High-Pressure Single-Crystal Neutron Scattering Study of Magnetic and Fe Vacancy Orders in (Tl,Rb)$_2$Fe$_4$Se$_5$ Superconductor

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The magnetic and iron vacancy orders in superconducting (Tl,Rb)$_2$Fe$_4$Se$_5$ single-crystals are investigated by using a high-pressure neutron diffraction technique. Similar to the temperature effect, the block antiferromagnetic order gradually decreases upon increasing pressure while the Fe vacancy superstructural order remains intact before its precipitous disappearance at the critical pressure $P_c = 8.3$ GPa. Combined with previously determined $P_c$ for superconductivity, our phase diagram under pressure reveals the concurrence of the block AFM order, the $\sqrt{5} \times \sqrt{5}$ iron vacancy order and superconductivity for the 245 superconductor. A synthesis of current experimental data in a coherent physical picture is attempted.

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The recently discovered metal-intercalated iron selenide superconductors $A_2$Fe$_4$Se$_5$ ($A=$K, Cs, Tl-K, Rb, Tl-Rb) (245) compounds, with $T_c \sim 30$ K, have attracted much interest. $^1,2$ A high transition-temperature ($T_N \approx 470$–560 K) and large magnetic moment ($3.3\mu_B$/Fe) block antiferromagnetic (AFM) order exists in the superconducting samples. $^3-5$ Magnetic order-parameter experiences an anomaly when $T_c$ is approached. $^4,5$ The superconductors crystallize with a highly ordered $\sqrt{5} \times \sqrt{5}$ superstructure, in which the Fe1 site of the $I4/m$ structure is only a few percents occupied and the Fe2 site is fully occupied. $^1,6$ The non-superconducting samples at low-$T$ also crystallize in the $I4/m$ structure, while both Fe sites are fractionally occupied. $^7,8$ since the numbers of the Fe vacancies in the samples and the vacant sites in the $\sqrt{5} \times \sqrt{5}$ pattern are mismatched. The partially ordered $\sqrt{5} \times \sqrt{5}$ vacancy order becomes one of three competing phases for temperature below room temperature up to $\sim 500$ K, namely, these phases are phase-separated and in the miscibility gap under the ambient condition. $^6,9$

Close to the miscibility gap, it is unsurprising that the nonstoichiometric 245 superconductors often contain several phases of different space-group symmetries. It has been a complex and controversial issue to determine the sample composition of the superconductors. The KFe$_{1.5}$Se$_2$ (234) of the orthorhombic Fe vacancy order has been proposed as the parent compound. $^10$ However, this phase is not even the ground state for KFe$_{1.5}$Se$_2$, and a partially ordered $\sqrt{5} \times \sqrt{5}$ vacancy superlattice is more stable at low temperature. $^9$ The KFe$_2$Se$_2$ (122) of $I4/mmm$ symmetry has also been proposed as the superconducting phase. $^11$ However, its existence in films grown by the molecular beam epitaxy method likely requires charge transfer with the substrate, and there is no trace of its existence in bulk superconducting samples. $^11,12$ Detected in the 245 superconductors is the alkaline metal deficient $A_x$Fe$_2$Se$_2$ ($x \sim 0.3-0.6$) phase embedded in $\sqrt{5} \times \sqrt{5}$ iron vacancy ordered superstructure, $12-14$ forming various microstructure patterns in the plane $^{15,16}$ or the heterostructure along the $c$-axis $^{9,14,17}$ depending on the sample preparation procedures. The average sample compositions of these superconductors are consistent with the phase diagram in Ref. $^8$. The question is what role the $A_x$Fe$_2$Se$_2$ ($x \sim 0.3-0.6$), the $\sqrt{5} \times \sqrt{5}$ superstructure and the AFM order play in the 245 superconductors.

High pressure adds an additional dimension to the complex composition phase-diagram of 245 superconductors, $^8$ offering a ‘clean’ way to investigate the relation among various phases. $^{18,19}$ The value of $T_c$ has been suppressed to zero at critical pressure $P_c \approx 6$ GPa for $A=$Rb, $^{19,20}$ 8 GPa for $A=$Cs. $^{21}$

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and 9 GPa for $A$–K and Tl–Rb superconductors.\cite{22} In the latter study, superconductivity of a higher $T_c = 48$ K is reported to re-emerge between 11 and 13 GPa.\cite{22} High-pressure x-ray powder diffraction experiments have been performed at room temperature, however, differing results have been reported: the $I4/m$ phase is replaced by an $I4/mmm$ phase at $P_c$ in one study,\cite{18} while the $I4/m$ phase remains up to 15.6 GPa well above $P_c$ in the other.\cite{20} In a high-pressure Mössbauer spectroscopic study, it has been concluded that the $A_1Fe_2Se_2$ phase in the sample remains intact up to 13.8 GPa. What has changed is the AFM order on the $\sqrt{5} \times \sqrt{5}$ superstructure, which is partially replaced by a new paramagnetic phase after the superconductivity is suppressed at the critical pressure $P_c$.\cite{20} Therefore, no consistent relationship has been established between the superconductivity and either the $A_1Fe_2Se_2$ phase, the $\sqrt{5} \times \sqrt{5}$ superstructure, or the AFM order in current high pressure studies.

In this Letter, we report a high-pressure single-crystal neutron diffraction study of the $(Tl,Rb)_2Fe_4Se_8$ superconductor up to 9 GPa, measuring simultaneously the AFM order and the crystal structure. The $\sqrt{5} \times \sqrt{5}$ vacancy order persists under pressure until its precipitous destruction near $P_c \approx 3.8$ GPa when the AFM order parameter is reduced progressively to zero. The disappearance of the magnetic and structural orders coincides with the suppression of superconductivity, revealing the importance of the block AFM order and the $I4/m$ vacancy order in stabilizing superconductivity in the 245 superconductor.

![Fig. 1. (Color online) Schematic diagram of the single-crystal neutron diffraction experiments at SNAP. The semi-white neutron beam reaches the sample inside the anvil cell and is diffracted into the position sensitive detectors.](image)

![Fig. 2. (Color online) (a) Magnetic (1,0,1) and (b) vacancy (1,2,1) peaks at selected pressures at 365 K. (c) Pressure dependence of the integrated intensity of the vacancy and magnetic peaks at 297 K. (d) The lattice parameters of the $I4/m$ structure as a function of pressure at 297 K.](image)

Figures 2(a) and 2(b) show the diffraction peak profile at selected pressures for the magnetic (1,0,1) and the vacancy superlattice (1,2,1) reflections at 365 K. Both peaks are smoothly suppressed in intensity without splitting or appreciable broadening. Fitting of the integrated intensities of the peaks as a function of pressure yields critical pressure $P_{c}(365$ K) $= 5.3(2)$ GPa for the AFM order and $P_{S}(365$ K) $= 5.9(2)$ GPa for the $\sqrt{5} \times \sqrt{5}$ Fe vacancy superstructure. Figures 3(a) and 3(b) show the contour plots of the diffraction data at 365 K. Clearly the magnetic
peak disappears at a lower pressure than the vacancy superlattice peak. Figures 3(d) and 3(e) present the contour plots for the same two Bragg peaks at 297 K. Both resolution-limited peaks indicate that the vacancy and magnetic orders remain long-ranged before their suppression by high pressure.

In Figs. 3(b) and 3(e), the (1,2,1) peak of the Fe vacancy order is suppressed more abruptly than the magnetic (1,0,1) peak in Figs. 3(a) and 3(d). Figure 2(c) shows the integrated intensity of the two peaks at 297 K, respectively. Compared to the gradual suppression of the AFM order, the Fe vacancy order exhibits a precipitous drop at \( P_c \approx 8.3 \) GPa. Such a behavior closely resembles the \( T \)-dependence of the two long-range orders at the ambient pressure observed in previous neutron diffraction studies.\(^\text{[4,5]}\)

Therefore, at both ambient and high pressures, the order parameter of the \( \sqrt{5} \times \sqrt{5} \) vacancy structure reaches the saturated value when there grows the block AFM order.

Figure 3(f) shows the nuclear (3,1,2) reflection which survives in the \( I4/mmm \) structure after the suppression of the \( \sqrt{5} \times \sqrt{5} \) superstructure under pressure. The lack of peak splitting and the absence of additional reflection in the pressure tuning between the \( I4/mmm \) and \( I4/m \) structures differ markedly from what have been observed in the temperature tuning of phase-separated samples.\(^\text{[22]}\)

There is an inflection in the peak position at \( P_c \) in Figs. 3(f), indicating lattice parameter relaxation after the sample experiences the pressure-induced \( I4/m \) to \( I4/mmm \) structural transition. The lattice parameters \( a \) and \( c \) from least-square refinements from a number of Bragg reflections including (1,0,1), (1,2,1), (3,1,2), and (5,0,3) at 297 K are shown in Fig. 2(d) as a function of pressure. Both shrink smoothly and do not exhibit any anomalies below \( P_c \) in the vacancy ordered state. Within the Fe vacancy-ordered \( I4/m \) phase, \((Tl,Rb)_2Fe_4Se_5\) exhibits moderate anisotropic compressibility: the lattice parameter \( c \) is reduced by about 9.3% and the in-plane lattice parameter \( a \) decreases by 5% at 7.5 GPa. This contrasts with the result found in \( \text{CaFe}_2\text{As}_2 \), where the \( c \)-axis collapses with the application of merely 0.4 GPa\(^\text{[26]}\) and the pressure-induced structure transition destroys the AFM order without introducing superconductivity.\(^\text{[26,27]}\)

Sample pressure was monitored \textit{in situ} by measuring the \( d \)-spacing of the lead (2,0,0) Bragg peak. Figure 3(c) shows an example of its clear pressure evolution. After releasing the pressure from above \( P_c \) back to zero at 297 K, all characteristic reflections associated with the magnetic and vacancy orders in the \( I4/m \) phase reappear. However, the intensity of the magnetic peak (1,0,1) is only 15% of the original value at ambient pressure, although the intensity of the vacancy order peak (1,2,1) and the main nuclear peak (3,1,2) are fully recovered. This indicates that the \( \sqrt{5} \times \sqrt{5} \) vacancy order can sustain the pressure-cycling while the AFM order cannot recover its original fully ordered state in the constant temperature cycle.

Fig. 3. (Color online) Contour plots of Bragg intensity of the magnetic peak (1,0,1) at (a) 365 K and (d) 297 K; the vacancy superlattice peak (1,2,1) at (b) 365 K and (c) 297 K; (f) the main nuclear Bragg peak (3,1,2) at 297 K. (c) The (200) Bragg peak of Pb inside the pressure anvil cell at 365 K. The weak pressure-independent intensity at \( d \)-spacing 2.51 Å is the diffraction from the pressure cell.

Fig. 4. (Color online) Pressure-temperature phase diagram of \((Tl,Rb)_2Fe_4Se_5\). Red circles denote the transition to the Fe \( \sqrt{5} \times \sqrt{5} \) vacancy order, and blue squares denote the block AFM order. The brown pentagon from the magnetization measurement denotes the superconducting transition at \( P = 0 \). \( T_c \), where both \( T_N \) and \( T_S \) are suppresed continuously by pressure, and the vacancy and AFM orders are absent at 9 GPa. The critical pressure coincides well with the pressure where the superconductivity was suppressed in the high-pressure resistivity and ac magnetic susceptibility works on \((Tl,Rb)_2Fe_4Se_5\).\(^\text{[22]}\) This phase diagram provides direct evidence indicating an intimate connection of the superconductivity with the block AFM order developing on the iron-vacancy superlattice in the 245 super-
conductor. While $T_S$ and $T_N$ track each other (Fig. 4), the superconducting transition temperature $T_c$ tracks the magnetic (1,0,1) Bragg intensity more closely than the superlattice (1,2,1) Bragg intensity under pressure.

Ksenofontov et al. reported that both the $A_xFe_2Se_2$ phase and the vacancy ordered $I4/m$ phase survive well above $P_c$, and there is no structural transition up to 15.6 GPa. The block AFM order only starts to slowly decrease above $P_c$ in their high-pressure studies. However, our results clearly show that the $\sqrt{5} \times \sqrt{5}$ Fe vacancy order and the AFM order are completely suppressed above $P_c$. The result for the vacancy superstructure order by Guo et al. is consistent with ours after the poor counting statistics in their high-pressure powder x-ray diffraction data is taken into account. [18] Thus there was likely either an error in the pressure calibration or too large a pressure gradient in the work of Ksenofontov et al. [20]

The nonsuperconducting samples, on the other hand, contain imperfect Fe vacancy order, which introduces substantial site disorder. The similar property has been shown in the Fe$_{1.4}$Se$_2$ films, in which random Fe vacancies serve as spin carrying scatterers, also shows the same microscopic behavior that is destructive to the local superconducting gap. [11]

Additionally, the $\sqrt{5} \times \sqrt{5}$ vacancy order with its associated AFM order is substantially more stable with the magnetostuctural energy gain through the formation of the Fe tetramers. It is thus conceivable that the few percent Fe at the minority Fe1 site in the average $I4/m$ structure of the 245 superconductors instead of being randomly distributed, aggregates to form nanoscale phase separation to save energy in breaking up the tetramers. Close interaction between the superconducting and AFM order parameters is therefore expected. When the excess Fe at the Fe1 sites aggregate on the $\sqrt{5} \times \sqrt{5}$ superlattice of fully ordered Fe2 sites, site disorder is minimized and thus is the pair-breaking electron scattering. The local composition inside the aggregation is $A_{0.4}Fe_2Se_2$ and outside it is $A_{0.6}Fe_{1.6}Se_2$, which average to an $A_{0.8}Fe_{1.6}Se_2$ sample composition. When the highly ordered $I4/m$ phase is suppressed at high pressure for the superconducting samples or is upset in nonsuperconducting samples, the energetics driving the formation of phase segregation are lost, thus is the superconductivity.

In summary, we have performed a high-pressure single-crystal neutron diffraction study on the magnetic and structural transitions in the (Tl,Rl)$_2$Fe$_4Se_8$ superconductor, and found that both the $\sqrt{5} \times \sqrt{5}$ Fe vacancy order and the block AFM order are suppressed at $P_c = 8.3$ GPa, where superconductivity also diminishes. As in previous temperature-dependent studies, the AFM order is also instrumental in the stability of the Fe vacancy order under pressure. Our results demonstrate that the highly ordered $\sqrt{5} \times \sqrt{5}$ vacancy order and the associated block AFM order are crucial ingredients in the realization of the 245 superconductors.

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