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# Effects on superconductivity of transition-metal doping in $\text{FeSe}_{0.5}\text{Te}_{0.5}$

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## Abstract

We investigate superconductivity in the compound  $\text{FeSe}_{0.5}\text{Te}_{0.5}$  and in its transition-metal-substituted derivatives  $\text{Fe}_{1-x}\text{TM}_x\text{Se}_{0.5}\text{Te}_{0.5}$ , where  $x = 5\%$  and the substituent ions studied were Mn, Co, Ni, Cu and Zn. Electronic and magnetic measurements indicate that doping with Mn or by Co acts respectively to cause a slight enhancement or suppression of the transition temperature. However, doping with this concentration of Ni or Cu destroys the superconductivity completely, and leads to semiconducting behaviour. Zn ions cannot be incorporated properly into the parent compound. The reasons for these contrasting effects are associated with the differing magnetic properties of the substituent ions, which determine their local impurity moments and the net carrier concentrations in the doped 11 system. The effects of magnetic ion substitution on superconductivity suggest that the pairing symmetry may not be either pure s wave or pure d wave.

(Some figures in this article are in colour only in the electronic version)

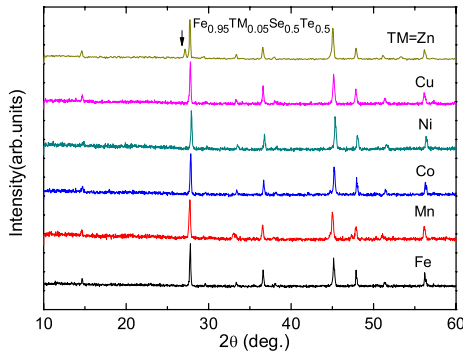
## 1. Introduction

The discovery of superconductivity with a transition temperature ( $T_c$ ) of 26 K in the ZrCuSiAs-type system  $\text{LaFeAsO}_{1-x}\text{F}_x$  was a major surprise which precipitated much research activity in the field [1]. These '1111' FeAs-based superconductors were found to give a maximum  $T_c$  of 55 K on appropriate rare-earth ion substitution, a value comparable to those for cuprate superconductors [2–6]. As part of this extensive investigation,  $\text{BaFe}_2\text{As}_2$  (the '122' system) was quickly found to be superconducting with a maximum  $T_c$  of 38 K when doped with potassium or cobalt [7]. Because single crystals of the 122 compounds are easier to synthesize, many intrinsic properties of the Fe-based superconductors have been studied in this system. A further breakthrough in the understanding of ferropnictide materials came with the synthesis of superconducting  $\text{Li}_{1-x}\text{FeAs}$  (the '111' system) [8].

The common foundation for all of the above Fe superconductors is the FeAs layer. However, fundamental research and potential applications of these materials may be limited by the presence of the poisonous element As. Thus the discovery of superconductivity in the As-free Fe(Se, Te) compound (the '11' system) constitutes exciting progress [9]. Many experiments indicate that the electronic and magnetic

properties of the 11 system are similar to those of FeAs-based materials, except that  $T_c$  is lower: the maximum  $T_c$  in the 11 series is approximately 15 K at ambient pressure, which is realized in  $\text{FeSe}_{0.5}\text{Te}_{0.5}$  [10]. However, this transition temperature can be raised dramatically by applying pressure, reaching 27 K in  $\text{FeSe}_{0.82}$  at 1.48 GPa [11], which indicates an important role for the pressure in controlling the electronic properties and superconductivity of the 11 system. Ion substitution is a convenient technique for generating effective internal 'chemical' pressure, which has been exploited widely in the 1111 system and in cuprate superconductors [12, 13]. The effect of chemical pressure has been studied in 11 systems by means of Se-site substitution [10]. From among the variety of possible substitutions, transition-metal (TM) ion substitution at the Fe site is the most informative as regards questions such as the pairing symmetry and the nature of the low-energy excitations.

Systematic studies of TM ion substitution in  $\text{FeSe}_{0.85}$  have been reported recently [14]. When the doping exceeds 3%, superconductivity can be sustained only in Mn-doped samples, whereas increasing doping with other transition-metal substituents was found to cause semiconducting behaviour. Separately, it has also been reported that 4% Cu doping drives a metal–insulator transition in  $\text{FeSe}_{0.85}$  [14].



**Figure 1.** X-ray powder diffraction patterns for  $\text{Fe}_{0.95}\text{TM}_{0.05}\text{Se}_{0.5}\text{Te}_{0.5}$  (TM = Mn, Fe, Co, Ni, Cu, Zn). The arrow marks the impurity phase ZnSe.

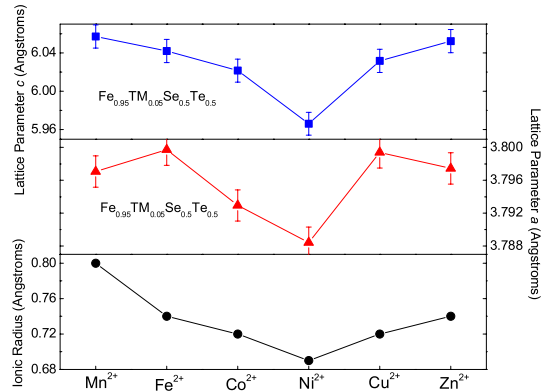
We have studied the effects of TM ion substitution on the electronic properties and superconductivity of  $\text{FeSe}_{0.5}\text{Te}_{0.5}$ , which is the 11 compound with the highest  $T_c$  value, 14.5 K. Our measurements indicate that superconductivity is maintained at 5% doping with both Mn and Co, with Mn ions even leading to a slight  $T_c$  enhancement. By contrast, samples with Ni and Cu dopants exhibit a semiconducting resistivity, while Zn ions simply cannot be incorporated into the parent compound. These results suggest that doping with TM ions in  $\text{FeSe}_{0.5}\text{Te}_{0.5}$  cannot be considered as a simple isovalent substitution. We compare our results with those for other Fe pnictides in order to discuss possible mechanisms for these effects, focusing on the impurity local moments and net carrier concentrations. The former in particular have an important role in determining the evolution of the electronic properties.

## 2. Experiments

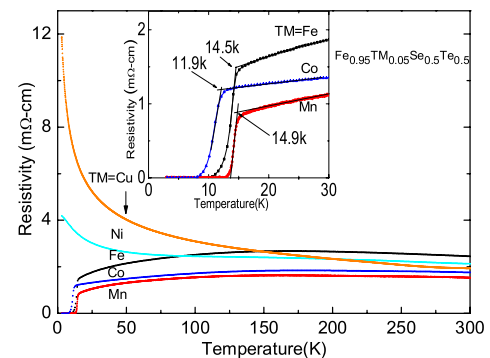
Polycrystalline samples of  $\text{Fe}_{0.95}\text{TM}_{0.05}\text{Se}_{0.5}\text{Te}_{0.5}$  (TM = Mn, Fe, Co, Ni, Cu, Zn) were prepared by solid-state reaction. Powders of Fe (99.99% purity), Se (99.9999% purity) and Te (99.9999% purity) were ground and mixed with the nominal stoichiometry. The fully mixed powder was cold-pressed into discs under a uniaxial pressure of 10 MPa, then sealed in an evacuated quartz tube at a pressure of less than  $10^{-2}$  Torr and annealed at 600 °C for 25 h. The bulk products were then reground into fine powder and re-pressed, sealed and subsequently sintered at 650 °C for a further 25 h. Structural characterization of the  $\text{Fe}_{0.95}\text{TM}_{0.05}\text{Se}_{0.5}\text{Te}_{0.5}$  powder samples was performed using an x-ray diffractometer with Cu  $K\alpha$  radiation generated at 35 kV and 25 mA. Resistivity measurements were made using a Quantum Design Physical Property Measurement System (PPMS), using the standard four-probe method with silver paste for the contacts. DC magnetic susceptibility measurements were conducted with the PPMS vibrating sample magnetometer (VSM).

## 3. Results and analysis

Powder x-ray diffraction patterns for all the samples  $\text{Fe}_{0.95}\text{TM}_{0.05}\text{Se}_{0.5}\text{Te}_{0.5}$  (TM = Mn, Fe, Co, Ni, Cu, Zn) are



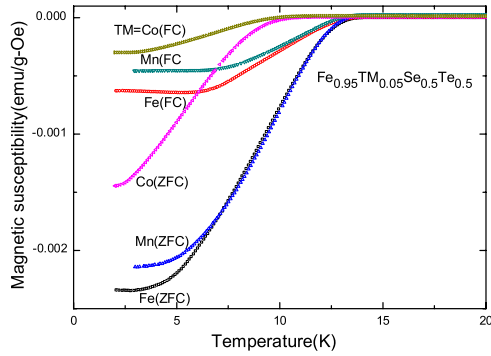
**Figure 2.** Lattice parameters for  $\text{Fe}_{0.95}\text{TM}_{0.05}\text{Se}_{0.5}\text{Te}_{0.5}$  (TM = Mn, Fe, Co, Ni, Cu, Zn). The ionic radii for the valence state 2+ are shown in the lower panel for comparison.



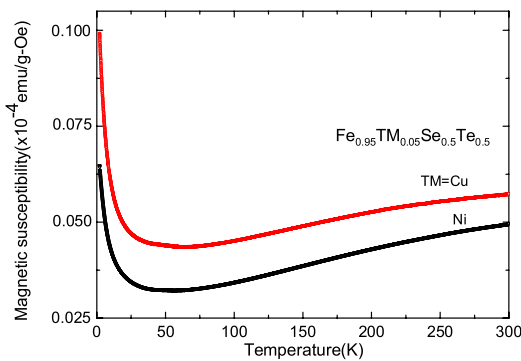
**Figure 3.** Temperature-dependent resistivities for  $\text{Fe}_{0.95}\text{TM}_{0.05}\text{Se}_{0.5}\text{Te}_{0.5}$  (TM = Mn, Fe, Co, Ni, Cu, Zn) samples. Inset: magnification near the superconducting transition temperatures. Note that the transition temperatures are taken from the extrapolated intersection of the low- and high-temperature sides.

shown in figure 1. All of the patterns are well described in terms of the tetragonal PbO-type structure. Apart from the Zn-doped sample, all of the others show no signature of secondary phases to within the limits of the resolution. The lattice parameters calculated from the diffraction data are shown in figure 2 together with the ionic radii of the substituents: the clear correspondence demonstrates that the doped ions have been properly and, from the width of the intensity peaks in figure 1, homogeneously incorporated into the host lattice. From this, in combination with the transport and magnetic measurements (below), it is safe to conclude from the data that impurity phases, if present at all, give negligible contributions. However, an obvious additional diffraction peak at  $2\theta$  26° is observed for the Zn-doped sample, which is found to be caused by ZnSe impurities. Thus Zn ions are not being doped effectively into the host system, a result consistent with [14] and to which we return below.

Figure 3 shows the temperature dependence of the resistivities. It is obvious that the behaviour of the samples with Ni and Cu doping is completely different from those of the parent compound and the Mn- and Co-doped samples. The latter three have clear superconducting transitions, which are also confirmed by the magnetic susceptibility measurements



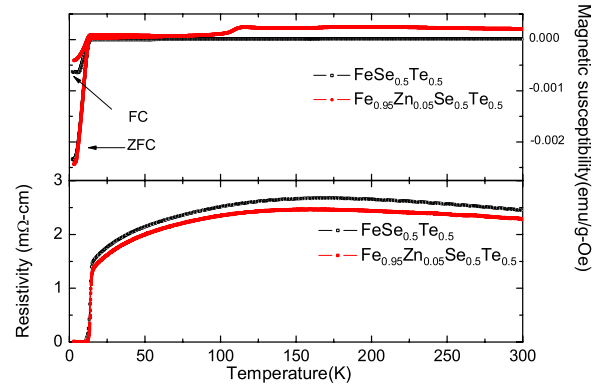
**Figure 4.** Variation with temperature of field-cooled and zero-field-cooled magnetic susceptibilities of  $\text{Fe}_{0.95}\text{TM}_{0.05}\text{Se}_{0.5}\text{Te}_{0.5}$  (TM = Mn, Fe, Co) samples, measured at a field of 100 Oe.



**Figure 5.** Variation with temperature of the magnetic susceptibility for  $\text{Fe}_{0.95}\text{Ni}_{0.05}\text{Se}_{0.5}\text{Te}_{0.5}$  and  $\text{Fe}_{0.95}\text{Cu}_{0.05}\text{Se}_{0.5}\text{Te}_{0.5}$ , measured at 2 T.

shown in figure 4. By contrast, the resistivities of the Ni- and Cu-doped samples show typical semiconducting behaviour, with respective activation energies of 1.6 and 5.7 meV. In their magnetic susceptibilities (figure 5), the nearly linear temperature dependence above 50 K is similar to that of other Fe-based systems (above), which has been described theoretically as the finite-temperature behaviour of a Heisenberg model for localized moments with nearest- and next-nearest-neighbour interactions [15]. The rapid increase with decreasing temperature below 50 K can be explained as the Curie contribution of the (uncorrelated) impurity magnetic moments.

The resistivity and magnetic susceptibility of the Zn-doped sample are presented in figure 6, with the corresponding quantities for the parent compound shown for comparison. Despite a small quantitative difference, essentially the same curvatures and transition temperatures can be seen for the two samples. Combining this with the information contained in the x-ray diffraction patterns, it appears reasonable to conclude that the Zn ions have not been incorporated into the host lattice to any effective degree. One possible reason for this result may be that ZnSe is preformed during the solid-state reaction due to the lower melting point of Zn (690 K). Another reason may be related to the absence of a magnetic moment for  $\text{Zn}^{2+}$  ions, whereas  $\text{Fe}^{2+}$  substitution by the other magnetic ions could be easier.



**Figure 6.** Temperature dependence of magnetic susceptibilities and resistivities for  $\text{FeSe}_{0.5}\text{Te}_{0.5}$  and  $\text{Fe}_{0.95}\text{Zn}_{0.05}\text{Se}_{0.5}\text{Te}_{0.5}$ . In the upper panel, which shows the magnetic susceptibilities at 100 Oe, the broad peak at approximately 115 K observed for the Zn-doped sample may originate from the impurity phase.

#### 4. Discussion

The effects of TM ion substitution on superconductivity which we find here are consistent with the results reported for other samples of 11 materials. For  $\text{FeSe}_{0.85}$ , 3% Mn doping was found to have only a slight influence on superconductivity, whereas 3% Cu doping caused complete destruction of the superconducting state and the development of semiconducting behaviour [14]. Similar results for Cu doping were also reported in  $\text{Fe}_{1.01}\text{Se}$  [16]. Somewhat surprisingly, the effects of TM substitution in FeAs superconductors are quite different from those of TM substitution in the 11 system: superconductivity is suppressed rapidly in  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$  by only a small amount of Mn doping, while  $T_c$  was not affected significantly by Zn doping [17]. Co and Zn doping have also been observed to have only a small effect on the superconductivity in LaFeAsO systems [18, 19].

We address first our result that the electronic properties of  $\text{Fe}_{0.95}\text{TM}_{0.05}\text{Se}_{0.5}\text{Te}_{0.5}$  exhibit a rather systematic evolution from superconducting to semiconducting with increasing atomic number of the TM ion. One explanation is that this evolution is caused by the effect of the local magnetic moment. An induced local moment has been estimated for in Cu-doped  $\text{Fe}_{1.01}\text{Se}$  [16], and in Mn- and Zn-doped  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$  [17], by fitting Mössbauer spectroscopy and DC magnetic susceptibility data with a Curie–Weiss law. The magnetic susceptibilities which we measure for the 11 compounds are quite similar in both magnitude and temperature dependence to those of the 122 compounds. On proceeding from  $\text{Mn}^{2+}$  to  $\text{Cu}^{2+}$ , the filling of the 3d orbitals changes from half-filling to almost full, and one expects in general that the local moment will decrease due to the interplay of Hund’s rules and crystal-field splitting effects. Thus to the extent that an effective magnetic impurity picture is appropriate, the increasing deviation from the magnetic moment of the host  $\text{Fe}^{2+}$  ions would result in an increasing influence on the electronic properties.

Another effect of TM substitution is that it acts to alter the carrier concentration. First-principles calculations have

shown that this substitution is equivalent to electron and hole doping in the 122 system [20]. Experiments indicate that the carriers in Fe(Se, Te) are holes [21]. Thus the hole concentration is raised effectively by Mn<sup>2+</sup> doping, which is harmless to superconductivity and even leads to a slight enhancement of  $T_c$ . Semiconducting behaviour arises naturally from the reduction of the carrier concentration in samples with Ni and Cu doping. However, this alone cannot explain the semiconducting behaviour observed in the FeSe<sub>0.85</sub> system with V and Cr doping [22], for which more detailed band structure considerations are required. We comment here that the slight enhancement of  $T_c$  for the Mn-doped sample indicates one direction for further studies aimed at understanding the mechanisms for higher  $T_c$  values in these systems.

The TM substitution effect being so different for 11 and FeAs-based superconductors may be a consequence of the quite distinct magnetic properties of the two types of system. Neutron scattering experiments have determined a magnetic ordering below the spin-density-wave transition temperature in the 11 parent compound more complicated than that found in any of the FeAs parent materials: this is bicollinear in 11 systems at low temperatures, as opposed to collinear in the FeAs parent compounds [23]. On the other hand, the electronic properties are also clearly distinct for these two classes of system, as shown by optical conductivity measurements [24]. The physics underlying this fundamental question in iron-based superconductivity requires further experimental and theoretical investigation.

A natural question is that of what can be learned about the superconducting state from TM substitution experiments in the 11 system. For a conventional BCS superconductor, magnetic impurities act strongly to suppress superconductivity, a result well understood in terms of pure s-wave pairing. By contrast, just a small amount of non-magnetic Zn<sup>2+</sup> doping is sufficient to destroy superconductivity completely in cuprates [25], which is a consequence of the d-wave pairing symmetry. Unfortunately, we are unable to investigate the effect of non-magnetic impurities on the superconductivity in FeSe<sub>0.5</sub>Te<sub>0.5</sub> because of the doping problems associated with Zn<sup>2+</sup> ions. However, some indications may still be obtained from the doping effects of the other ions, which can be classified into two categories: Mn<sup>2+</sup> and Co<sup>2+</sup> have a slight influence on  $T_c$  while Ni<sup>2+</sup> and Cu<sup>2+</sup> have a dramatic effect. This behaviour is characteristic of neither the conventional s-wave nor the standard d-wave pairing scenario. Angle-resolved photoemission and other experiments have suggested that extended s<sub>±</sub>-wave pairing is the most likely symmetry in the multi-orbital iron-based superconductors [26, 27], and our substitution results also indirectly support such a pairing symmetry.

## 5. Conclusions

In summary, we have synthesized the superconducting parent compound FeSe<sub>0.5</sub>Te<sub>0.5</sub> and substituted the transition-metal ions Mn, Co, Ni, Cu and Zn for iron with 5% doping. Transport and magnetic measurements show that the  $T_c$  values

are altered only slightly, to 14.9 and 11.9 K respectively, by the substitution of Mn and Co. However, the superconductivity is destroyed completely in the samples with 5% Ni and Cu doping. The evolution of this behaviour with substituent atomic number depends on the local impurity moment and the carrier concentration induced by the TM substitution. The results for 11 systems differ very strongly from TM substituent effects in FeAs materials, a contrast which may be attributable to the different magnetic properties of the two types of system. The effect of substitution on superconductivity also implies that the pairing symmetry in FeSe<sub>0.5</sub>Te<sub>0.5</sub> cannot be described by either a simple s-wave or a simple d-wave picture.

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