Superconductivity in PbO-type tetragonal FeSe nanoparticles

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ABSTRACT

The existence of a high-temperature superconducting phase with $T_c \sim 40$ K in PbO-type tetragonal β-FeSe has been demonstrated by application of high pressure. We have used a rapid, solvent-less reaction under autogenic pressure at elevated temperature (RAPET) process to synthesize superconducting Fe–Se nanoparticles. The nanoparticles obtained are mainly the superconducting β-FeSe phase. Detailed magnetization measurements on these nanoparticles show that in addition to the superconducting transition at $\sim 10$ K, we observe an anomaly in magnetic susceptibility measurements suggesting the presence of a superconducting transition at $\sim 30$ K in the synthesized nanoparticles. The superconducting volume fraction depends on the chemical composition of the starting materials and also on the processing time.

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1. Introduction

The recent discovery of superconductivity in iron-based compounds breaks the conventional wisdom that Fe atoms are detrimental to superconductivity [1–5]. Subsequently, intensive activities were devoted to the search for new superconductors and a better understanding of the origin of superconductivity in this intriguing class of materials, particularly the interplay between magnetism and superconductivity [6]. Among all the Fe-based superconductors, the tetragonal PbO-type β-FeSe (denoted as Fe–Se hereafter) with P4/mmm symmetry has the simplest structure and thus serves as an ideal platform to investigate the origin of superconductivity in Fe-based compounds [4,7].

An important follow-up after the discovery of Fe–Se superconductor was the observation of an extremely large pressure enhancement in the superconducting transition temperature $T_c$ [8]. The maximum $T_c$ is $\sim 37$ K [9]. The result strongly suggests that there may intrinsically exist a superconducting phase with much higher transition temperature in Fe–Se. Another critical issue, which is in fact still unresolved, was a report of high sensitivity of the superconductivity to the chemical stoichiometry in Fe–Se [10]. A small amount of excess Fe appears to suppress the superconductivity completely. However, on the other hand, results reported earlier suggest that Se deficiency is probably more important to the occurrence of superconductivity [4,11].

It was also found right after the discovery of Fe–Se that there exists a low-temperature structural distortion in this compound [4,11]. More detailed studies confirmed that there is a strong correlation between superconductivity and the low-temperature structural distortion in Fe–Se. All the results show that if there is no low-temperature structural distortion there is no superconductivity. One may then immediately ask what the origin of this low-temperature distortion is, and if there is any correlation between the chemical stoichiometry and the low-temperature structural distortion.

In order to gain more information to better answer the questions mentioned above, we decided to develop processes to prepare superconducting Fe–Se in nanoparticle form. Such a synthetic capability for nanodimensional Fe–Se is important for several reasons. The nanoparticle materials may intrinsically exhibit certain strain so that the high-temperature superconducting phase that appears under high pressure may show up in the sample. The superconducting nanoparticles may provide a better platform to investigate the effect of chemical stoichiometry on superconductivity. In addition, interesting size-dependent phenomena have been discovered for other superconductors when synthetic routes have better size and dimensional control.

There are several approaches reported for the preparation of nanodimensional iron chalcogenide materials. Core–shell nanofibers of carbon-coated β-FeSe and FeSe$_2$ and FeTe$_2$ nanoparticles have been obtained using solution-based solvothermal reduction [12]. There were also successful attempts to synthesize nanocrystalline iron sulfide and selenide phases, including FeS$_2$, Fe$_2$S$_3$, and impure NiAs-type β-FeSe. However, there have been no reports of a low-temperature solution-based chemical route to prepare superconducting PbO-type β-FeSe, as well as the other related iron chalcogenides. In this paper, we report a relatively simple, rapid, and solvent-less RAPET (reaction under autogenic pressure at elevated temperature) process to fabricate Fe–Se and related compounds in nanodimensional form.
2. Experimental details

2.1. Synthesis of $\beta$-FeSe nanoparticles

Here, we describe a rapid, solvent-less RAPET (reaction under autogenic pressure at elevated temperature) approach for the fabrication of nanoparticles. The starting materials include iron (Fe) powder (99.5%, 200 mesh) and selenium (Se) powder (99%, 325 mesh); both were from Alfa–Aesar. The Fe was first mixed with Se powder and introduced into a 2 ml stainless steel Swagelok union reactor at room temperature in an N$_2$-filled glove box. The filled reactor was sealed tightly with another plug and placed at the center of the tube’s furnace. The temperature of the furnace was raised to 700 °C at a rate of 20 °C/min, and the temperature was kept at 700 °C for various lengths of time, and then the reactor was gradually cooled (over a period of 5 h) to room temperature and opened.

2.2. Properties characterizations

The magnetic properties were measured on a SQUID magnetometer (MPMS, Quantum Design Inc.). The electrical resistivity was measured with a Quantum Design PPMS system, which is capable of high magnetic field (up to 9 T) and lowest temperature close to 300 mK. X-ray diffraction and transmission electron microscopy (TEM) were used to determine the exact crystal structure of the nanoparticles prepared.

3. Results and discussions

Fig. 1 displays the X-ray diffraction patterns of the as-grown nanoparticles with three different starting chemical compositions. The patterns were fitted and indexed to the tetragonal space group $P4_{1}/nmm$ of the PbO-type $\beta$-FeSe phase. The lattice parameters of the samples are listed in Table 1. Unfortunately, a small amount (less than about 10%) hexagonal phase also exist in the samples; the associated peaks are marked with H.

Fig. 2 shows the TEM image of an as-grown nanoparticle with stoichiometry Fe$_{1.03}$Se. The shape of the particle is relatively irregular, with typical size $\sim$300 nm. The electron diffraction pattern confirms the tetragonal symmetry of the particle. And the chemical composition analysis using energy-dispersive X-ray spectroscopy (EDX) suggests in fact that the sample is Se rich, even though the starting material is Fe rich. However, these results seem to be consistent with the observation of about 10% hexagonal phase being present in the samples from X-ray measurements.

It is rather difficult to measure the electrical properties of the nanoparticles using the set-up that exists in our laboratory. Thus, we first used the SQUID magnetometer to determine the magnetic responses of the nanoparticles prepared. Figs. 3–5 show the magnetic susceptibility of Fe–Se nanoparticles of different compositions prepared at the same temperature but with different holding times. We only show the zero-field-cooled (ZFC) data for clarity. All samples measured show a superconducting transition but with different superconducting content. It is observed that the superconducting volume fraction of the sample depends on the Fe/Se ratio and the processing time. For Fe-deficient samples (Fe$_{0.97}$Se) or samples close to 1:1 Fe/Se ratio (the starting composition) the materials processed with 6 h holding time give the highest volume fraction. On the other hand, the results for Fe-rich samples have less dependence on the processing time. As shown in Fig. 5, all Fe-rich samples processed with different times exhibit about the same superconducting volume fraction, which is the highest among all samples investigated.

The most interesting observations were the onset of a superconducting-like (diamagnetic) transition with an onset temperature at $\sim$30 K in most of the samples after 12 h processing time. It is particularly clear in the sample with Fe$_{1.03}$Se starting stoichiometry, which shows about 15% diamagnetic signal within the total superconducting signal observed. This observed anomaly is unlikely due to the $\sim$10% hexagonal phase detected by X-ray analysis, as the temperature of the transition is also not consistent with the magnetic order in the hexagonal phase (which has order temperature close to 130 K). This diamagnetic-like anomaly is suppressed by the magnetic field. However, the
anomaly is very sensitive to the magnetic field, as shown in the inset of Fig. 5, suggesting that it has extremely low critical field if it is related to a superconducting transition. It is interesting to note that a similar anomaly appearing at relatively higher temperature was observed in an electron-doped CaFe$_2$As$_2$ superconductor [13]. The observed anomaly was carefully examined by the authors and was argued to be associated with an interfacial or filamentary superconducting transition.

It is noted that the magnetic anomaly observed, especially the result on the Fe$_{1.03}$Se sample, is consistent with a recent more detailed electrical resistivity measurement on single-crystal Fe–Se, which reveals that there may exist a higher superconducting phase. This is shown in Fig. 6, which displays the temperature derivative of the resistivity as a function of temperature; an anomaly with onset at about 30 K ($T_c$) is clearly observed. The data also confirm the presence of a resistive anomaly $T_m$ at about 100 K, which is obviously associated with the low-temperature structural distortion.

To further understand whether we have indeed stabilized a higher superconducting phase in the nanoparticle samples we prepared bulk materials from the nanoparticle powder using a spark plasma sintering (SPS) process. Then we measured the electrical resistance of the processed samples. The results are shown in Fig. 7. The results do not show unambiguously the presence of a resistive transition signature, which is the onset of superconductivity. Though the overall behavior is the same as that of the single crystal.

In fact, it was not totally surprising that we were not able to observe a clear resistive transition at higher temperature even though the magnetic data strongly suggests the existence of a higher $T_c$ phase in the nanoparticle samples. This is because the bulk samples may not retain the true behavior of the nanoparticles as we have to process the sample at elevated temperature. Consequently, the nanoparticles will aggregate into larger grains. A proper tool, such as high-resolution low-temperature scanning transmission electron microscopy (STEM), will be essential to further examine the nature of the transition at $\sim$40 K observed by the magnetic measurements. We have also carried out a detailed TEM study in an attempt to find out the possible origin of the higher $T_c$ phase. In addition, we also hoped to examine more accurately the exact chemical stoichiometry of the samples using high-resolution electron microscopy. Unfortunately, we are not able to gain more detailed information due to the relatively low resolution and the lack of proper low-temperature environment of our TEM system.

4. Conclusion

We have developed a simple, rapid, one-step RAPET process to synthesize superconducting Fe–Se nanoparticles. All the nanoparticles synthesized with different starting chemical compositions contain the PbO-type tetragonal FeSe as the main phase, with about 10% hexagonal phase. A clear bulk superconducting transition with onset at $\sim$10 K is observed in all samples. The superconducting transition volume fraction of the nanoparticles obtained depends on the chemical composition of the starting materials. For samples that are Se rich or have 1:1 Fe/Se stoichiometry, the superconducting fraction also depends on the process time. An intermediate process time (6 h in our studies) gives the best results on these samples. However, the sample with highest superconducting fraction comes from slightly Fe-rich compound, and its superconducting volume fraction is less process-time dependent. An interesting superconducting-like signal, which is about 15% of the total diamagnetic transition, at $\sim$30 K is clearly observed in the Fe$_{1.03}$Se nanoparticles. Such a signal, but less obvious, can also be seen in the other two samples. Currently, we are trying to use high-resolution microscopy including low-temperature STM and TEM, to provide more detailed information to answer whether such a relatively higher temperature transition in the nanoparticles and the high $T_c$ transition observed in bulk samples under the application of pressure have the same origin.
Fig. 6. (left) Temperature dependence of resistivity of Fe–Se single crystals. The inset shows the magnetic field dependence of the resistive transition. (right) Temperature derivative of the resistivity of single-crystal Fe–Se (dR/dT) as a function of the temperature. The inset is a plot with a different scale to reveal the transitions more clearly (associated with a structural distortion at $T_s \sim 100$ K; and an anomaly at $\sim 30$ K, which may be related to the higher $T_c$ observed phase under pressure, and the bulk $T_c$ at $\sim 10$ K.)

Fig. 7. Resistance of bulk Fe–Se samples prepared by pressing nanoparticles with the SPS process.

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References