Superconductivity and magnetism in $Rb_{0.8}Fe_{1.6}Se_2$ under pressure

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High-pressure magnetization, structural, and ^{57}Fe Mössbauer studies were performed on superconducting $Rb_{0.8}Fe_{1.6}Se_{2.0}$ with $T_c = 32.4$ K. The gradual decrease of T_c with increasing pressure up to 5 GPa is followed by a step-like suppression of superconductivity at higher pressures. No structural phase transition in the Fe vacancy-ordered superstructure is observed in synchrotron x-ray diffraction (XRD) studies up to 15.6 GPa. The Mössbauer spectra above 5 GPa reveal the appearance of a new paramagnetic phase, exhibiting magnetic order below 80 K, coinciding with the irreversible disappearance of superconductivity. We interpret these changes as due to a pressure-induced diffusion of Rb ions between the two phases, responsible for the antiferromagnetism and superconductivity in $Rb_{0.8}Fe_{1.6}Se_{2.0}$.

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The family of high-temperature Fe-based superconductors attracts broad scientific interest due to a fascinating interplay of superconductivity and magnetism.[1] Recently, a new class of Fe-based superconductors, namely $A_xFe_{2-y}Se_2$ (A = K, Rb, Cs, and Tl) with T_c values above 30 K, has been discovered.[2] Neutron scattering, muon spin rotation (μSR), transport, magnetic, and calorimetric investigations have revealed a coexistence of superconductivity and antiferromagnetic (AFM) order with large static magnetic moments and Nèel temperatures around 500 K.[3] This coexistence has been questioned by transmission-electron microscopy reporting on a phase separation in the potassium intercalated compound.[4] Subsequent high-resolution nanofocused x-ray diffraction studies provided further experimental evidence that magnetism and superconductivity occur in spatially separated regions,[5] which is also supported by recent Mössbauer spectroscopy[6] and optical measurements.[7] The real-space structure of these two different phases has been suggested to correspond to a layered arrangement of AFM and superconducting sheets stacked along the c axis[8] with the stoichiometry of the superconducting phase corresponding to $Rb_{0.3}Fe_2Se_2$.[9]

The iron-based superconductors exhibit a pronounced dependence of the superconducting transition temperature on pressure: T_c of the simplest Fe-based superconductor FeSe amounts to 8 K at ambient pressure and reaches 37 K around 8 GPa.[10,11] However, recent studies of $K_{0.8}Fe_{1.7}Se_2$,[12–14] $Rb_{0.8}Fe_2Se_2$,[15] and $Cs_{0.8}Fe_2Se_2$[13,16] have shown that T_c is only slightly increased by pressure to a maximum value of 33 K and superconductivity is completely suppressed by further increasing pressures up to 9 GPa. The origin of the suppression of superconductivity in $A_xFe_{2-y}Se_2$ systems with pressure is still an open question. Here we present the results of magnetization, synchrotron x-ray diffraction, and Mössbauer studies of $Rb_{0.8}Fe_{1.6}Se_2$ as a function of pressure, which indicate that the existence of superconducting and AFM phases are either directly related to each other or bound to a third parameter susceptible to pressure.

Single crystals of $Rb_{0.8}Fe_{1.6}Se_2$ were grown employing the Bridgman method. Details of preparation and sample characterization were published elsewhere.[17] The single-crystal quality of the grown samples was confirmed by x-ray diffraction. The samples exhibit an onset of the superconducting transition at 32.4 K. For high pressure studies, loading of the high pressure cells was performed in a glove box in an atmosphere of pure nitrogen containing less than 0.1 ppm of oxygen and water to avoid sample decomposition.

Magnetic susceptibility measurements were performed using a high-pressure cell made from a nonmagnetic hardened Cu-Ti alloy, equipped with SiC anvils with flats of 0.8 mm in diameter and CuBe gaskets with sample holes 0.3 mm in diameter. The cell allows quasihydrostatic pressures up to 12 GPa.[18] The hole was filled with a single crystalline $Rb_{0.8}Fe_{1.6}Se_2$ flake and Daphne oil as a pressure transmitting medium. The pressure was measured via ruby fluorescence from small ruby chips distributed over the sample. The pressure inhomogeneity was determined to be 0.5 GPa across the sample at the highest pressure.

High-pressure x-ray diffraction experiments were performed at room temperature on the beamline 01C2 of the NSRRC synchrotron facility, Taiwan. Grained samples of $Rb_{0.8}Fe_{1.6}Se_2$, consisting of preferentially oriented small single-crystalline flakes, were loaded in a diamond-anvil cell with culets of 450 μm in diameter and a tungsten gasket with a sample chamber of 150 μm in diameter. Silicon oil was used as pressure-transmitting medium. The x-ray beam ($\lambda = 0.496$ Å) was collimated to 100 μm, with the image plate detector set perpendicular to the beam. Cerium dioxide was used as external standard to determine the beam center,

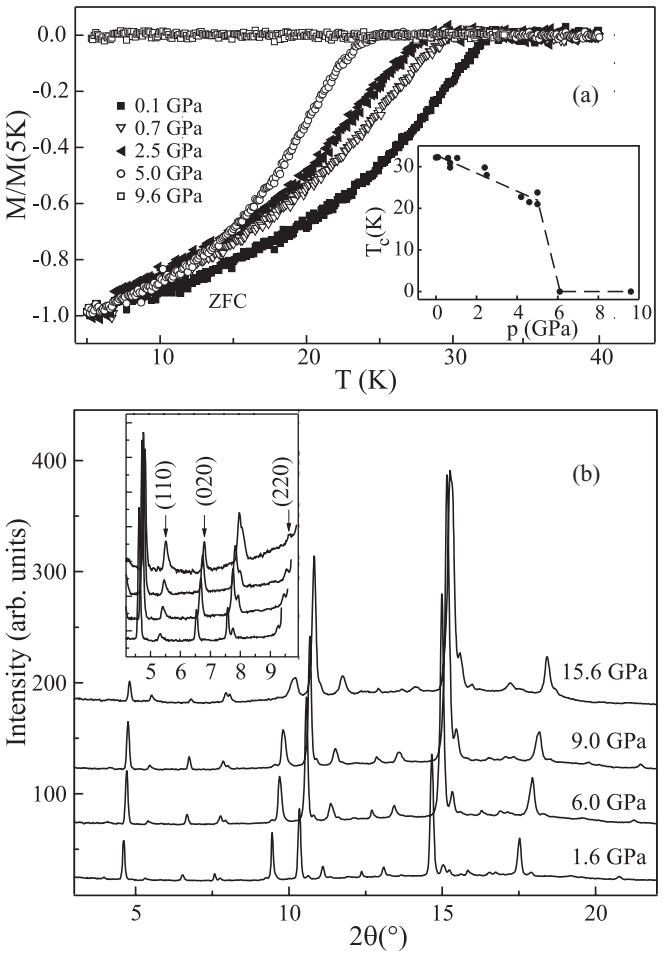

FIG. 1. (a) Temperature dependence of the ZFC magnetization M of $Rb_{0.8}Fe_{1.6}Se_2$ at different pressures measured in a magnetic field of 20 Oe, the magnetization was normalized to the values at 5 K. Inset: variation of the superconducting transition temperature T_c under pressure. (b) Powder diffraction patterns of $Rb_{0.8}Fe_{1.6}Se_2$ at different pressures. Inset: the superstructure reflections (110), (020), and (220) demonstrate the $\sqrt{5} \times \sqrt{5}$ superstructure persist up to the highest pressure of 15.6 GPa.

sample-to-detector distance, and tilting angle of the image plate. Collected full-circle powder patterns were processed with FIT2D software.

^{57}Fe-Mössbauer spectra were using a ^{57}Co(Rh) point source with an active spot diameter of 0.5 mm. Grained $Rb_{0.8}Fe_{1.6}Se_2$ samples were prepared with enriched ^{57}Fe (20%) and measured in a diamond-anvil pressure cell with silicon oil as a pressure-transmitting medium.[10] Due to the granular character of the sample (like in the XRD studies), the ^{57}Fe spectra exhibit strong texture effects which were carefully taken into account in the analysis of the Mössbauer spectra.[6] The isomer shifts are quoted relative to that of α-Fe at 295 K.

Figure 1(a) shows the temperature dependence of the zero-field cooled (ZFC) magnetization of $Rb_{0.8}Fe_{1.6}Se_2$ as a function of pressure. T_c was determined from the intersection of two extrapolated straight lines drawn through the data points in the normal state and the steepest part in the superconducting state. Similarly to observations in the K- and Cs-intercalated superconductors,[12–14,16] T_c of $Rb_{0.8}Fe_{1.6}Se_2$ shows a moderate decrease with a rate of -2.1 K/GPa up to 5 GPa. Then, a sudden suppression of the diamagnetic ZFC signal occurs at pressures close to 6 GPa and T_c drops to zero. These results are in excellent agreement with recent pressure-dependent electrical resistivity studies of $Rb_{0.8}Fe_2Se_2$, especially with the steep decrease of T_c from 15.5 K at 5 GPa to zero at 5.6 GPa.[15] It resembles also the pressure behavior of T_c in the related $Cs_{0.8}Fe_2Se_2$ compound.[16] In $K_{0.8}Fe_{1.7}Se_2$ and $K_{0.8}Fe_{1.78}Se_2$, however, a more continuous decrease of T_c up to critical pressures around 9 GPa is reported.[12] The suppression of superconductivity in the present $Rb_{0.8}Fe_{1.6}Se_2$ sample with pressure is found to be irreversible: no recovery of the diamagnetic signal was observed on the release of pressure from 10 GPa to ambient pressure. This behavior is different to the observations for $K_{0.8}Fe_{1.7}Se_2$, where superconductivity was reported to reappear after release of pressure.[12]

The x-ray diffraction patterns shown in Fig. 2(b) reveal the absence of any structural phase transitions in the magnetic majority phase up to pressures of 15.6 GPa. Although a rigorous structural refinement was not performed due to a highly textured sample with different orientations of the flakes, the superstructure reflections (110), (020), and (220) corresponding to the $I4/m$ structure persist up to the highest pressures indicating the stability of the vacancy-ordered $\sqrt{5} \times \sqrt{5}$ superstructure far above the suppression of superconductivity. The present findings are in excellent agreement with a recent XRD study of Svitlyk *et al.*, where for $Rb_{0.85}Fe_{2-y}Se_2$ the pressure dependence of lattice parameters and of the superstructure reflections were studied in detail up to ~11.0 GPa.[19] We therefore conclude that the suppression of superconductivity in $Rb_{0.8}Fe_{1.6}Se_2$ is not connected with a structural phase transition in the magnetic majority phase. This is in contrast to the assumptions in Ref. 12, where the observed suppression of superconductivity was attributed to the loss of the superstructure reflections in the magnetic phase without considering that magnetism and superconductivity are occurring in $A_xFe_{2-y}Se_2$ systems in strictly separated phases.[4–6,9] The pressure-induced suppression of superconductivity in $Rb_{0.8}Fe_{1.6}Se_2$ is also not caused by a structural phase transition in the minority phase, as observed in superconducting FeSe,[10] as evidenced in the corresponding Mössbauer data presented in the following.

The left panel of Fig. 2 shows pressure-dependent Mössbauer spectra of $Rb_{0.8}Fe_{1.6}Se_2$, recorded at room temperature. At pressures below 5.2 GPa, the spectra consist of a magnetic sextet which corresponds to the magnetically ordered component with a $\sqrt{5} \times \sqrt{5}$ superstructure (denoted as phase **I**) and a paramagnetic (PM) doublet (phase **II**) with relative fractions of 88(1)% and 12(1)%, respectively, exactly the same as observed at ambient pressure.[6] The appearance of these two components is attributed to two different phases and associated with the majority AFM phase and the minority metallic/superconducting phase.[5,6] The derived hyperfine parameters for the magnetic hyperfine field H_{hf}, the isomer shift IS, and the quadrupole splitting QS at the lowest pressure of 2.5 GPa, H_{hf}(**I**) = 252.2(7) kOe, IS(**I**) = 0.53(1) mm/s, QS(**I**) = 1.11(3) mm/s and IS(**II**) = 0.55(2) mm/s, QS(**II**) = $-$0.24(2) mm/s, are close to those at ambient pressure.[6]

Remarkable changes in the Mössbauer spectra are observed starting from 5.2 GPa, where an additional new PM doublet

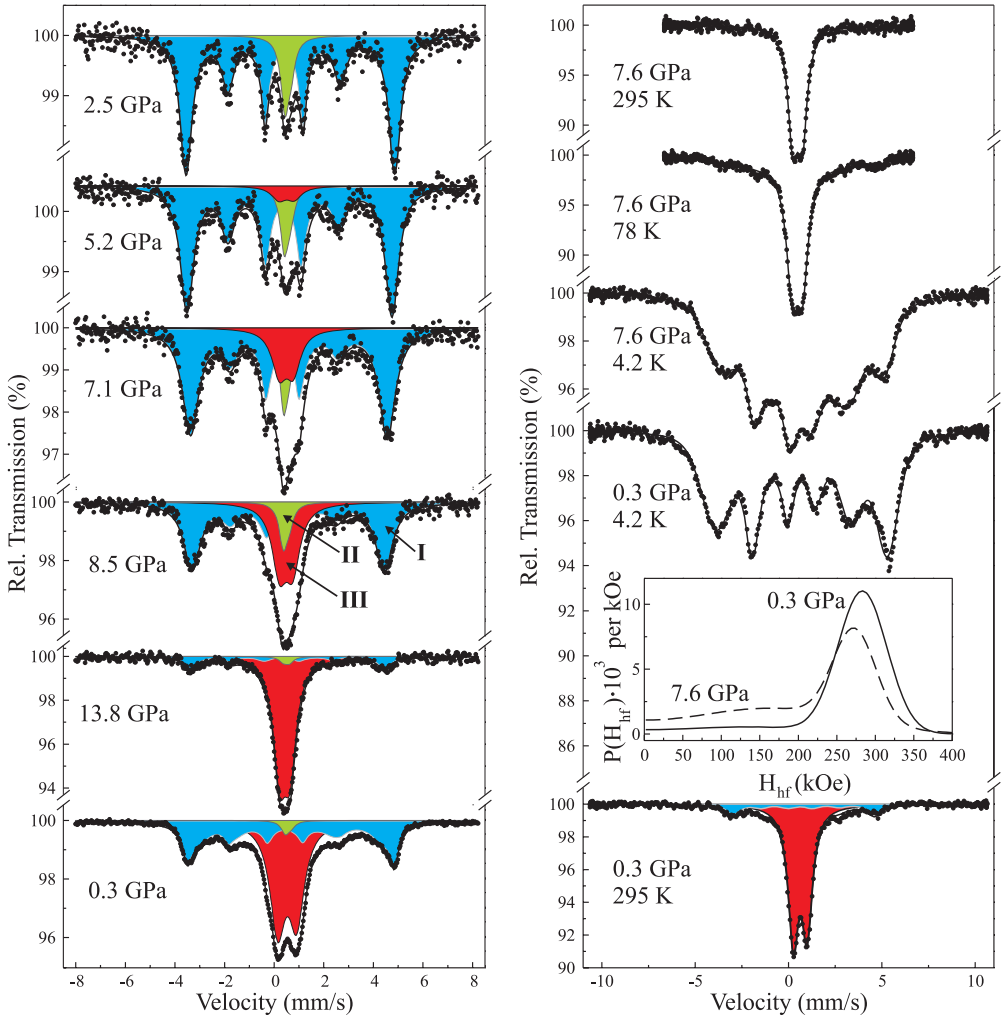

FIG. 2. (Color online) Left panel: Room temperature ^{57}Fe-Mössbauer spectra of $Rb_{0.8}Fe_{1.6}Se_2$ measured at different pressures. Subspectra of the magnetic Fe sites are marked in blue (AFM phase **I**), subspectra of nonmagnetic Fe sites (phase **II**) are shown in green. At 5.2 GPa a new PM phase **III** (doublet shown in red) emerges from the AFM phase **I**. Right panel: Second run of Mössbauer measurements of $Rb_{0.8}Fe_{1.6}Se_2$ performed at different pressures and temperatures. Sequence of measurements is presented from the top to the bottom. Inset: distribution function $P(H_{hf})$ of magnetic hyperfine fields on Fe atoms in $Rb_{0.8}Fe_{1.6}Se_2$ measured at $p = 7.6$ GPa (dashed line) and $p = 0.3$ GPa (solid line) at $T = 4.2$ K. The Mössbauer spectrum measured at $p = 0.3$ GPa and $T = 295$ K is dominated by the PM doublet shown in red. Subspectrum of the magnetic Fe sites is marked in blue.

appears. The corresponding intensity ratios reveal that this spectral component emerges mostly from the AFM sextet, indicating a partial transformation of the AFM phase into a PM state. The hyperfine parameters of this new PM phase (denoted as phase **III**) at $p = 6.5$ GPa are: IS(**III**) = 0.50(2) mm/s and QS(**III**) = 0.64(4) mm/s. They are quite different from those observed in the PM phase **II,** but close to the corresponding parameters of the still dominant AFM phase **I** at 6.5 GPa: IS(**I**) = 0.50(1) mm/s, QS(**I**) = 0.85(4) mm/s. This indicates that in the new PM phase **III** the local crystal arrangement of Fe atoms, as well as their electronic properties, namely an Fe^{2+} high-spin state with orbital contributions to the electric field gradient as established in Ref. 6, are similar to those in the AFM phase. The relative fraction of the new PM phase **III** progressively increases with increasing pressure and attains 80(1)% of the total spectral area at 13.8 GPa [see Fig. 3(a)]. The transformation of the AFM phase **I** into the PM phase **III** is not complete, and 17(1)% of phase **I** can still be observed at $p = 13.8$ GPa. The fraction of the PM phase **II** decreases similarly to phase **I** and amounts to 3(1)% at 13.8 GPa. The observed pressure-induced magnetic transition is in part irreversible. The Mössbauer spectrum measured after release of pressure to $p = 0.3$ GPa is dominated by the new PM phase **III** with 53(1)% intensity, while the AFM phase **I** recovers with broadened spectral features and relative intensity of 45(2)%. The component **II** with intensity below 3% can hardly be detected.[20]

The pressure dependence of the magnetic hyperfine field H_{hf}(**I**) in the AFM phase **I** is presented in Fig. 3(b). H_{hf}(**I**) remains almost unchanged up to 4.2 GPa, but the clear decrease of H_{hf}(**I**) from 249(1) kOe at 5.2 GPa to 235(1) kOe at 8.5 GPa points to a significant change of the local magnetic and electronic properties at the Fe sites in the $\sqrt{5} \times \sqrt{5}$ superstructure. The latter is also reflected in a concomitant

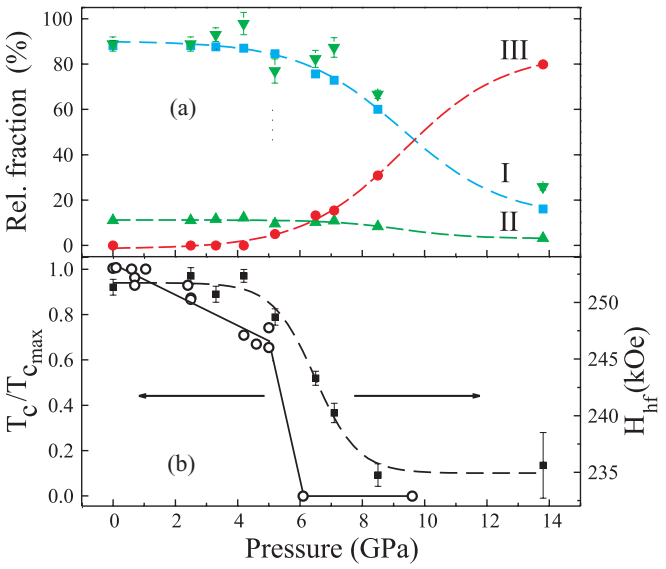

FIG. 3. (Color online) (a) Pressure dependence of the relative fractions of the PM component **II** (up triangles), the PM component **III** (solid circles), and the AFM fraction **I** (squares). Down triangles result from rescaling the amount of the PM fraction **II**. This procedure makes evident that under pressure the PM phase **II** behaves similarly to the AFM phase **I**, and that a new component **III** develops at the expense of both phases **I** and **II**. (b) Left scale: normalized variation of T_c/T_{cmax} (open circles) in $Rb_{0.8}Fe_{1.6}Se_2$. Right scale: pressure dependence of the magnetic hyperfine field H_{hf}(**I**) in the AFM phase **I**. The pressure dependence of the phase fractions and of H_{hf} is described by sigmoidal curves (dashed lines).

decrease of QS(**I**) = 1.04(4) mm/s at 5.2 GPa to 0.84(4) mm/s at 8.5 GPa. At higher pressures, the variation of H_{hf}(**I**) is again very small: H_{hf}(**I**) = 236(3) kOe at 13.8 GPa. Of specific interest are the values of the respective hyperfine parameters after release of pressure to 0.3 GPa: H_{hf}(**I**) = 240(4) kOe, which is almost identical to the value observed at 13.8 GPa, while the value of QS(**I**) = 1.13(3) mm/s corresponds to the initial ambient pressure value. A similar trend is observed for the new PM phase **III,** where QS(**III**) increased from 0.42(1) mm/s at 13.8 GPa to 0.77(1) mm/s at 0.3 GPa.

The most prominent feature presented in Fig. 3 is the clear relation between the disappearance of superconductivity above 5 GPa and the onset of a transformation of the AFM phase **I** into a new PM phase **III**, concomitant with a marked reduction of H_{hf}(**I**), pointing to a change in the magnetic properties. The pressure dependence of the different phase fractions and H_{hf}(**I**) could be well described by sigmoidal curves (Fig. 3), which supports a scenario of nucleation-like phase transformations and confirms that the magnetic transformation starts already in the SC state but is close to the breakdown of superconductivity. This fact is especially remarkable in view of the recently established phase separation in alkali-intercalated magnetic superconductors $A_xFe_{2-y}Se_2$.[5–9] According to this concept, only the minority fraction is metallic and superconducting, whereas the major fraction is antiferromagnetic and insulating. According to our recent Mössbauer studies,[6] the superconducting phase (PM component **II**) has hyperfine parameters close to those observed in FeSe. Therefore, one can expect that a similar scenario of suppression of the superconductivity under pressure associated with a structural phase transition occurs.[10] However, as we found in the present investigation, the relatively abrupt and irreversible suppression of superconductivity is not accompanied by a structural phase transition in the dominant $\sqrt{5} \times \sqrt{5}$ phase **I** and also not with strong spectral changes of the minority phase **II**. The present data demonstrate that the suppression of superconductivity in $Rb_{0.8}Fe_{1.6}Se_2$ coincides with the onset of a sluggish transformation of parts of the dominant AFM phase into a new PM phase and is also connected with the change of the local magnetic and electronic properties of the AFM phase. Since also the minority phase **II**, responsible for superconductivity, is reduced by the same relative amount (see Fig. 3), one has to look for the responsible mechanism, reflecting also the irreversibility of both the suppression of superconductivity in phase **II** and the formation of the new phase **III**. Of actual interest are also the magnetic properties of this new phase **III**. For this reason a second series of high-pressure Mössbauer spectra of the same sample were recorded, now also a low temperatures.

The Mössbauer spectrum recorded first at $p = 7.6$ GPa and room temperature clearly shows only phase **III**, while phases **I** and **II** are not detectable (right panel of Fig. 2). The spectrum measured at $T = 78$ K exhibits beside the dominant phase **III** an additional subspectrum with a broadened magnetic splitting, indicating the onset of magnetic order. Further cooling to 4.2 K reveals a full transformation of the paramagnetic phase **III** into a broad static magnetic spectrum. Fitting this spectrum based on a model with a distribution of hyperfine parameters provides the distribution function $P(H_{hf})$ of magnetic hyperfine fields with the main peak located at $H_{hf} = 274(2)$ kOe (inset of Fig. 2, right panel). A remarkable feature of the distribution function at 7.6 GPa is a plateau below $H_{hf} \leqslant 200$ kOe, indicating that part of the Fe moments are reduced by pressure. The release of pressure leads to essential recovery of the Fe moments, as demonstrated by the Mössbauer spectrum measured at $T = 4.2$ K and $p = 0.3$ GPa, which can be well fitted with a sharper distribution function centered at $\langle H_{hf} \rangle = 284(2)$ kOe. This value and also the average quadrupole splitting $\langle QS \rangle = 1.1(1)$ mm/s, almost identical to that of the initial sample at ambient pressure,[6] signify the close relation between the pressure-modified magnetic phase with random order and the original well-ordered magnetic phase **I**. It is important to note that the paramagnetic fraction **II** is completely absent in this well-resolved spectrum. The room temperature Mössbauer spectrum measured at the end of the second pressure cycle at $p = 0.3$ GPa exhibits 85(1)% of the PM phase **III** with QS(**III**) = 0.74(1) mm/s. The residual fraction of the broad magnetic subspectrum with $H_{hf} = 226(2)$ kOe is 15(1)%, significantly less than the corresponding amount of phase **I** remaining at the end of the first pressure cycle (see Fig. 2). This indicates that the pressure-induced changes in the magnetic properties of $Rb_{0.8}Fe_{1.6}Se_2$ are accumulated during both pressure runs.

The observed irreversibility in the superconducting and magnetic properties in $Rb_{0.8}Fe_{1.6}Se_2$ induced by pressure suggests some irreversible local structural changes without a global change of the crystal symmetry, especially of the $\sqrt{5} \times \sqrt{5}$ superstructure. Remarkably, the magnetic and superconducting properties of the AFM (phase **I**) and PM

(phase **II**) mixture stay intact up to pressures of 5 GPa. The suppression of superconductivity with further increase of pressure is connected with the onset of the transformation of parts of the AFM phase **I** and the minority phase **II**, associated with the superconductivity, into the PM phase **III**. The Mössbauer spectra from the second pressure cycle indicate a complete and irreversible disappearance of this minority fraction **II.** These spectra also show that the average values $\langle H_{hf}\rangle$ and $\langle QS\rangle$ are after release of pressure close to the corresponding values of the AFM majority phase before application of pressure. This indicates that on the average the local magnetic moments of Fe atoms and their local surroundings are conserved. However, the strong broadening of the spectral lines indicates that pressure induces local disorder and thus diminishes the electronic and magnetic differences of both phases. Therefore we suppose that the pressure-induced disorder is caused by short-range diffusion of Rb ions within the layers above a threshold pressure of 5 GPa. Such a diffusion process of the Rb ions seems to be thermodynamically much more probable than that of Fe ions, as documented by the preservation of the $\sqrt{5} \times \sqrt{5}$ superstructure up to 15.6 GPa. In this context, one should consider the enormous difference in the Rb layer density between the magnetic $Rb_{0.8}Fe_{1.6}Se_2$ phase and the superconducting $Rb_{0.3}Fe_2Se_2$ phase,[9] intimately connected with an enormous amount of phase boundaries due to the filamentary shape of the minority phase.[4,5,7] The observed sharp disappearance of the superconductivity above 5 GPa might be also attributed to the fact that the new PM phase **III** is growing in the phase boundaries between the phases **I** and **II** and exhibiting metallic behavior with conduction electrons penetrating into the superconducting phase **II**.

Indeed, a pressure-induced change from semiconducting towards metallic behavior is reported in Ref. 12, coinciding with the disappearance of superconductivity. Joint conduction bands of the new phase **III**, which orders magnetically at low temperature, and of the metallic phase **II** would suppress superconductivity, especially if one considers the large values of the local magnetic moment of Fe ions (approximately 3 μ_B) and the corresponding huge exchange/transferred fields far exceeding second critical fields. The same holds, if the still dominant AFM phase would became metallic at pressures above 5 GPa. Apparently, any incomplete compensation of these moments due to their random magnetic order could destroy the neighboring superconducting state, as proposed in Ref. 21.

The present Mössbauer experiments demonstrate that pressure above 5 GPa causes irreversible local changes in $Rb_{0.8}Fe_{1.6}Se_2$ presumably due to Rb diffusion between the two phases. In this respect, one can suppose that the new PM component **III** observed here is related to the paramagnetic phase in $A_xFe_{2-y}Se_2$ systems (A = K, $Tl_{0.6}Rb_{0.4}$) occurring above the suppression of superconductivity and below the reentrant superconductivity at higher pressures reported in Ref. 22. The observed decrease of the magnetic moments under pressure, as reflected by their hyperfine fields (Fig. 2, inset), could tend to a nonmagnetic ground state at higher pressures.

In summary, our pressure experiments show that the dominating AFM phase and the superconducting minority phase in $Rb_{0.8}Fe_{1.6}Se_2$ are reduced above 5 GPa with increasing pressure on the expense of a new paramagnetic phase, appearing concomitantly with the suppression of superconductivity. Here we propose as a possible reason for the appearance of the new phase as well as for the suppression of superconductivity a pressure-assisted diffusion of Rb atoms, which irreversibly alters the electronic and magnetic properties of both phases. The growth of the new PM phase might be associated with the reentrant superconductivity observed at higher pressure in superconducting $A_xFe_{2-y}Se_2$ systems.[22]

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