Pressure Effects on Superconductivity and Magnetism in FeSe$_{1-x}$Te$_x$

Chien-Lung HUANG, Chih-Chieh CHOU, Kuo-Feng TSENG, Yi-Lin HUANG$^1$, Fong-Chi HSU$^1$, Kuo-Wei YEH$^1$, Mau-Kuen WU$^1$, and Hung-Duen YANG$^*$

Department of Physics, Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung 804, Taiwan

$^1$Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan

(Received May 14, 2009; accepted May 27, 2009; published July 27, 2009)

The pressure ($P$) dependence of AC susceptibility and electrical resistivity of FeSe$_{0.88}$ and FeSe$_{0.5}$Te$_{0.5}$ has been studied. The superconducting transition temperature ($T_c$) of FeSe$_{0.5}$Te$_{0.5}$ is found to be more sensitive to $P$ than it is in FeSe$_{0.88}$, which is believed to arise from the strongly distorted structure. The enhancement of $T_c$ by $P$ is mainly attributed to an increase of density of states, which implies that the superconductivity in FeSe$_{1-x}$Te$_x$ favors pairing mechanism in the context of strong-coupling BCS theory.

KEYWORDS: iron-based superconductor, FeSe, pressure effect, electrical resistivity, AC susceptibility

DOI: 10.1143/JPSJ.78.084710

1. Introduction

Recently, the newly discovered superconductor LaFeAsO$_{1-\delta}$F$_{\delta}$ (1111),$^{1,2}$ with a relatively high $T_c$ of 26 K, has sparked tremendous interest, and the substitution of La by other lanthanoids (Ce,$^3$ Nd,$^3$ Sm,$^4$,$^5$) and the fluorine-free Gd$_{1-\delta}$Th$_{\delta}$FeAsO$_6$ quickly raised the $T_c$ up to 56 K. There are three impressive features in iron-based superconductors: (1) among the non-cuprate superconductors, this series has the highest $T_c$ which exceeds the predicted limit of BCS theory, (2) the FeAs and LaO both form into alternating layered structure analogous to the CuO or CuO$_2$ layers in cuprate superconductors, and (3) the Fe ion, which has strong short-range magnetic coupling, is commonly thought to be antagonistic to superconductivity. However, defying the traditional wisdom, not only is Fe a key element in 1111 compound, it is essential in the occurrence of superconductivity that might couple with the spin fluctuations in the normal state or they coexist even below $T_c$. Spin-density-wave (SDW) and magnetic ordering seem to coexist and compete with the superconducting state.$^6$$^8$ No sooner had the 1111 superconductors been discovered, superconductivity in (Ba,Sr)$_{1-x}$K$_x$Fe$_2$As$_2$,$^{9,12}$ (122) and the ternary LiFeAs$^{13}$ was also reported, and all these have led to a surge of related publications.

Very recently, the binary FeSe$_{1-x}$ was found to also be superconducting, and Se deficiency is necessary for stabilizing the superconducting phase.$^{14}$ FeSe$_{1-x}$ has attracted a lot of attention because of its simple structure similar to the Fe–As layers in 1111 and 122 series. It is understood that the Fe–As layer plays a key role for superconductivity in Fe–As superconductors, and therefore studying physical properties of FeSe$_{1-x}$ thus will be helpful in clarifying the underlying physics of the iron-based superconductors. The pressure effect, furthermore, is a simple yet powerful tool to investigate the superconducting properties by varying the primary parameters without doping, which may introduce complicating atomic disorder: the electronic density of states at the Fermi energy, $N(E_F)$, phonon frequency, and electron–phonon coupling constant. In the pressure range of present work, there are indeed pressure-effect studies on the FeSe$_{1-x}$ superconductors,$^{15,16}$ however, none of them alluded to the pairing mechanism. In this work, based on the pressure dependence of $T_c$, we found the superconductivity of FeSe$_{0.88}$ could be explained in the context of BCS theory within the strong-coupling regime. In addition, as mentioned previously, Se deficiency stabilizes the superconducting phase in FeSe$_{1-x}$. The Te substitution for Se in FeSe has the similar scenario with enhanced $T_c$ though the reason is not yet clear.$^{17,18}$ However, the widened range of stoichiometry in the Fe–Se systems provides a broader scope to examine the origin of superconductivity. As the $T_c$ increased in FeSe$_{1-x}$Te$_x$ reaches a maximum at $x \sim 0.5$,$^{17,18}$ we further studied the pressure effects on optimally-doped FeSe$_{0.5}$Te$_{0.5}$ to see how a varied stoichiometry such as that in FeSe$_{1-x}$Te$_x$ changes its superconductivity.

2. Experimental

The polycrystalline samples of FeSe$_{0.88}$, FeSe$_{0.5}$Te$_{0.5}$ were prepared by a solid reaction method. The detailed synthesis procedure has been described elsewhere.$^{14,17}$ The AC susceptibility under pressure was measured by a homemade BeCu piston–cylinder type cell.$^{19}$ The sample was placed in a Teflon cell with 3M Fluroinert FC-77 as a pressure-transmitting medium. We measure the $T_c$ of lead as a pressure gauge. The sample sizes were made as small as approximately 1 mm$^3$ for the sake of reducing the pressure inhomogeneity across the samples. The temperature changing rate was set at 0.2 K/min to ensure good thermal equilibrium before data taking. Each measurement included several cooling and warming cycles near $T_c$, in which repeatability of the data guaranteed negligible temperature gradient. The pressure dependence of resistivity measurements were performed with a physical property measurement system (Quantum Design). A standard four-probe method was applied with AC current $I = 10$ mA (rms) and frequency $f = 30$ Hz. Pressure was determined by measuring the resistivity of a Sn manometer located in the vicinity of sample. Both of which are merged in Pentane as the pressure-transmitted medium.

3. Result and Discussion

Figure 1 presents temperature dependent AC susceptibility of FeSe$_{0.88}$ and FeSe$_{0.5}$Te$_{0.5}$ under hydrostatic pressure.
At ambient pressure, $T_c^{\text{mag}}$ ($T_c$ as determined by magnetic susceptibility) of FeSe$_{0.88}$ and FeSe$_{0.5}$Te$_{0.5}$ are 8.69 and 8.47 K, respectively. The broad superconducting transition probably implies the sample inhomogeneity, which makes precise determination of $T_c$ a challenge, but in general, the $T_c^{\text{mag}}$ values are lower than those reported in refs. 15, 17, 18 based on resistivity measurement. Both samples show positive pressure coefficients $dT_c^{\text{mag}}/dP$, as shown in Fig. 2, though with different trends. The $T_c^{\text{mag}}$ of FeSe$_{0.88}$ increases moldly with pressure, consistent with previous reports, while the $T_c^{\text{mag}}$ of FeSe$_{0.5}$Te$_{0.5}$ increases sharply at low pressure and then gradually saturates above $P \sim 16$ kbar [see Fig. 3(b)]. The initial pressure coefficient $dT_c^{\text{mag}}/dP$ is 1.47 K/kbar for FeSe$_{0.5}$Te$_{0.5}$, which is much larger than that for FeSe$_{0.88}$, where $dT_c^{\text{mag}}/dP \sim 8.36 \times 10^{-2}$ K/kbar. Such a huge difference probably results from the more distorted lattice for the Te doped sample under pressure, because the c-axis length of the Te doped sample is larger than that of the undoped sample.\(^{17}\) Mizuguchi et al. reported a 27 K superconducting transition for FeSe at 14.8 kbar and $dT_c/dP \sim 9.1 \times 10^{-1}$ K/kbar,\(^{15}\) and Li et al. reported $dT_c/dP \sim 4 \times 10^{-1}$ K/kbar for FeSe$_{0.88}$.\(^{16}\) The discrepancy between these values and present work may be rooted in the variation of stoichiometry of the FeSe$_x$ (not addressed in ref. 15). Moreover, traceable Fe impurity, which contributes a positive background in the susceptibility data,\(^{14-16,20}\) may also have contributed to the differences.

Superconductivity was often expected to be correlated with the suppression of SDW ordering, and indeed, in some 1111 and 122 compounds, the SDW ordering can be suppressed by doping, such as in NdFeAsO$_{1-x}$F$_x$.\(^{3}\)
Ba$_{1-x}$K$_x$Fe$_2$As$_2$,\cite{30} or by pressure, such as in LaFeAsO\cite{21} and SrFe$_2$As$_2$,\cite{22} and superconductivity does emerge in both cases. However, there are also other inconsistent reports showing no superconducting transition down to $T = 5\,\text{K}$, leaving this an open question for future work.\cite{22,33} For the binary Fe–Se systems, to be considered as a fundamental structural unit of the more complex Fe-based superconductors, one would be curious about their superconducting pairing mechanism. On the one hand, to be specific, if the superconductivity of FeSe$_{0.88}$ is truly related to spin instabilities, a positive pressure coefficient would be expected on an unconventional superconducting basis. On the other hand, as we have argued previously, a slight structure distortion could be responsible for the larger pressure coefficient of FeSe$_{0.5}$Te$_{0.5}$ due to the larger atomic size of Te, which seems plausible that the superconductivity in FeSe$_{0.88}$ may be associated with the crystal lattice vibration, i.e., the phonons. To further investigate this issue, we analyze the data by applying the McMillan theory,\cite{25} underlying which is the phonon-mediated superconductivity, to see whether the BCS theory can account for the pairing mechanism in FeSe$_{0.88}$.

From the McMillan equation, $T_c$ can be described as

$$T_c = \left(\frac{\theta_D}{1.45}\right) \exp\left[\frac{1.04(1 + x)}{\lambda - \mu^*(1 + 0.62\lambda)}\right]$$

(1)

where $\theta_D$ is the Debye temperature, $\mu^*$ is the Coulomb pseudopotential, and $\lambda$ is the electron–phonon coupling constant given by

$$\lambda = \frac{N(E_F)(\langle \omega^2 \rangle)}{M(\langle \omega^2 \rangle)}$$

(2)

($\langle \omega^2 \rangle$ being the averaged square electronic matrix element of electron–phonon interactions, $M$ the atomic mass, and $\langle \omega^2 \rangle$ the averaged square of phonon frequency. From eq. (1), in principle, we can determine the sign of $d\theta_D/dP$ according to the variation of $\theta_D$ and $\lambda$ at high pressure (usually $\mu^*$ and $\langle \omega^2 \rangle$ are less pressure dependent and can be neglected), but actually $\theta_D$ and $\lambda$ are two correlated quantities. $\theta_D$, as a linear term in eq. (1), is coupled with $\lambda$, which is in turn a function of $\langle \omega^2 \rangle$ as given in eq. (2). $\theta_D$ generally increases with pressure because of phonon hardening, and therefore reduces $\lambda$. This usually leads a decrease in $T_c$. Therefore, the positive pressure coefficient for FeSe$_{0.88}$ and FeSe$_{1-x}$Te$_x$ should originate from the increase of $N(E_F)$, which enhances the electron–phonon coupling constant $\lambda$ [eq. (3)] and outweighs the lattice stiffening effect. In addition, external pressure usually causes a shift of $E_F$ and a broadening of bandwidth, both of which could also end with an increased $N(E_F)$. The same result is found in LaFeAsO$_{1-x}$F$_x$ under a pressure of 3 GPa.\cite{30} Given that $\mu^* = 0.1$ and $\theta_D = 1.88\,\text{K}$ from heat capacity measurements,\cite{13} we can calculate $\lambda \approx 0.82$ for FeSe$_{0.88}$ at ambient pressure based on eq. (1). The value is comparable with that in the strong electron–phonon coupling superconductor, such as MgC$_{11}$,\cite{35} but is inconsistent with the result ($\lambda = 0.17$) from density functional calculations.\cite{36} If we neglect the pressure dependence of $\mu^*$ and follow approximations suggested by Loa et al.,\cite{30} we can get

$$\frac{d\ln T_c}{dP} \approx C \frac{d\ln N(E_F)}{dP} + (1 - 2C) \frac{\gamma}{B_0}$$

(3)

with $C = (1.04 + 0.4\mu^*)/\lambda(1 - \mu^*(1 + 0.62\lambda))^2$. Assuming the Grüneisen parameter $\gamma \approx 1$, bulk modulus $B_0 = 320\,\text{kbarr}$,\cite{30} and $d\ln N(E_F)/dP = 9.3 \times 10^{-3}\,(\text{eV}\cdot\text{kbarr})^{-1}$ from the present work, we obtain an increase of $N(E_F)$ with $P$, $d\ln N(E_F)/dP$, of $9.37 \times 10^{-3}\,(\text{eV}\cdot\text{kbarr})^{-1}$ for FeSe$_{0.88}$. The order of magnitude of this value is comparable to that obtained in most superconductors (e.g., $d\ln N(E_F)/dP = 1.2 \times 10^{-3}\,(\text{eV}\cdot\text{kbarr})^{-1}$ for a strong-coupling BCS superconductor $\gamma = 2$\cite{37}). Hence, the superconductivity in FeSe$_{0.88}$ can be explained in the framework of the strong-coupling BCS theory, which is consistent with both a muon-spin-rotation study describing the nodeless superconductivity in FeSe$_{0.88}$\cite{38} and a specific heat study in FeSe$_{0.5}$Te$_{0.5}$.\cite{33} However, our results are inconsistent with the NMR study which suggested unconventional superconductivity.\cite{39} If the extended $s_d$-wave symmetry, as applied to Fe pnictide superconductors, can indeed describe the pairing mechanism in FeSe$_{1-x}$Te$_x$, such a disagreement can be reconciled.\cite{40}

Furthermore, we have also performed transport measurements under pressure for the FeSe$_{0.5}$Te$_{0.5}$. Figure 3(a) shows the resistivity data from $T = 1.8$ to $300\,\text{K}$ at $P = 1\,\text{bar}$, 0.22, 12.7, 18.6, and 25.3 kbar. Upon applying pressure, the distorted structure seems to gradually get aligned, resulting in a decrease in resistivity. The grain boundary effect might be appreciable in our samples and can be reduced with applying pressure. Dissimilar to the results of FeSe presented by Mizuguchi et al.,\cite{15} the normal state of FeSe$_{0.5}$– Te$_{0.5}$ shows semiconducting behavior at low pressure, then undergoes a gradual change to metal-like behavior as the pressure increases. Although the reason for such a semiconductor–metal transition is intriguing, more work is necessary to better understand it as it is not clear if this transition would persist in single crystals. In addition, the data at ambient pressure is incompatible with the result from ref. 18 showing metallic behavior. This may be accounted for by an uncertainty in the stoichiometry.\cite{20} The resistivity $\rho_N$ at $T_c$ onset is plotted as a function of $P$ in Fig. 3(b). Interestingly, $\rho_N(P)$ and $T_{c_{\text{res}}}(P)$ appear to be correlated, that is, as $P$ increases, the decrease in $\rho_N$ and increases in $T_{c_{\text{res}}}$ both tend to taper off. A smaller $\rho_N$ may have been an indicator of better sample perfection, which hence favors higher $T_c$, consistent with the results from a single-crystal-synthesis study.\cite{33} The pressure dependence of $T_{c_{\text{res}}}$ ($T_c$ as determined by resistivity) of FeSe$_{0.5}$Te$_{0.5}$ is plotted in Fig. 3(b) along with $T_{c_{\text{mag}}}$. The $T_{c_{\text{res}}}$ is determined by the midpoint of the transition, with the transition width defined by the 90–10% drop of resistivity. Values of $T_{c_{\text{res}}}$ and $T_{c_{\text{mag}}}$ are different partly due to the inhomogeneous sample stoichiometry and use of different methods to determine the $T_c$. The optimal $T_{c_{\text{res}}}$ of 20 K occurred at $P \sim 19\,\text{kbar}$, above which the $T_{c_{\text{res}}}$ decreased to 19.6 K at $P = 25.3\,\text{kbar}$.

There are two possible scenarios for the behavior of $T_{c_{\text{res}}}(P)$: (1) at low pressure, the grains in the samples are tightly packed, hence showing a higher $T_c$. At modest pressure, an increase of $N(E_F)$ or shift of $E_F$ would further enhance the superconductivity, but as the pressure continues to rise, the lattice stiffening effect comes in to weigh down the $T_c$, or (2) the FeSe$_{0.5}$Te$_{0.5}$ undergoes a structure transition at $P \sim 19\,\text{kbar}$, which either enhances the lattice stiffening effect or leads to a high-pressure phase that favors non-superconductivity, hence gives a decreased $T_c$. Recently,
several groups have reported that FeSe would reach its maximal $T_c \sim 33-37$ K at $P \sim 70-100$ kbar, but the $T_c$ would then decrease as $P$ further increases, wherein the FeSe undergoes a partial phase transition from a superconducting tetragonal structure to a non-superconducting hexagonal structure.\textsuperscript{36-38} These results are inconsistent with other studies reporting either the absence of superconductivity\textsuperscript{39} or enhanced $T_c$ under high pressure.\textsuperscript{40} While further works are necessary, we believe FeSe$_{0.5}$Te$_{0.5}$ has a more distorted lattice than that of FeSe, and thus could exhibit more structural instability, i.e. the structural phase transition may occur at a pressure that is lower in FeSe$_{0.5}$Te$_{0.5}$ than in FeSe. To address this issue, an analysis of structures under pressure in single crystalline FeSe$_{0.5}$Te$_{0.5}$ would be helpful.

4. Summary

To summarize, the pressure-dependent AC susceptibility and resistivity measurements on FeSe$_{0.88}$ and FeSe$_{0.5}$Te$_{0.5}$ have been performed. The larger pressure coefficient is found in FeSe$_{0.5}$Te$_{0.5}$, believed to arise from the more distorted lattices as compared to those in FeSe$_{0.88}$. From the McMillan theory, we argue that the positive pressure coefficients indicate an increase of $N(E_F)$ as pressure is applied, suggesting that a phonon mediated mechanism can well describe the superconductivity for FeSe$_{1-x}$Te$_x$. Finally, the normal-state resistivity data exhibit a semiconductor-metal transition when under pressure, but the exact nature for the transition demands further investigation, as we are not certain if the same phenomenon would persist in single crystalline samples.

Acknowledgments

The authors acknowledge Professor W. N. Mei and Professor Quark Chen for fruitful discussions. C.L.H. thanks Professor Y. Uwatoko and Dr. K. Matsubayashi for their hospitality during his visit to the University of Tokyo and helpful discussions on high pressure experiments. This work was supported by the National Science Council of Taiwan under Grant Nos. NSC 96-2112-M-110-001 and NSC 97-2112-M-110-005-MY3.