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Published in:
Journal of Magnetism and Magnetic Materials

DOI:
j.jmmm.2014.01.037

Publicerad: 01/01/2014

Please cite the original version:

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Evolution of the internal magnetic field in chalcogenide superconductors FeTe$_{1-x}$S$_x$ for various $x$ values

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1. Introduction

Chalcogenide superconductors belong to a very suitable class among the iron-based superconductors for studying hyperfine interactions. Effects like the coexistence of magnetism and superconductivity, presence of spin density waves make these materials attractive for various kinds of investigations [1–5].

Superconductivity in the simple unsubstituted FeTe phase cannot be achieved even if an external pressure is applied as in FeSe [6,7]. Iron telluride shows an antiferromagnetic ordering with a Néel temperature around 70 K, but by using substituting elements a suppression of the magnetic ordering occurs. Substitution of tellurium by sulphur or selenium can be used to induce superconductivity. Depending on the concentration of the substituting atom superconductivity will appear and develop into filamentary or bulk type and finally disappear for exceeding quantities of the substituent [8–10]. Earlier studies of Fe-based superconductors indicate that the enhancement of $T_c$ is related to changes in the crystal lattice or magnetic properties of the material. In FeTe$_{1-y}$S$_y$ the sulphur atoms occupy the sites of tellurium and create a chemical pressure in the lattice owing to the difference in the atomic sizes.

Although bulk superconductivity in conducting materials usually develops from paramagnetic parent phases, studies of the new Fe-based superconductors reveal coexistence of antiferromagnetic ordering and superconductivity [11,12]. Previously it was believed that by substituting a part of tellurium by sulphur the magnetic ordering is completely suppressed and superconductivity is induced but later the presence of a hyperfine magnetic field in superconducting FeTe$_{1-x}$S$_x$ was observed [1,10]. The addition of sulphur atoms to FeTe makes the magnetic ordering at low temperatures incommensurate even for a very small concentration of substituents [10]. Also in Fe$_{1-x}$Te$_{1+y}$S$_y$ with $y=0.03$ and $x=0.40–0.5$ a magnetic ordering at low temperatures was found [5,24]. It was experimentally found that at temperatures below ~80 K (the exact ordering temperature depends on the substitution level) magnetically ordered fractions appear and below the superconducting transition temperature coexistence of magnetism and superconductivity is observed [5]. In contrast, Fe$_{1-x}$Te has an incommensurate magnetic structure [25]. In the bulk superconductor FeTe$_{0.5}$Se$_{0.5}$ only paramagnetic iron was observed at all temperatures [5,26].

In FeTe$_{1-x}$S$_x$ the maximum for the superconducting transition temperature $T_c$ is reached at $x \approx 0.2$. For other sulphur concentrations the superconducting volume fraction is smaller and can exhibit filamentary structure. An enhancement of the superconducting volume fraction can be achieved by changing the sulphur content, but also by applying additional procedures during or after the final step of synthesis [13–17]: it has been shown that an oxygen annealing leads to a sharper superconductivity transition and increases the transition temperature. Air-exposure of the materials also shows a good result for improving superconductivity in FeTe$_{1-x}$S$_x$. The solubility limit of sulphur atoms causes some obstacles for choosing an optimal synthesis method [6]. Several ways of synthesis are used for producing FeTe$_{1-x}$S$_x$: melting method, Bridgman method and solid-state reaction [20,21].
Apparently, a solid-state reaction method gives a better combination for the desired properties in the synthesized materials, however, it also leads to a broadening of the superconductivity transition to zero resistivity, but at the same time a reduced presence of impurity phases is observed.

Owing to the simple process of synthesis we focus our attention on the Fe(Te,S) system for studies on the incipient hyperfine magnetic effects at temperatures around the superconductivity transition. Sulphur-substituted iron telluride samples were produced and the development of superconductivity properties and behavior of the hyperfine magnetic field below 77 K were studied and compared with the earlier results obtained for an optimally substituted sample [18,19].

2. Experimental

For studies of the magnetic properties of superconducting FeTe$_{1-x}$S$_x$ samples with $x=0.05$, $x=0.10$ and $x=0.20$ were synthesized using a solid-state reaction scheme. Stoichiometric mixtures of iron (99.9%), tellurium (99.9%) and sulphur (99.9%) powders were sealed into quartz tubes under vacuum and slowly heated from room temperature to 1050 °C for 20 h and kept at this temperature for 30 h. The obtained samples were reground inside a glove box with an inert Ar atmosphere, pressed into pellets at 10 kbars, sealed into evacuated quartz tubes and sintered again at 800 °C for 20 h. The oxygen-annealing was used as an additional synthesis step for the synthesis of the FeTe$_{0.8}S_{0.2}$ sample [19].

The superconductivity properties were checked with resistivity measurements using a home-built four-probe setup and with magnetic measurements in zero-field cooling and field-cooling regimes using a SQUID magnetometer (Quantum Design, MPMS-XL). According to the literature FeTe$_{0.95}S_{0.05}$ is not superconducting, FeTe$_{0.9}S_{0.1}$ starts to show superconductivity properties. The samples purity was characterized with an X-ray powder diffractometer (PanAnalytical X’pert Pro MPD, CuKα1 radiation) and the data were analyzed by the Rietveld method using the software program FullProf [27].

Mössbauer spectra were recorded in the temperature range from 6.8 K up to 300 K in transmission geometry using maximum Doppler velocities of 1.70 mm/s and 10.00 mm/s. High-velocity spectra were used for checking the presence of impurity phases. Low-velocity spectra were used for extracting the hyperfine interactions of the main phase. A 25 mCi Cyclotron Co. $^{57}$Co:Rh source was used for producing the gamma quanta. For low-temperature measurements an Oxford continuous-flow cryostat with liquid He as a coolant below 77 K and liquid N$_2$ at and above 77 K was used. The spectra of FeTe$_{0.9}S_{0.1}$ were fitted using a model that includes one paramagnetic doublet from the main phase and

![Fig. 1. X-ray powder diffraction patterns for the FeTe$_{0.95}S_{0.05}$, FeTe$_{0.9}S_{0.1}$ and FeTe$_{0.8}S_{0.2}$ samples.](image)

![Fig. 2. $^{57}$Fe high-velocity Mössbauer spectra of FeTe$_{0.95}S_{0.05}$ (upper panel) and FeTe$_{0.9}S_{0.1}$ (lower panel) recorded at room temperature. Components due to the paramagnetic doublet (green solid) and the magnetic Fe$_3$O$_4$ impurity (blue dashed) are indicated. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)](image)
two magnetic sextets from magnetic impurities. For fitting the spectra that were recorded below 77 K three singlets and one doublet were used. Two of the three singlets can be associated with the third lines of the magnetic sextets with high internal fields. The third singlet was used for fitting the paramagnetic main component together with a broadened doublet. For FeTe$_{0.95}$S$_{0.05}$ the fitting model includes only one paramagnetic doublet at all temperatures. All spectra of the investigated materials exhibit a texturized structure and the angle between the wave vector and the principal axis of the electric field gradient was entered as a free fit parameter. Isomer shift values were taken relative to α-Fe at room temperature.

Obtained hyperfine parameters for 0.05 and 0.10 sulphur-substituted samples were compared with properties of the sample with x=0.20 reported earlier [18,19].

3. Results and discussion

The XRD analyses showed Fe(Te,S) as the main phase but other phases were also observed. They were identified as FeTe$_{2.1}$Fe$_{0.87}$Te and FeS and their amounts were found to be dependent on the substitution level of sulphur. The results of the multiphase Rietveld refinements are presented in Fig. 1. The main phase Fe(Te,S) is strongly c-axis oriented and this was taken into account to enable the quantification of the fractional phases. A March–Dollase function was applied to account for the orientation effect and the resulting refined value (C = 0.57 < 1) suggests a plate-like texture in the present samples. No sulphur-containing impurities were observed for the x=0.05 and 0.10 samples and only 1% of the FeS impurity phase was detected for the x=0.20 sample. This indicates that the S-for-Te substitution is rather successful. This is supported by the lattice parameter behavior: the cell volume decreases with increasing x. As the X-ray scattering power is different enough for Te and S, we also studied the fractional occupancies in their crystallographic positions. This was done at the final stage of the refinement so that the chemically fixed occupancy of S was released. This somewhat improved the results and gave 1.8, 6.1 and 9.5% as the actual amount of S in the x=0.05, 0.10 and 0.20 samples, respectively. Comparison of the c-axis value for the chemically analyzed samples would give slightly different results (4.9, 7.6 and 7.8%) [28]. This is probably explained by the fact that some of the Fe and Te is bonded in the parasitic phases but the reality should be something in between. The high-velocity Mössbauer spectrum recorded at room temperature revealed also the presence of Fe$_3$O$_4$ in the FeTe$_{0.95}$S$_{0.05}$ sample (Fig. 2). But this impurity was not observed in the FeTe$_{0.95}$S$_{0.05}$ sample. Paramagnetic FeTe$_2$ and Fe$_{0.05}$Te impurities were not detected in the high-velocity Mössbauer spectra. The much more intensive main doublet probably masks these two phases in the Mössbauer spectra, as both these impurities are paramagnetic at room temperature [22,23,29]. The isomer shift and quadrupole coupling constant of the main phase were $\Delta IS=0.44$ mm/s and $eQV_{zz}=-0.78$ mm/s at 77 K for x=0.10 and $\Delta IS=0.45$ mm/s and $eQV_{zz}=-0.83$ mm/s at 77 K for x=0.05. For the FeTe$_{0.8}$S$_{0.2}$ sample these values were $\Delta IS=0.52$ mm/s and $eQV_{zz}=-0.71$ mm/s at 77 K [19].

The FeTe$_{0.95}$S$_{0.05}$ sample did not show any superconducting transition in the magnetization nor the resistivity data. In FeTe$_{0.9}$S$_{0.1}$ the zero-field cooling (ZFC) magnetization measurement shows a broad drop at ~10 K (Fig. 3). As expected, the x=0.20 sample shows bulk superconductivity: a sharp drop of the magnetization curve is observed at ~9 K (Fig. 3). This value of the transition temperature is confirmed by the resistivity measurement. The hump in the susceptibility observed at 125 K on the field-cooling curve is compatible with the Verwey transition in magnetite. A sharper superconducting transition is seen on the resistivity versus temperature curve, Fig. 3, with $T_c$ ~8 K. The resistivity curve also shows a weak Verwey transition at ~125 K. Low-velocity Mössbauer spectra of the FeTe$_{0.95}$S$_{0.05}$ and FeTe$_{0.9}$S$_{0.1}$ samples (Fig. 4) were recorded in the temperature range from room temperature to 6.8 K. The spectra exhibit a broadening of the line width of the main components with decreasing temperature, in particular in the range from 77 K to 6.8 K. The broadened doublets were fitted with a histogram distribution of hyperfine magnetic fields. The temperature dependencies of the
hyperfine fields for the FeTe_{0.95}S_{0.05} and FeTe_{0.9}S_{0.1} samples are presented in Fig. 5. In the upper panel of Fig. 5 an increase of the magnetic field with decreasing temperature continues down to the lowest temperature. In FeTe_{0.9}S_{0.1} the magnetic field of the main component grows up to approximately 8.5 K and drops upon further decreasing temperature. A similar behavior was also observed in the FeTe_{1-x}S_{x} samples with a higher content of sulphur (x ≈ 0.20) [18,19] and is presented for comparison in Fig. 5. The obtained dependencies of the hyperfine magnetic fields agree with the concept of a competition between magnetism and superconductivity in the FeTe_{1-x}S_{x} system for the samples which exhibit various degrees of superconductivity. Also, there seems to be a relationship between the peak of the hyperfine magnetic field and the value of the superconductivity transition temperature.

By comparing the average internal fields of the x=0.05 and x=0.10 samples and the earlier investigated optimally substituted sample with x=0.20 it is noticed that in the non-superconducting FeTe_{0.95}S_{0.05} sample the magnetic volume fraction linearly grows with the decreasing temperature, whereas for the two superconducting samples the curves show a faster than linear growth up to the superconducting transition temperature and a sharp down turn at temperatures below T_c. Also, it was observed for the earlier studied sample [19] that the increase of the hyperfine magnetic field has a weaker character and the maximum value of the hyperfine magnetic field is considerably lower than that for the FeTe_{0.9}S_{0.1} sample.

A conclusion that superconductivity in the FeTe_{1-x}S_{x} system suppresses the magnetic ordering below transition temperature can be drawn which is in contrast to the results for Fe_{1+y}Te_{1-x}Se_{x} where the volume of the region with the coexistence of the magnetic ordering and superconductivity is increasing even below the superconductivity transition. Therefore in FeTe_{1-x}S_{x} rather a competition and suppression of the magnetic ordering by superconductivity takes place in agreement with our previous results for the bulk superconductor [19].

4. Conclusions

The evolution of the magnetic hyperfine field for FeTe_{1-x}S_{x} samples with various x has been studied. The temperature dependencies of the internal field for a non-superconducting sample and the samples that show a superconducting transition were obtained. The sharp drop of the magnetic field value below...
the superconducting transition temperature suggests a suppression of the magnetic ordering by the emerging superconductivity. This is in contrast to the reported mutual coexistence of magnetic ordering and superconductivity in some Fe-based superconductors.

Fig. 5. Average internal fields vs. temperature for FeTe$_{0.95}$S$_{0.05}$ (upper panel), FeTe$_{0.9}$S$_{0.1}$ (middle panel), and FeTe$_{0.8}$S$_{0.2}$ (lower panel) [19]. The lines are guides for the eye.

References
