Pressure induced magnetic order in FeSe

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The magnetic order induced by the pressure was studied in single crystalline FeSe by means of muon-spin rotation (μSR) technique. By following the evolution of the oscillatory part of the μSR signal as a function of angle between the initial muon-spin polarization and 101 axis of studied crystal it was found that the pressure induced magnetic order in FeSe corresponds either to the collinear (single-stripe) antiferromagnetic order as observed in parent compounds of various FeAs-based superconductors or to the Bi-Collinear order as obtained in FeTe system, but with the Fe spins turned by 45°. The value of the magnetic moment per Fe atom was estimated to be $\sim 0.13 - 0.14 \mu_B$ at $p \approx 1.9$ GPa.

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Since their discovery in 20081 iron chalcogenide superconductors has attracted much interest. Being composed of a single layer of square Fe lattice tetrahedrally coordinated by chalcogen (Ch) atoms (Ch= Se, Te, S), FeCh consists just of a fundamental building blocks of Fe-based high-temperature superconductors (Fe-HTS). The iron selenide, FeSe, superconducts at ambient conditions (0.4 K) with the transition temperature $T_c \approx 8$ K. Early muon spin rotation (μSR) experiments on FeSe revealed that the system is non-magnetic at ambient pressure down to $T \simeq 0.02$ K.2 The first pressure experiments also do not detect the magnetic order up to pressures at least $p \sim 20$ GPa.2 This is in striking contrast to the other Fe-HTSs that usually exhibit static magnetic order in the parent compounds.5,10 Shortly after, the NMR studies showed a wipeout of the signal that revealed an incipient magnetic phase transition under pressure.2 It was further realized that pressure promotes the static magnetism in FeSe which was confirmed in μSR experiments by Bendele and coworkers.10 The static magnetic orders which competes with superconductivity was set in above $p \gtrsim 0.8$ Gpa and both ground states were found to coexist on an atomic length for pressures exceeding $\sim 1.2$ GPa.

So far the only confirmation of pressure induced bulk magnetic order in FeSe was obtained from μSR data.15 Only very recently the appearance of bulk magnetism in high-quality FeSe single crystalline samples was confirmed in Mössbauer under pressure experiments by Kothapalli et al.12 and NMR studies of Wang et al.15 It should be emphasized, however, that the exact magnetic spin arrangement in FeSe is still unknown. The problem stems from the low value of the ordered magnetic moment on the Fe site ($m_{Fe}$). Following μSR studies, for pressures $p \leq 2.5$ GPa $m_{Fe}$, do not exceed 0.2 $\mu_B$.14 Recent Mössbauer experimenter results in similar estimate of $m_{Fe}$ for $p \lesssim 4$ GPa.15 Such small values of $m_{Fe}$ makes the determination of the magnetic structure by means of neutron experiments to be quite challenging. We are only aware of one neutron diffraction measurement allowing to set the upper limit of $m_{Fe} < 0.5 - 0.7 \mu_B$ for pressures $p \lesssim 4.5$ GPa.15

Experimentally, the antiferromagnetic (AFM) collinear structure consistent of stripes of parallel spins (the 'Collinear1' structure, Fig. 1) was established for parent compounds of FeAs-based Fe-HTSs.5,11 The so-called 'Bi-collinear' order (denoted as 'Bi-Collinear1', Fig. 1) was resolved for parent compounds of iron tellurides.4,12,13 For FeSe the direct measurements are still missing and only theoretical considerations were made till now. For bulk FeSe the 'Collinear2' type of order was proposed in Ref. 14 based on first principle calculations. The AFM 'Pair-checkerboard' order in bulk and mono-layer FeSe was considered by Cao et al.14 For the mono-layer and the bi-layer FeSe films the 'Checkerboard' and the mixture of the 'Checkerboard' and 'Collinear1' orders were predicted in Ref. 16. The purely 'Pair-Checkerboard' order in bulk and thin-film FeSe was obtained in Refs. 17. The authors of Ref. 18 have reported that the 'Pair-Checkerboard' and the 'Collinear1' stripe orders are realized in thin-film and bulk FeSe, respectively.

The aim of this paper was to identify the type of the pressure induced magnetic order in FeSe single crystalline sample by means of muon-spin rotation technique. In addition to the mentioned above, the 'Bi-Collinear2' order which differs from the 'Bi-Collinear1' one by spins turned to 45° (see Fig. 1 and Refs. 10,19) as well as several magnetic structures suggested by Christensen et al.19 for various electron- and hole-doped Fe-HTSs were considered. This includes the collinear order denoted as 'Collinear-Z', two type of spin vortex crystal (SVC) phases and the charge-spin density wave (CSDW) phase. Note that SVC1, SVC2, and CSDW phases preserves the tetragonal symmetry of the system, while the rest of the structures could be observed in both, the orthorhombic and the tetragonal magnetic unit cells. By following the evolution of the oscillatory part of the μSR signal as a function of angle between the initial muon-spin polarization and 101 axis of studied crystal it was shown that the pressure induced magnetic order in FeSe may correspond...
either to the "Collinear1" or the 'Bi-Collinear2' type of the order (see Fig. 1).

The FeSe single crystal was synthesized by means of floating zone technique as is described in Ref. 20. The x-ray experiment confirms that crystal exhibit a single preferred orientation of a tetragonal (101) plane.\(^\text{[20]}\) The muon-spin rotation (µSR) experiments were carried out at the µE1 beam line by using the dedicated GPD spectrometer (Paul Scherrer Institute, Switzerland). The zero-field (ZF) and 3 mT weak transverse-field (TF) µSR measurements were performed at temperatures ranging from \(\sim 5\) to 60 K and pressure \(p \approx 1.9\) GPa. The typical counting statistics were \(\sim 20 \cdot 10^6\) positron events for each data point. The experimental data were analyzed by using the MUSRFIT package.\(^\text{[21]}\) The pressure was generated in a double-wall piston-cylinder type of cell made of MP35N alloy. As a pressure transmitting medium 7373 Daphne oil was used. The details of the experimental setup for conducting µSR under pressure experiments are given in Ref. \(\text{[22]}\).

Figure 2a shows the schematic of the experiment. The sample, placed inside the pressure cell, was rotated in a way allowing to change the angle \(\theta\) between the initial muon-spin polarization \(P(0)\) and 101 crystallographic axis of the sample. The zero-field µSR muon time spectra measured at \(T = 15\) K and \(p \approx 1.9\) GPa for \(\theta = -10^\circ\) and \(-100^\circ\) are shown in Fig. 2. The solid lines are fits of the following function to the experimental data:

\[
A(t) = A_s(0)P_s(t) + A_{pc}(0)P_{pc}(t),
\]

Here \(A_s(0)\) and \(A_{pc}(0)\) are the initial asymmetries and \(P_s(t)\) and \(P_{pc}(t)\) are the muon-spin polarizations belonging to the sample and the pressure cell, respectively. The polarization of the pressure cell \(P_{pc}(t)\) was obtained in separated set of experiments.\(^\text{[22]}\) The polarization of the sample was described by the following functional form:

\[
P_s(t) = f_{osc}e^{-\lambda_T t} \cos(\gamma \mu B_{int} t) + (1 - f_{osc}) e^{-\lambda_L t}.
\]

Here \(B_{int}\) is the internal field on the muon stopping site, \(\gamma \mu = 2\pi \cdot 135.5\) MHz/T is the muon gyromagnetic ratio, and \(\lambda_T\) and \(\lambda_L\) are the transverse and the longitudinal exponential relaxation rates, respectively. The oscillating \((f_{osc})\) and non-oscillating \((1 - f_{osc})\) µSR signal fractions originate from the magnetic field components which are transversal to the initial muon-spin polarization and \(101\) crystallographic axis, and the non-precessing longitudinal field components \(\parallel P(0)\), respectively. Note that in powder sample, where all possible angles between \(B_{int}\) and \(P(0)\) are equally possible, \(f_{osc} \equiv 2/3\).

From the experimental data presented in Fig. 2b two important points emerge: (i) The spontaneous muon-spin precession with \(B_{int} \simeq 42.7\) mT is clearly detected on the ZF µSR time spectra. Consequently, the static magnetic order in FeSe crystal studied here is established below the Neél temperature \(T_N\) in agreement with the results of previous µSR experiments on FeSe powders.\(^\text{[23]}\) and recent Mössbauer experiments of high-quality single crystals.\(^\text{[23]}\) (ii) The value of the oscillatory component \(f_{osc}\) depends on the angle between \(P(0)\) and 101 axis of the crystal. \(f_{osc}\) for \(\theta = -10^\circ\) is obviously smaller than that for \(\theta = -100^\circ\). Consequently, by measuring \(f_{osc}\) as a function of \(\theta\), the direction of the internal field \(B_{int}\) on the muon stopping position might be determined.

The dependence of \(f_{osc}\) on \(\theta\) is shown in Fig. 3a. It has \(180^\circ\) periodicity with the maximum \((f_{max})\) and minimum \((f_{min})\) corresponding to \(\theta = 90^\circ + n \cdot 180^\circ\) and

![FIG. 1: The in-plane view of ten magnetic phases tested in the present study. The red and the blue arrows(circles) represent Fe spins. Green rectangles denote the in-plane magnetic unit cell. SVC1, SVC2, and CSDW phases preserves the tetragonal magnetic unit cells.](image)

![FIG. 2: (a) The schematic of the experiment. The rotation of cylindrically shaped FeSe crystal placed inside the pressure cell allows to change the angle \(\theta\) between the initial muon-spin polarization and 101 crystallographic axis. (b) ZF-µSR time spectra measured at \(T = 15\) K, \(p = 1.9\) GPa for \(\theta = -10^\circ\) (red symbols) and \(-100^\circ\) (black symbols). The solid lines are fits by using Eq. 1.](image)
et. al. in FeSe were previously calculated by Bendele at muon stopping sites were carried out. The muon sites information, calculations of corresponding internal fields as they presented in Fig. 1. To obtain more quantitative make any firm conclusion about other magnetic phases 'Collinear1' type of order do not allow us, however, to

The above obtained consistency between \( f_{\text{osc}}(\theta) \) and 'Collinear1' type of order do not allow us, however, to

\[
B_{\text{int},i} \simeq B_{\text{dip},i}, \quad (3)
\]

with \( B_{\text{dip}} \) at position \( r \) within the lattice unit cell calcu-

\[
B_{\text{dip}}(r) = \frac{\mu_0}{4\pi} \sum_{j, \beta} \frac{m_j^\beta}{R_i^3} \left( \frac{3R_i^\alpha R_j^\beta}{R_j^2} - \delta^{\alpha\beta} \right). \quad (4)
\]

Here \( R_j = r - r_j \), \( \alpha \) and \( \beta \) denote the vector components \( x, \ y, \) and \( z \), \( r_j \) is the position of \( j \)-th magnetic ion in the unit cell, and \( m_j^\beta \) is the corresponding magnetic moment. The summation is taken over a sufficiently large Lorentz sphere of radius \( R_L \). Note that Eq. 3 differs from its general form which includes also the so-called contact field term \( B_{\text{cont}} = A_{\text{cont}} \sum_{k=1}^N m_k \) \( (A_{\text{cont}} \) is the contact constant and the summation is made over the \( N \) nearest neighboring magnetic moments). \( B_{\text{dip}} \) becomes zero for all structures presented in Fig. 1 with the magnetic unit cell doubled in comparison with the chemical one along the crystallographic \( c \)-directions, and for all structures except both 'Bi-Collinear' ones for a case without doubling. The results of internal field calculations for various magnetic structures presented in Fig. 1 and \( m_{\text{Fe}} = 1 \mu_B \) are summarized in Table 1 in the Supplemental part. The part of the data denoted as 'II' corresponds to the case when the magnetic and the chemical unit cell have similar \( c \)-axis constants (the magnetic order along the \( c \)-axis is ferromagnetic). For the part denoted as 'II' the magnetic unit cell along the \( c \)-direction is doubled in comparison to the chemical one and the magnetic order along the \( c \)-axis becomes antiferromagnetic. The last column shows the value of \( m_{\text{Fe}} \) as calculated from the experimentally obtained \( B_{\text{int}} \simeq 0.0427 \) T (see Fig. 2 b).

Several magnetic phases could be excluded from the consideration based entirely on the dipolar field calcula-

\[
\theta (\text{degree})
\]

| Oscillating fraction, \( f_{\text{osc}} \) | \[
\begin{array}{|c|c|c|c|}
\hline
\theta (\text{degree}) & \text{FeSe, ZF, } T = 15 \text{ K, } p = 19 \text{ kBar} \\
\hline
\theta (\text{degree}) & \text{FeSe, ZF, } T = 15 \text{ K, } p = 19 \text{ kBar} \\
\hline
\end{array}
\]

\( B_{\text{int}} \parallel 100, 010, \) and \( 001 \) crystallographic directions (Fig. 3 b and the Supplemental part) is consistent to the chemical one and the magnetic order along the \( c \)-axis becomes antiferromagnetic. The last column shows the value of \( m_{\text{Fe}} \) as calculated from the experimentally obtained \( B_{\text{int}} \simeq 0.0427 \) T (see Fig. 2 b).
tions. The 'Collinear2' structure results in zero internal field on the muon stopping position. The 'SVC1' and 'SVC2' result in different $B_{\text{int}}$’s. Both these findings are inconsistent with the experimentally observed single finite internal field value (see Fig. 2 b and Refs. 7,8).

Values of $m_{\text{Fe}}$ for 'CSDW' structure were estimated to be 0.70 and 1.04 $\mu_B$ for the magnetic unit cell with and without doubling along the crystallographic $c$-direction, respectively. These values are bigger than the upper estimate of $m_{\text{Fe}} < 0.5 - 0.7 \mu_B$ set in neutron diffraction experiment 2.

Following the above discussion, our data are consistent with the internal field on the muon stopping position aligned along the crystallographic $c$-direction. Among the magnetic phases left, the 'Collinear1' phase, which was already proposed in Ref. 7, satisfy such criteria. In the magnetic phases left, the 'Collinear1' phase, which was already proposed in Ref. 7, satisfy such criteria. In the magnetic phases left, the 'Collinear1' phase, which was already proposed in Ref. 7, satisfy such criteria.

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