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Re-emerging superconductivity at 48 kelvin in iron chalcogenides

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Pressure has an essential role in the production[1] and control[2,3] of superconductivity in iron-based superconductors. Substitution of a large cation by a smaller rare-earth ion to simulate the pressure effect has raised the superconducting transition temperature T_c to a record high of 55 K in these materials[4,5]. In the same way as T_c exhibits a bell-shaped curve of dependence on chemical doping, pressure-tuned T_c typically drops monotonically after passing the optimal pressure[1–3]. Here we report that in the superconducting iron chalcogenides, a second superconducting phase suddenly re-emerges above 11.5 GPa, after the T_c drops from the first maximum of 32 K at 1 GPa. The T_c of the re-emerging superconducting phase is considerably higher than the first maximum, reaching 48.0–48.7 K for $Tl_{0.6}Rb_{0.4}Fe_{1.67}Se_2$, $K_{0.8}Fe_{1.7}Se_2$ and $K_{0.8}Fe_{1.78}Se_2$.

The recent discoveries of superconductivity at 30–32 K in a new family of iron-based chalcogenide superconductors[6–9] $A_{1-x}Fe_{2-y}Se_2$ (where A = K, Rb or Cs, with possible Tl substitution) bring new excitement to the field of superconductivity[10]. These superconductors have unusually large magnetic moments up to $3.3\mu_B$ per Fe atom and a Fe-vacancy ordering in the Fe square lattice[11]. How superconductivity with such a high T_c can exist on such a strong magnetic background remains perplexing[10]. It has been established that superconductivity in strongly correlated electronic systems can be dictated by their crystallographic structure, electronic charge, and orbital and spin degrees of freedom, which can all be manipulated by controlling parameters such as pressure, magnetic field and chemical composition[12–15]. Pressure is a 'clean' way to tune basic electronic and structural properties without changing the chemistry. High-pressure studies are thus very useful in elucidating mechanisms of superconductivity as well as in searching for new high-T_c superconducting materials.

We studied single crystals of $Tl_{0.6}Rb_{0.4}Fe_{1.67}Se_2$, $K_{0.8}Fe_{1.7}Se_2$ and $K_{0.8}Fe_{1.78}Se_2$ grown by the Bridgman method[6,16,17]. We conducted both high-pressure resistance and susceptibility measurements to detect superconductivity *in situ* at high pressures and low temperatures. Figure 1 shows the temperature dependence of the electrical resistance at different pressures for $Tl_{0.6}Rb_{0.4}Fe_{1.67}Se_2$ single crystals. Here we define T_c as the intersection of the tangent through the inflection point of the resistive transition with a straight-line fit of the normal state just above the transition. As can be seen, T_c starts at the maximum of 33 K at 1.6 GPa, shifts to lower temperatures at increasing pressures, and vanishes near 9 GPa in our experimental temperature range, which is 300–4 K for our high-pressure resistance measurements (Fig. 1a). At slightly higher pressures, however, an unexpected superconducting phase re-emerges with an onset T_c as high as 48.0 K at 12.4 GPa (Fig. 1b). The sample is not superconducting at pressures higher than 13.2 GPa. We repeated the measurements with new samples in three independent experiments, and the results were reproducible.

To confirm the pressure-induced changes of superconductivity in $Tl_{0.6}Rb_{0.4}Fe_{1.67}Se_2$, we also performed magnetic alternating-current susceptibility measurements *in situ* at high pressures (Fig. 2). The value of T_c is taken to be the onset of superconductivity defined by the intersection of a line drawn through the steep slope of the curve and the region of zero slope above the transition. The magnetic study showed that T_c decreased with increasing pressure and vanished at 9.8 GPa in the first superconducting phase SC-I (Fig. 2a). With further increasing pressure, the material enters a new superconducting phase SC-II and its transition temperature reaches 40.2 K at 12.2 GPa (Fig. 2b). The magnetic measurements yield T_c values consistent with the resistivity data within the experimental uncertainties. These results provide convincing evidence for the existence of two distinct superconducting phases in $Tl_{0.6}Rb_{0.4}Fe_{1.67}Se_2$.

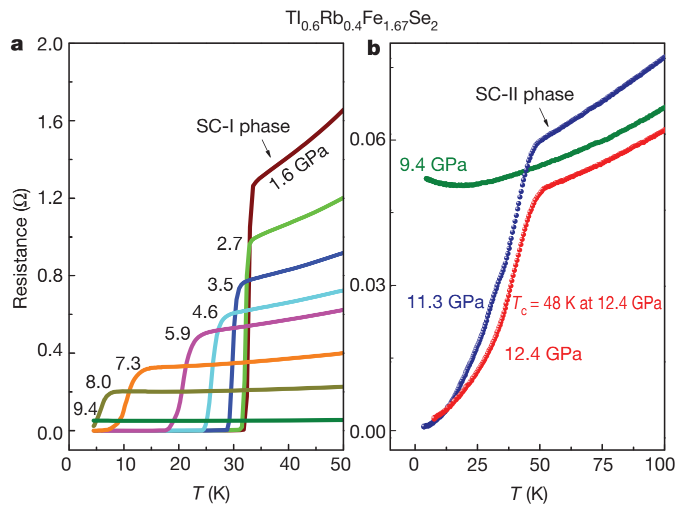

Figure 1 | Temperature-dependence of electrical resistance for $Tl_{0.6}Rb_{0.4}Fe_{1.67}Se_2$ at different pressures. **a**, Resistance–temperature curves in the initial superconducting phase (SC-I) up to 9.4 GPa. T_c was observed to shift to lower temperature with increasing pressure. Superconductivity disappears at 9.4 GPa. **b**, Electrical resistance curves for the same single crystal at higher pressures. A new superconducting state re-emerges upon further compression. The pressure-induced superconducting phase (SC-II) has a T_c of 48 K, which is much higher than the maximum in SC-I. Cryogenic resistance measurements were performed in a diamond-anvil cell. Diamond anvils with 600-μm and 300-μm tip flats were used with sample chambers of diameter 300 μm and 100 μm, respectively. Four electrical leads were attached to the single-crystal sample insulated from the rhenium gasket, and loaded into the sample chamber. NaCl powders were employed as a pressure medium. The ruby fluorescence method was used to gauge pressure[20].

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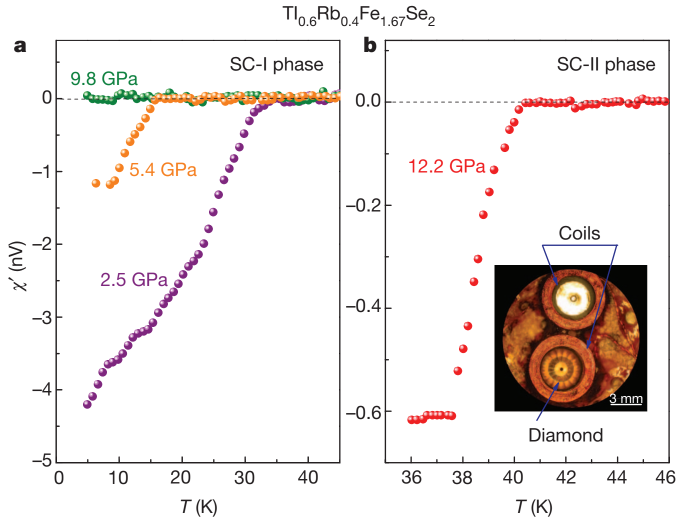

Figure 2 | Temperature dependence of the alternating-current susceptibility for $Tl_{0.6}Rb_{0.4}Fe_{1.67}Se_2$ at different pressures. **a**, Superconducting transitions observed in the real susceptibility component of the sample at pressures of 2.5, 5.4 and 9.8 GPa in SC-I. The superconducting transition shifts downward to lower temperature with increasing pressure. At 9.8 GPa the susceptibility component remains constant upon cooling down to 4 K, indicating that the sample is no longer superconducting. **b**, The real component of the susceptibility versus temperature for the crystal in SC-II at a pressure of 12.2 GPa. The inset shows the set-up for alternating-current susceptibility measurements in a diamond-anvil cell, with a signal coil around the diamond anvils and a compensating coil. The alternating-current susceptibilities were detected within a lock-in amplifier[21]. The crystals were loaded into the sample chamber, which is a hole in the centre of the nonmagnetic gaskets, with Daphne 7373 as the pressure medium.

To investigate whether the pressure-induced re-emergence of superconductivity was unique to $Tl_{0.6}Rb_{0.4}Fe_{1.67}Se_2$ or more general among iron chalcogenides, we conducted parallel electrical resistance measurements on $K_{0.8}Fe_{1.7}Se_2$ single crystals, and observed nearly identical behaviour (Fig. 3). The initial T_c of 32 K at 0.8–1.6 GPa decreased monotonically with increasing pressure and became undetectable at 9.2 GPa. At a slightly increased pressure, the second superconducting phase of $K_{0.8}Fe_{1.7}Se_2$ re-emerged and reached the maximum T_c of 48.7 K at 12.5 GPa. We repeated the experiment six times using six single crystals cut from different batches, and the results were reproducible. We further repeated the measurements with a slightly different composition, $K_{0.8}Fe_{1.78}Se_2$, and again, observed similar pressure-induced behaviour.

We summarized the pressure dependence of T_c of $Tl_{0.6}Rb_{0.4}Fe_{1.67}Se_2$, $K_{0.8}Fe_{1.7}Se_2$, and $K_{0.8}Fe_{1.78}Se_2$ in Fig. 4 and Supplementary Tables 1 to 4. The diagram clearly reveals two distinct superconducting regions: the initial superconducting phase SC-I and the pressure-induced superconducting phase SC-II. In the SC-I region, T_c is suppressed with applied pressure and approaches zero between 9.2 and 9.8 GPa. At higher pressures, the SC-II region appears, in which the T_c is even higher than the maximum T_c of the SC-I region. The SC-II region has a maximum T_c of 48.7 K for $K_{0.8}Fe_{1.7}Se_2$ and 48.0 K for $Tl_{0.6}Rb_{0.4}Fe_{1.67}Se_2$, higher than previously observed in chalcogenide superconductors. The SC-II region appears in a narrow pressure range. Unlike the usual parabolic pressure-tuning curve of T_c, the high T_c in SC-II appears abruptly above 9.8 GPa and disappears equally abruptly above 13.2 GPa. Intermediate $T_c < 38$ K is not observed even with small pressure increment steps of 0.1 GPa. A similar re-emergence of superconductivity has been observed in some other strongly correlated electronic systems, such as heavy-fermion[12] and organic systems[18].

Our preliminary high-pressure polycrystalline X-ray diffraction results of the two iron chalcogenides $K_{0.8}Fe_{1.7}Se_2$ and $K_{0.8}Fe_{1.78}Se_2$ confirm that, to the first degree, the basic tetragonal crystal structure persists throughout the pressure range studied (Supplementary Information). Therefore, the disappearance of T_c in SC-I, the re-emergence of higher T_c in SC-II, and the final non-superconducting region reflect detailed structural variances within the basic tetragonal unit cell, which await future in-depth investigation with advanced diagnostic probes. For instance, the possible change in magnetic-ordering structures would require high-pressure neutron diffraction, and the possible superlattice and Fe vacancy ordering would require high-pressure single-crystal X-ray structural investigations.

The pressure dependence of T_c in the SC-I region is expected but its mechanism is still much debated. Quantum criticalities are thought to affect superconductivity for strongly correlated electronic systems[19]. A characteristic feature of the new iron chalcogenide superconductors is

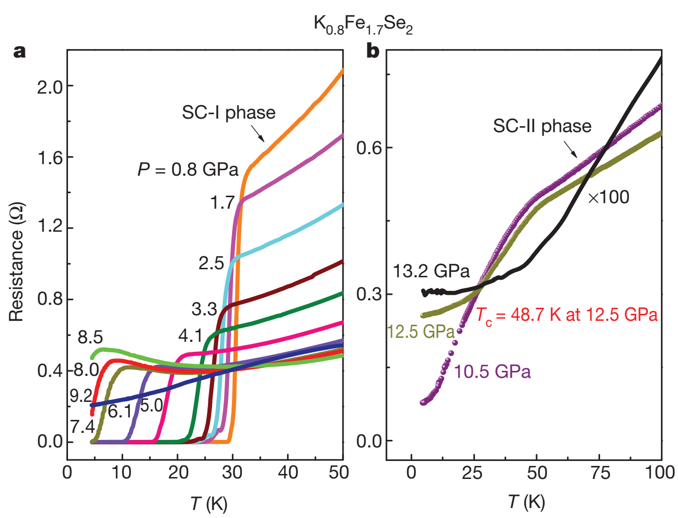

Figure 3 | Temperature dependence of the resistance for $K_{0.8}Fe_{1.7}Se_2$ at different pressures. **a**, SC-I. The resistance–temperature curves showing the T_c reduction with increasing pressure and its disappearance at 9.2 GPa. **b**, SC-II. The resistance measurements reveal another superconducting phase above 10.5 GPa. The T_c reaches 48.7 K at 12.5 GPa and disappears at 13.2 GPa. The black curve has been multiplied by 100.

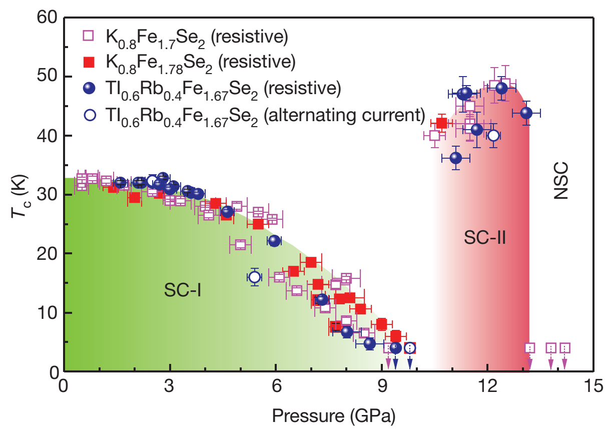

Figure 4 | Pressure dependence of the T_c for $Tl_{0.6}Rb_{0.4}Fe_{1.67}Se_2$, $K_{0.8}Fe_{1.7}Se_2$ and $K_{0.8}Fe_{1.78}Se_2$. The symbols represent the pressure–temperature conditions for which T_c values were observed from the resistive and alternating-current susceptibility measurements; symbols with downward arrows represent the absence of superconductivity to the lowest temperature (4 K). All $Tl_{0.6}Rb_{0.4}Fe_{1.67}Se_2$, $K_{0.8}Fe_{1.7}Se_2$ and $K_{0.8}Fe_{1.78}Se_2$ samples show two superconducting regions (SC-I and SC-II) separated by a critical pressure at around 10 GPa. NSC, the non-superconducting region above 13.2 GPa. The maximum T_c is found to be 48.7 K in $K_{0.8}Fe_{1.7}Se_2$ at a pressure of 12.5 GPa. At higher pressures above 13.2 GPa, the samples are non-superconducting. Error bars are one standard deviation.

the existence of Fe-vacancies in the Fe-square lattice, ordered by a $\sqrt{5} \times \sqrt{5}$ superstructure[11]. It remains unclear whether pressure could destroy the vacancy ordering at a critical value and drive the materials into a disordered lattice. Detailed structural studies of these superconducting behaviours in the iron chalcogenide superconductors are currently being conducted. Their magnetic properties at high pressures should help us to understand the interplay of magnetism and superconductivity in these iron chalcogenides.

This observation of the SC-II region with the re-emerging higher T_c is unexpected. It will certainly stimulate a great deal of future experimental and theoretical studies to clarify whether the observed re-emergence of superconductivity in iron chalcogenides is associated with the quantum critical transition, magnetism, superstructure, vacancy ordering or spin fluctuation.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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