Effect of Co Impurities on Superconductivity of FeSe$_{0.4}$Te$_{0.6}$ Single Crystals

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The effect of Co doping on the superconductivity of FeSe$_{0.4}$Te$_{0.6}$ single crystals is investigated. The superconducting transition temperature decreases linearly for Co doping at a rate of $-0.75$ K/(Co %). On the other hand, the increase in residual resistivity is less than 50 $\mu$cm for 4% Co doping. These data are consistent with the interband scattering mechanism of superconductivity with the sign change ($s_\pm$ symmetry).

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1. Introduction

Fe-based superconductors$^{1,2}$ have attracted much attention from condensed-matter physicists and chemists since Fe, which is “the representative” of magnetic atoms, occupies the most essential part of the crystal structure and plays the dominant role in the emergence of 50 K class superconductivity. Soon, it was found both theoretically$^3$ and experimentally$^4$ that many Fe bands contribute to superconductivity, and the mechanism of superconductivity for such a novel type of multiply gapped superconductor is of central importance. Mechanisms based on spin fluctuation, where the interband anti-ferromagnetic scattering between hole bands around the $\Gamma$ point and electron bands around the M point plays an essential role, favor the condensate wave function with the so-called $s_\pm$ symmetry.$^7,8,10$ On the other hand, mechanisms based on the orbital fluctuation favor the $s_{++}$ symmetry with the same sign of the order parameter for both hole bands and electron bands. The absence of coherence enhancement in the temperature dependence of spin relaxation rate$^{2,11}$ and microwave conductivity$^{12-15}$ in many materials suggests the sign-changing $s_\pm$ wave. A more detailed study of the coherence factor by scanning tunneling microscopy (STM) in FeSe$_{1-x}$Te$_x$ (the so-called 11 material)$^{16}$ also suggests the presence of the $s_\pm$ wave definitely. However, a neutron scattering experiment$^{17}$ and its interpretation,$^{18}$ and an investigation of the impurity effect$^{19}$ suggest the presence of the $s_{++}$ wave. There have been many studies on the disorder effect,$^{20-24}$ whose results are complicated and there is no consensus on the possible pairing mechanisms, so far as the pair breaking effect is concerned.

For instance, a Co doping study of the 1111 material showed that $T_c$ decreases by 12 K when Co is substituted by 5%. According to a theoretical estimation,$^{25}$ only the doping of impurities by 1% is expected to destroy superconductivity completely when the impurity potential is high in the case of the $s_\pm$ wave. This seems to be in strong contradiction to experimental results. However, even in the $s_\pm$ scenario, the decreasing rate of $T_c$ can become comparable to the experimentally observed rate, when the impurity potential is very low. To check impurity potential, one of the most important measurable quantities is residual resistivity. Thus, for the discussion of the symmetry of the condensate wave function in terms of the pair-breaking effect, it is crucially important to discuss the decrease in $T_c$ and the increase in residual resistivity, simultaneously. Regarding this, in the experiments on polycrystalline samples$^{19-21}$ a high additional resistivity at the grain boundary masks the intrinsic behavior of residual resistivity. In addition, the effect of impurities in the 1111 material, where 5 elements exists in the sample other than the intentionally doped impurities, might be very complicated.

Recently, studies of the effect of impurities (disorders) using single crystals of the 122 material have been conducted.$^{22-24}$ Although all of these studies showed a considerable decrease in $T_c$ with small amounts of disorders, their conclusions were different. In addition, a recent theoretical re-investigation of the effect of disorders$^{26}$ suggests that there is a transition from the $s_\pm$ state to the $s_++$ state with increasing amount of disorders. Thus, there is almost no consensus on the effect of disorders on Fe-based superconductors, both experimentally and theoretically. Thus, we focus on the simplest material among Fe-based superconductor family members, the so-called 11-type chalcogenide, Fe(Se,Te).$^{27}$ This material has $T_c$ values of 14–15 K in a bulk form. By preparing good films,$^{28,29}$ we can increase $T_c$ up to 16$^{30}$ to 20 K$^{31}$ We have prepared a series of single crystals of Fe$_{1-x}$Co$_x$Se$_{0.4}$Te$_{0.6}$ with $x = 0, 1, 2,$ and 4%, and investigated how superconductivity changes with $x$, together with residual resistivity. Our results are consistent with $s_\pm$ pairing, which suggest that the spin-fluctuation mechanism with interband scattering is the appropriate description of superconductivity in Fe chalcogenides.

2. Experimental Methods

Prior to the single crystal study, we investigated the series of substitution studies of the polycrystalline samples of Fe 11 materials for Cr, Mn, Co, Ni, Ru, Pd, Pt, and Ir, and found that Co did substitute the Fe site. Thus, we chose Co as the representative in the substitution study.

Single crystals of Fe$_{1-x}$Co$_x$Se$_{0.4}$Te$_{0.6}$ with $x = 0, 1, 2,$ and 4% were prepared by a method described elsewhere.$^{15}$ Composition analysis by the energy dispersive X-ray spectroscopy (EDX) method revealed that the samples with the nominal composition of Fe : Se : Te : Co = 0.98 : 0.4 : 0.6 : 0.02 show the actual ratio of Fe : Se : Te : Co = 1 : 0.32 : 0.64 : 0.03. Considering the possible measurement errors in the EDX method, the result shows that Co substitutes the Fe site with almost the same amount as the nominal one. One delicate issue is that the material has two different Fe sites, and the above EDX result does not give us any detailed information on these. An exact experi-
mental estimation of the amount of Fe atoms for each site is very difficult. In general, however, if a change in the distribution of Fe atoms among these two different sites affects \( T_c \), it should accompany a large change in resistivity (both magnitude and temperature dependence), which was not observed in our experiment, as will be shown below. Thus, we believe that the change in the Fe distribution between the two different sites is negligible, or at least, is small so that the main conclusion of the paper is not affected at all.

Lattice constants were measured using an X-ray diffractometer. DC resistivity was measured by the four-probe method. To obtain good reproducibility, the use of Au paste (Tokuriki 8560) was found to be crucial. Superconductivity was also checked by measuring dc magnetization using a superconducting quantum interference device (SQUID) magnetometer.

### 3. Results

Figure 1 shows the \( a \)- and \( c \)-axis lattice constants as a function of Co doping up to 4%. Very slight changes in \( a \) and \( c \) parameters suggest that the possible change of carrier concentrations by the introduction of Co is very small (almost negligible).\(^{32}\)

Figure 2 shows the temperature dependence of the dc susceptibility of the samples with \( x = 0, 1, 2, \) and 4%. Both zero-field cooled data and field cooled data are shown.

Figure 3 shows the temperature dependence of dc resistivity of four different pieces of the \( x = 1\% \) sample. The inset shows the enlarged plot around \( T_c \).

Figure 4 shows the temperature dependence of dc resistivity of samples at different Co concentrations \( (x = 0, 1, 2, \text{and } 4\%) \). Within this range of Co concentrations, the temperature dependence of resistivity is almost the same. This suggests that Co behaves as nonmagnetic impurities. With further Co doping, the resistivity shows an upturn at the lowest temperatures. Thus, we will discuss the Co doping effect within the Co concentration range shown in Fig. 4.

From the data in Figs. 2 and 4, we plotted the superconducting transition temperature \( T_c \) as a function of Co concentration in Fig. 5. \( T_c \) was found to decrease almost linearly, with the rate \( dT_c/dx = -0.75 \text{K/(Co \%)} \). We also obtained almost the same result in polycrystals, so far as the decrease in \( T_c \) is concerned.
The above results show that \( T_c \) decreases with Co doping. For each concentration, error bars come from the scattering of the measured resistivity among four crystals with the same Co content. From this data, the maximum possible increase in \( \rho_0 \) is found to be 50 \( \mu \Omega \text{cm} \) for 4\% Co doping [12.5 \( \mu \Omega \text{cm}/(\text{Co } \%) \)].

4. Discussion

The above results show that \( T_c \) decreases with Co doping. It is well established that superconductivity is robust for nonmagnetic disorders for conventional s-wave superconductivity. Magnetic disorders alone affect superconductivity, leading to the decrease in \( T_c \). However, as was already mentioned, Co is considered to behave as a non-magnetic disorder in these materials. Thus, we do not expect the decrease in \( T_c \) by 3 K for only 4\% Co doping by the pair-breaking effect. Even in the case of nonmagnetic disorders, a slight decrease in \( T_c \) is expected for two-dimensional superconductors when one takes into account the weak localization effect. In this case, however, there must be a change in the temperature dependence of resistivity at low temperatures. This is not the case for our present data. Essential physics should be the same even for multiband superconductors with the same sign of the superconducting gaps for all Fermi surfaces. It should also be considered that the two-dimensional nature is rather weak in the 11 material. Thus, in any case, our results are difficult to understand in terms of the so-called \( s_{++} \) wave pairing, unless carrier concentration changes largely even in the case of a very small Co substitution, which might cause the decrease in \( T_c \). However, for \( T_c \) to be decreased by the change in carrier concentration in the Fe(Se,Te) system, this is accompanied by a large change (increase) in resistivity. Therefore, it is unlikely that the change in \( T_c \) shown here is caused by the change in carrier concentration.

An alternative possibility is the pair-breaking effect in superconductors with \( s_{\pm} \) pairing. In the \( s_{\pm} \) pairing, the interband scattering is strongly affected by the presence of disorders, leading to a very rapid decrease in \( T_c \) with even a very small amount of disorders. Even nonmagnetic disorders play the same role as the magnetic impurities in conventional (or \( s_{++} \)) superconductors. We check this possibility quantitatively, using our resistivity data. According to Kontani, when one takes the effective mass ration as \( m^*/m = 10 \), the ration of the change in \( T_c \) to the change in residual resistivity, \( \Delta T_c/\Delta \rho_0 \), is about \(-0.3 \text{K}/(\mu \Omega \text{cm})\). Thus, we expected that the increase in residual resistivity to Co concentration is 3 \( \mu \Omega \text{cm}/(\text{Co } \%) \), which we plotted in Fig. 6 as a straight line. Our results do not contradict the expectation for the \( s_{\pm} \) pairing, in contrast to the argument in ref. 19. The reason for the difference in the conclusion is that our data are obtained from single crystals, which are free from the additional resistivity generated at grain boundaries characteristic of polycrystals.

Indeed, the microwave conductivity data for the same material showed that low-temperature penetration depth shows the \( T^2 \) behavior, meaning that there are a large number of disorders even in Co-free materials. This is also consistent with the \( s_{\pm} \) scenario.

5. Conclusions

The effect of Co doping on the superconductivity of FeSe\(_0.5\)/Te\(_{0.5}\) single crystals is investigated. The superconducting transition temperature decreases linearly for Co doping at a rate of \(-0.75 \text{K}/(\text{Co } \%) \). On the other hand, the residual resistivity increase is less than 50 \( \mu \Omega \text{cm} \) for 4\% Co doping. These data are consistent with the interband scattering mechanism of superconductivity with the sign change (\( s_{\pm} \) symmetry).

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