Superconductivity in the PbO-type structure \( \alpha \)-FeSe


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The recent discovery of superconductivity with relatively high transition temperature (Tc) in the layered iron-based quaternary oxypnictides La\([O_{1-x}F_x]\)FeAs by Kamihara et al. [Kamihara Y, Watanabe T, Hirano M, Hosono H (2008) Iron-based layered superconductor La\([O(1-x)F_x]\)FeAs \(x = 0.05–0.12\) with \(T_c = 26\,K\). J Am Chem Soc 130:3296–3297.] was a real surprise and has generated tremendous interest. Although superconductivity exists in alloy that contains the element Fe, LaOMnPn (with \(M = \text{Fe, Ni}; \text{and } \text{Pn} = \text{P and As}\)) is the first system where Fe plays the key role in the occurrence of superconductivity. LaOMnPn has a layered crystal structure with an Fe-based plane. It is quite natural to search whether there exists other Fe-based planar compounds that exhibit superconductivity. Here, we report the observation of superconductivity with zero-resistance transition temperature at 8 K in the PbO-type \( \alpha \)-FeSe compound. A key observation is that the clean superconducting phase exists only in those samples prepared with intentional Se deficiency. FeSe, compared with LaOFeAs, is less toxic and much easier to handle. What is truly striking is that this compound has the same, perhaps simpler, planar crystal sublattice as the layered oxypnictides. Therefore, this result provides an opportunity to better understand the underlying mechanism of superconductivity in this class of unconventional superconductors.

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**Although superconductivity exists in alloy (1) that contains the element Fe, LaOMnPn (2–9) (with \(M = \text{Fe, Ni}; \text{and } \text{Pn} = \text{P and As}\)) is the first system where Fe plays the key role in the occurrence of superconductivity. LaOMnPn has a layered crystal structure with an Fe-based plane. It is quite natural to ask whether other Fe-based planar compounds exist that exhibit superconductivity. Here, we report the observation of superconductivity with zero resistance transition temperature at 8 K in the PbO-type \( \alpha \)-FeSe compound. Although FeSe has been studied quite extensively (10, 11), a key observation is that the clean superconducting phase exists only in those samples prepared with intentional Se deficiency.

FeSe comes in several phases: (i) a tetragonal phase \( \alpha \)-FeSe with PbO-structure, (ii) a NaAs-type \( \beta \)-phase with a wide range of homogeneity showing a transformation from hexagonal to monoclinic symmetry, and (iii) an \( \text{FeSe}_2 \) phase that has the orthorhombic marcasite structure. The most studied of these compounds are the hexagonal Fe\text{Se}_6, which is a ferrimagnet with Curie temperature at \( \sim 125\,K\), and monoclinic Fe\text{Se}_6.

Unlike the high-temperature (high-Tc) superconductors (12) discovered more than 20 years ago that have a Cu\text{O}_2 plane that is essential for the observed superconductivity, the tetragonal phase \( \alpha \)-FeSe with PbO structure has an Fe-based planar sublattice equivalent to the layered iron-based quaternary oxypnictides, which have a layered crystal structure belonging to the P4/nmm space group (2). The crystal of \( \alpha \)-FeSe is composed of a stack of edge-sharing Fe\text{Se}_6 tetrahedra layer by layer, as shown schematically in Fig. 1. Polycrystalline samples with nominal concentration Fe\text{Se}_{1-x} (\(x = 0.03\) and 0.18) were synthesized and studied. X-ray diffraction analysis of the samples in Fig. 2 shows that \( \alpha \)-FeSe is dominant, and \( \beta \)-FeSe phases exist in trace amounts. This result is reasonable because in the Fe-Se binary alloy system, the \( \alpha \)-phase is considered as a slightly Se-deficient phase \([45–49.4\text{ atomic percent (at\% Se)}]\) and the \( \beta \)-phase, in contrast, persists in a wide range of compositions from slightly Fe-rich to Se-rich \((49.5–58\text{ at\% Se})\) (13). In Fe\text{Se}_{0.82}, the possible iron oxide impurity phases could come from either starting materials \((99.9\% \text{ Fe})\) or surface oxidation during sintering, and the silicides might be the product of reactions between the sample and silica ampoules. Nevertheless, the samples contained only trace amounts of these impurity phases (note that the y axis of Fig. 2 is in log scale). The calculated lattice constants are \(a = 0.37693\,(1)\,\text{nm and } c = 0.54861\,(2)\,\text{nm for FeSe}_{0.82}\), and \(a = 0.37676\,(2)\,\text{nm and } c = 0.54847\,(1)\,\text{nm for FeSe}_{0.88}\). The lattice constant slightly expands in the a axis and shrinks in the c axis for both samples as compared with those of \( \alpha \)-FeSe in the Joint Committee on Powder Diffraction Standards Card (85-0735, unpublished) (13) \((a = 0.3765\text{ nm and } c = 0.5518\text{ nm})\). This

![Fig. 1. Schematic crystal structure of \( \alpha \)-FeSe. Four unit cells are shown to reveal the layered structure.](image)

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The authors declare no conflict of interest.

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dependence of the upper critical field, and the experimental strengths. The Right Inset shows the resistive measurements at various magnetic fields. The room temperature-to-250 K and exhibits metallic characteristics before the onset of the superconducting transition. The temperature-to-residual resistance ratio is \( \approx 6 \). Interestingly, an anomalous downturn in resistivity at \( \approx 100 \) K is observed. As the temperature is lowered further, the zero-resistance transition occurs at \( \approx 8 \) K. The transition width is rather broad, suggesting the inhomogeneous nature of the sample. Superconducting critical transition temperature \( (T_c) \) in variety of applied magnetic field up to 9 T was determined by taking the temperature where the resistance drops to 50% of that at the onset (50% \( R_n \)). Fig. 3 Left Inset shows the resistive measurements at various magnetic field strengths. The Right Inset of Fig. 3 shows the temperature dependence of the upper critical field, and the experimental result was fit to the relationship, \( H_{\text{c}2}/H_{\text{c}2}(0) = 1 - (T/T_c(0))^2 \), shown by the blue line. The estimated upper critical field \( H_{\text{c}2}(0) \) is \( \approx 16.3 \) T, which gives a coherence length \( \xi \approx 4.5 \) nm.

The magnetic susceptibility as a function of temperature was measured at 30-G field strength, as shown in Fig. 4A. The zero field cool (ZFC) susceptibility is essentially temperature independent, indicating that the sample is a Pauli paramagnet before the onset of superconductivity. A sharp drop, indicating the magnetic onset of superconductivity, appears at \( \approx 8 \) K, which is the same as the zero-resistance temperature. The susceptibility shows a relatively large Pauli susceptibility in the normal state. This relatively large positive background above \( T_c \) can possibly be attributed to the existence of trace Fe impurity. A relatively small magnetic anomaly occurs at \( \approx 105 \) K, which is more pronounced in the field-cool measurement. This magnetic anomaly occurs at the same temperature as that observed in the resistive measurement. Further confirmation of superconductivity is shown in the Inset of Fig. 4A, which displays the typical magnetic hysteresis curve for a superconductor. Fig. 4B shows the specific heat of the FeSe\(_{0.88}\) sample. In the normal state, the electronic coefficient of specific heat \( \gamma = 9.17 \) mJ/mol-K\(^2\), which can be seen from the zero-temperature intercept. The superconducting transition at \( T_c \) is relatively broad, and the estimated \( \Delta C_p/\gamma T_c \) is \( \approx 0.61 \). In the superconducting state, the best fit of data over the temperature range \( 1 < T_c/T < 1.8 \) leads to \( \text{Ces}/\gamma T_c = 7.69 \exp(-1.58T_c/T) \). But it does not follow the BCS relation over the full temperature range below \( T_c \), as shown in the

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**Fig. 2.** Powder x-ray diffraction patterns of FeSe\(_{0.82}\) and FeSe\(_{0.88}\). The patterns show that the resulting sample with starting composition of Fe (53%)/Se (47%) composes of primarily PbO-type tetragonal FeSe\(_{1-x}\) (P4/mmm), the \( \alpha \)-phase, and partly of NiAs-type hexagonal FeSe (P6\(_3\)/mmc), the \( \beta \)-phase. The sample with higher initial iron content, Fe (55%)/Se (45%), shows no \( \beta \)-phase but trace amounts of possible impurity phases including elemental selenium, iron oxide, and iron silicide (marked with an asterisk). Question marks in the figure represent unknown phases.

**Fig. 3.** Temperature dependence of electrical resistivity (\( \rho \)) of FeSe\(_{0.88}\). The Left Inset shows the resistive measurement in magnetic fields (H) of 0, 1, 3, 5, 7, and 9 T below 12 K. \( T_c \) decreases linearly with increasing magnetic field. The Right Inset displays the temperature dependence of upper critical field (\( H_{\text{c}2} \)), with the fit shown in blue.

**Fig. 4.** Magnetic susceptibility and specific heat of FeSe\(_{0.88}\). (A) Temperature dependence of magnetic susceptibility measured in a 30-G magnetic field. A small magnetic anomaly is observed at \( \approx 105 \) K, which is more pronounced in the FC measurements. Inset shows the magnetic hysteresis of the sample measured at 2 K. It confirms the superconducting characteristic of the sample. (B) Low temperature-specific heat of FeSe\(_{0.88}\). The red dotted line is the curve fitting of phonon and electronic contribution to the specific heat. The intercept at zero temperature gives \( \gamma = 9.17 \) mJ/mol-K\(^2\). A specific jump appears at \( \approx 8 \) K, which coincides with the zero-resistance temperature that confirms the superconducting transition. The Inset shows the semilogarithmic Ces/\( \gamma T_c \) vs. \( T/T_c \) in the superconducting state. The measured plot displays deviation from the linear curve of the fully gapped superconductor (solid blue straight line).
Detailed refinement of the diffraction data suggests that the crystal structure changes from the tetragonal (P4/nmm) symmetry to the triclinic (P-1) symmetry, with the lattice parameters at 6 K of $a = 0.3773$ nm, $b = 0.3777$ nm, $c = 0.5503$ nm; both angles $\alpha$ and $\beta$ remain at 90°, but the $\gamma$-angle increases from 90 to $\sim 90.3^\circ$. Fig. 5B Inset shows the temperature dependence of $\gamma$-angle fit with P-1 symmetry. Whether this observed structural change at low temperature is related to the appearance of superconductivity is currently under intensive investigation. In summary, we have confirmed the existence of superconductivity in the binary alloy FeSe$_{1-x}$ that exhibits PbO-type structure. Transport measurements show that the upper critical field of these compounds is in the order of 17 T, which implies a coherence length of $\sim$40 Å. In the superconducting state, the specific heat data can only fit to the BCS relation over a relatively narrow range, 1 < $T_c$/T < 1.8. This observation suggests that superconductivity in FeSe$_{1-x}$ is most likely unconventional. An interesting low-temperature phase transition at $\sim$100 K from P4/nmm symmetry to P-1 symmetry was observed. This structural change, which only affects the lattice parameters without breaking the magnetic symmetry, may strongly correlate with the origin for superconductivity.

Materials and Methods

Polycrystalline bulk samples were prepared with the following procedure. High-purity (99%) powder of selenium and iron with appropriate stoichiometry (FeSe = 0.98) was mixed and ground with an agate mortar and pestle. The grinding process was carried out in a fume hood with strong ventilation. The ground powder was cold-pressed into discs with 400 kg/cm$^2$ uniaxial stress. The discs were sealed in an evacuated quartz tube (10−5-torr vacuum) and slowly ramped to 700°C, which is a little above the boiling point of Se, at the rate of 100°C/hr. Finally, the temperature was kept at 700°C for 24 h. After cooling to room temperature at the rate of 300°C/hr, the loose sample was reground, pressed, sealed in a quartz tube, sintered again at 700°C for 24 h, and finally annealed at 400°C for 36 h. All of the samples were kept in vacuum desiccators before measurement. The sample resistance was measured by using the standard four-probe method using silver paste for contact. Measurements were carried out with a Quantum Design Physical Property Measurement System (model 6000, PPMS) (Fig. 3). DC magnetic susceptibility measurements were performed in a Quantum Design superconducting quantum interference device vibrating sample magnetometer (SQUID-VSM) (Fig. 4A). The FeSe$_{0.88}$ powder sample was measured in two ways: (i) the sample was cooled without an initial external magnetic field applied, and the susceptibility was measured as a function of temperature. After initializing, a 30-G magnetic field was applied, and the susceptibility was measured as a function of temperature. The temperature dependence of the x-ray powder diffraction Fig. (5) was measured by using the synchrotron source at BL12B2 in Spring 8 with incident beam wavelength of 0.995 Å.

ACKNOWLEDGMENTS. We acknowledge fruitful discussions with T. K. Lee and Sungkit Yip. This work was partially supported by a National Science Council of Taiwan Grant and the U.S. Air Force Office of Scientific Research through its Tokyo Asian Office of Aerospace Research and Development Grant 084049.

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