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Pressure-restored superconductivity in Cu-substituted FeSe

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Copper doping of FeSe destroys its superconductivity at ambient pressure, even at low doping levels. Here we report the pressure dependent transport and structural properties of $Fe_{1.01-x}Cu_xSe$ with 3 % and 4 % Cu doping and find that the superconductivity is restored. Metallic resistivity behavior, absent in Cu-doped FeSe, is also restored. At the low pressure of 1.5 GPa, superconductivity is seen at 6 K for 4 % Cu doping, somewhat lower than the 8 K T_c of undoped FeSe. T_c reaches its maximum of 31.3 K at 7.8 GPa, lower than the maximum superconducting temperature in the undoped material under pressure (T_c max of 37 K) but still very high. X-ray diffraction shows that applied pressure decreases the lattice parameter in the basal plane, counteracting the structural effect of Cu doping, providing a possible explanation for the restoration of the superconductivity.

After the discovery of the layered iron based superconductors in 2008[1], interest in understanding the origin of their high T_cs grew quickly. The superconductors display a variety of crystal structures, in all but one case consisting of two-dimensional layers of tetrahedrally coordinated Fe atoms interleaved with inert intermediary layers. The '1111' system, typified by LaFeAs(O,F), at 55 K exhibits the highest T_cs in the iron arsenides[2–4]. Both simpler structures, e.g. the 122 system typified by $BaFe_2As_2$, superconducting with a maximum T_c of 38 K,[5] and more complex structures e.g. the perovskite arsenide intergrowth phases typified by $Sr_3V_2O_6Fe_2As_2$ are known[6]. The simplest superconductor in the family, FeSe, prototype of the '11' system, was found to be superconducting below 8 K[7]. Of all the compounds FeSe is the simplest structurally, as it is the one case with no intermediary layer. In spite of that simplicity, however, the superconductivity in this compound has proven to be much more sensitive to small deviations in chemical stoichiometry than the others, and further, can be completely suppressed by both magnetic and non magnetic dopants at the level of only a few percent[8,9]. These observations suggest that FeSe is barely stable in the superconducting state.

Cu doping of FeSe leads to a rapid suppression of superconductivity. Even at the 3% level, no evidence for superconductivity is seen, and, above 3%, all doped compositions are non-metallic. At 12% Cu, spin glass behavior has been suggested[8]. Density functional calculations have been interpreted as indicating that the origin of the metal-insulator transition in Cu doped FeSe is Anderson localization[10]. The calculations show that enhanced static magnetic susceptibility should appear with increasing Cu content, until at a 12 % doping level a spin glass is formed; this is in agreement with experiment. The calculations further show that until this doping level is reached, only minor changes in the electronic structure of the compound should occur. Critically, the Fermi surface nesting is still present at small dopings, and it was therefore proposed that the disappearance of superconductivity in FeSe at small doping levels is due to an increase of the static susceptibility rather than changes in the electronic structure. The theoretical analysis further indicated that this increased static magnetic susceptibility would naturally result as a consequence of the experimentally observed increase in the in-plane lattice parameter a on Cu doping[8].

Several groups have reported a very strong enhancement of T_c under applied pressure in undoped FeSe[11–16]. This suggests that studies of a doped non-superconducting phase of FeSe under pressure may be of interest; at low doping levels the Fermi surface nesting is still present, and because pressure is likely to reduce the lattice parameter a in the basal plane, superconductivity might be restored if the picture based on the electronic structure calculations is correct. By investigating the pressure dependence of the normal state magnetic susceptibility, it would be possible to determine whether the appearance of superconductivity in the doped phase under pressure, if it occurs, is accompanied by a decrease in the static susceptibility, as predicted, or whether the enhancement of the ($q \neq 0$) spin fluctuations[17] that accompany the increase in T_c under pressure in undoped FeSe lead to an enhancement of the static susceptibility along with the increasing T_c in the doped case.

Here we report investigations of initially non-superconducting $Fe_{1.01-x}Cu_xSe$ with small doping levels, 3 % and 4 %, under pressure. Magnetic susceptibility measurements, transport measurements and X-ray diffraction are employed. We find that the superconductivity is indeed restored, reaching temperatures of approximately 31 K at 8 GPa, and that the in-plane lattice parameter does indeed decrease under pressure, consistent with the theoretical models for FeSe and its doped variants. We discuss the relation of the restoration of SC in Cu-doped FeSe under pressure to the possible mechanism of superconductivity in Fe based compounds.

Polycrystalline samples were prepared by solid state reaction as described elsewhere[8]. High pressure angle dispersive X-ray diffraction studies were performed at room temperature at beamlines BL12B2 of SPring-8 (Japan) and 01C2 of NSRRC (Taiwan). For these studies, the samples were loaded in a diamond anvil cell (DAC) with mineral oil as the pressure transmitting medium. Susceptibility measurements were performed in a CuBe cell, allowing hydrostatic pressure up to 1 GPa to be obtained. This cell was mounted in a SQUID-magnetometer (MPMS-XL-5, Quantum Design). A DAC was used for electrical resistance measurements under high pressures. For insulating the gasket, a cubic BN/epoxy mixture was used, and, for the electrical leads, platinum foil. The diameter of the flat working surface of the diamond anvil was 0.5mm and the diameter of the hole in the gasket was 0.07mm. The hole was filled with polycrystalline sample. The resistance was measured with a dc current source and voltmeter in a two probe configuration. The pressure was measured at room temperature and below via the Ruby scale from small chips scattered across the sample. The sample pressure inhomogeneity was about 0.05 GPa. The temperature was measured with a calibrated Si diode with an accuracy of 0.1 K attached to the DAC. T_c was determined from the onset of the resistivity drops.

In terms of the structural response on compression, $Fe_{1.01-x}Cu_xSe$ is very similar to undoped FeSe. At a pressure of 8 GPa, the onset of a phase transition into a high-pressure phase with NiAs-type structure is observed. A broad pressure range of coexistence of both phases is found (up to 14 GPa), similar to what is seen in undoped FeSe. Fig. 1 shows the decrease of the in-plane lattice parameter a as a function of pressure for different Cu concentrations. Cu doping at ambient pressure increases the a parameter[8], and thus applied pressure counteracts the structural effect of doping; Fig. 1 shows that the lattice parameter a can be restored to its original size with modest application of pressure, between 1 and 2 GPa.

Resistivity measurements of $Fe_{0.97}Cu_{0.04}Se$ under pressure were performed up to 13.7 GPa (Fig.2). At a pressure of 1.55 GPa, a superconducting transition was observed at 6.6 K. Above T_c, the compound shows metallic behavior, resembling the behavior of undoped superconducting $Fe_{1.01}Se$[8]. Thus, a pressure of only 1.55 GPa is sufficient to turn non-superconducting, semiconducting $Fe_{0.97}Cu_{0.04}Se$ into a metallic superconductor. The superconducting transition temperature increases up to a pressure of 7.8 GPa, reaching its maximum of 31.3 K. At higher pressures, it decreases slowly until 13.7 GPa, where it quickly disappears. At 13.7 GPa, the finite resistance indicates that the sample is no longer superconducting. The flattening and decrease of the slope of the R(T) curve at this pressure indicates that the material has a low fraction of conducting phase present. Figure 3 shows the dome-like shape of the curve of T_c versus applied pressure for Cu-doped FeSe compared to undoped FeSe. The curve for the Cu-doped material has the same general character as the one for pure FeSe, but is shifted to higher pressures by about 3 GPa. The dome-shaped curve of Tc vs pressure for Cu-doped FeSe is narrower than for the undoped material because the onset of Tc occurs at higher pressures in the present case but for both doped and undoped materials the superconducting tetragonal FeSe phase structurally transforms to the hexagonal non-superconducting phase at about the same pressure (above 12 GPa). The maximum T_c is encountered at similar pressures for the doped and undoped phases, and no superconductivity is observed in either doped or undoped compounds above 12 GPa[15].

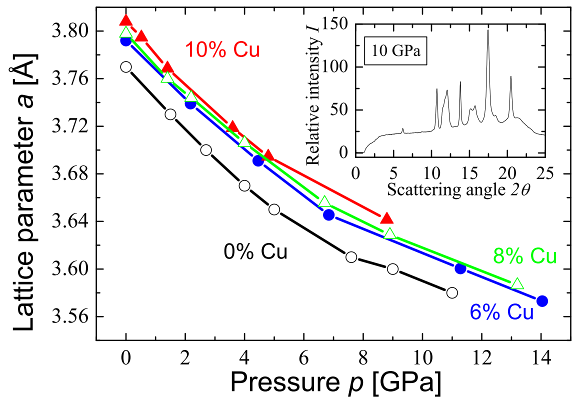

FIG. 1. The lattice parameter a as a function of pressure in $Fe_{1.01-x}Cu_xSe$. The data for FeSe are taken from[14]. The insert shows the diffraction pattern for $Fe_{0.95}Cu_{0.06}Se$ at 10 GPa, where both tetragonal and hexagonal FeSe phases are present.

Susceptibility measurements under pressure, up to 1 GPa, were performed on $Fe_{0.98}Cu_{0.03}Se$. The temperature dependence of the zero field cooled (ZFC) magnetization, measured at 20 Oe at different pressures, normalized to the value at 15 K, is shown in Fig.4. The dc magnetization at ambient pressure shows no superconducting transition and exhibits an increasing static susceptibility at low temperatures. At 0.82 GPa the magnetization decreases from 15 K to 8 K; at lower temperatures, it increases, showing a residual moment at 2 K. At a pressure of 0.98 GPa, the magnetization decreases monotonically below 14 K and displays a downturn below ca. 6 K. While the decrease of the residual low temperature magnetization up to pressures of 0.82 GPa can be considered as a reduction of the static susceptibility, the sudden decrease of the magnetization below 3 K at 0.98 GPa is due to the appearance of a superconducting transition.

Doping of very small amounts of Cu or Fe into $Fe_{1.01}Se$ lowers T_c strongly[8]; even $Fe_{0.995}Cu_{0.015}Se$ and $Fe_{1.03}Se$ are not bulk superconductors[8,18]. The restoration of the superconductivity in Cu-doped FeSe under pressure im-

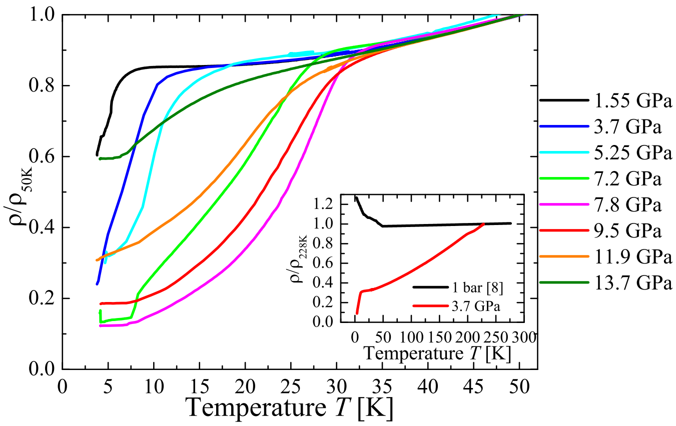

FIG. 2. Normalized electrical resistivity of $Fe_{0.97}Cu_{0.04}Se$ at different pressures. The data are normalized to the value at 50K. The inset shows the normalized resistivity over a wider temperature range at ambient pressure and at 3.7 GPa. The transition from semiconducting to metallic behavior with pressure is illustrated. The data at ambient pressure were taken from[8].

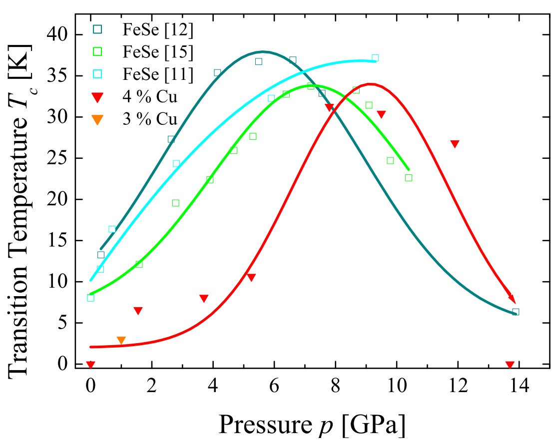

FIG. 3. T_c versus pressure for $Fe_{0.97}Cu_{0.04}Se$ and FeSe. Since the pressure dependence of FeSe varies in the literature, data from three different publications were added for better comparison. The data were taken from[11,12,15].

plies the restoration of the specific important features of the undoped compound that had been disrupted by Cu doping. In the low Cu regime we argue that the character of disruption is almost purely geometrical. There can be little smearing of energy bands due to random disorder from very small amounts of Cu, and the increase of the Fermi energy must be very small. Cu doping decreases c and increases a, so the applied pressure, which decreases both lattice parameters c and a effectively compensates the effect of Cu doping on the a parameter. We attribute the restoration of the superconductivity to this geometrical effect.

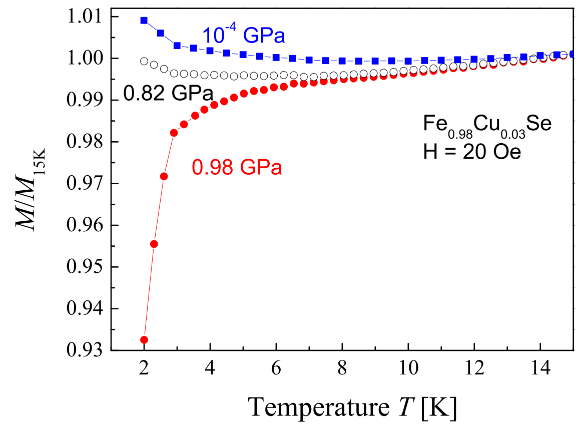

FIG. 4. Susceptibility measurement of $Fe_{0.98}Cu_{0.03}Se$ at different pressures. The slope changes at 1 GPa.

Calculations have indicated that an increase of the in-plane lattice parameter a in Cu-doped FeSe should cause a localization of the magnetic moments associated with the Fe atoms, which has been proposed as the reason for the disappearance of superconductivity at such low doping levels[10]. Mößbauer spectroscopy shows that Cu-doping does indeed cause the appearance of a magnetic component in the Mößbauer spectrum[8], which can be interpreted as being due to either the formation of a spin glass or the development of long lived magnetic fluctuations, consistent with this picture. Because applied pressure decreases the lattice parameter a in Cu-doped FeSe, the reappearance of superconductivity under pressure is consistent with the overall understanding of this phase: our observation that a decrease in the static susceptibility accompanies the appearance of T_c supports the theoretical picture that magnetism and superconductivity compete as a function of in-plane lattice size in FeSe.

In summary we have observed the restoration of superconductivity in Cu doped FeSe under pressure. This result is distinct from prior experiments on pressure-induced superconductivity in $SrFe_2As_2$ and $BaFe_2As_2$[19], because superconductivity was first suppressed with doping and then restored with pressure in the current case, whereas in the 122 compounds, initially nonsuperconducting materials were made superconducting under pressure. An increase of the lattice parameter a accompanies the suppression of the superconductivity at low Cu-doping levels in FeSe, and calculations attribute the disappearance of the superconductivity to the enhancement of magnetism with increased lattice parameter. We have shown that pressure brings the in-plane lattice parameter a to its original size, suppresses the static susceptibility and stabilizes superconductivity, consistent with the theoretical picture. It may be of interest to examine other iron arsenide superconductors in their non-superconducting composition regimes to determine whether their superconducting properties are as sensitive to lattice size as has been found here, or whether FeSe again represents a special case among iron pnictide superconductors due to the near instability of its superconducting state.

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