (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 $\gamma$-quanta with a $^{57}$Fe nucleus in Mössbauer spectroscopy experiments 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 $m \approx 0.19$ to be substantially lower than that found at the Fe site by Mössbauer spectroscopy ($m \approx 0.96$).
- 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 $36^\circ$ and $176^\circ$ 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 satisfactorily 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.