Observation of lattice softening at $T_c$ in the FeSe$_{0.5}$Te$_{0.5}$ superconductor

J. Lindén a,*, J.-P. Libäck a, M. Karppinen b, E.-L. Rautama b, H. Yamauchi b

a Department of Physics, Åbo Akademi, FI-20500 Turku, Finland
b Laboratory of Inorganic Chemistry, Department of Chemistry, Aalto University, FI-00076 Aalto, Finland

A R T I C L E   I N F O

Article history:
Received 6 August 2010
Received in revised form 5 October 2010
Accepted 5 November 2010
Available online 13 November 2010

Keywords:
A. Pnicotide superconductors
B. Lattice softening
E. $^{57}$Fe Mössbauer spectroscopy
E. Hyperfine interactions

A B S T R A C T

Polycrystalline samples of FeSe$_{0.5}$Te$_{0.5}$ were synthesized using a conventional solid-state reaction method. The onset of bulk superconductivity transition was confirmed by SQUID magnetometry at 12.5 K. $^{57}$Fe Mössbauer spectra in transmission geometry were recorded at temperatures between 6.0 and 320 K. Both the isomer shift and the total absorption started to drop about $T_c$, indicating a softening of the lattice. The drop is estimated to correspond to at least 60 K from the original Debye temperature $\theta_D \approx 460$ K. Seebeck measurements indicate that the samples are n-type conductors at low temperatures with a crossover to p-type conductivity around 135 K. The zero Seebeck coefficient is seen below 10.6 K.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Superconductivity above 20 K in iron pnictides was reported two years ago [1]. Since then the number of iron-pnictide phases has grown considerably, but the highest critical temperature has remained below 60 K. However, the value falls short only of that of the high-$T_c$ superconductive cuprates. Nonetheless, Fe as a natural constituent in superconductive materials is fascinating and somewhat unexpected. In none of these iron-pnictide phases does iron order magnetically in the superconductive state, though some non-superconductive parent phases exhibit antiferromagnetic spin-density waves [2]. Some of the superconductive iron phases have simple structures, e.g. the chalcogenide phase FeSe [3]. Like the high-$T_c$ cuprate superconductors, Fe-based phases also have layered structures, in which the superconductive charge carriers reside at edge-shared FeX$_4$ ($X =$ Group 15 or 16 element) tetrahedra. The geometry is important for both types of superconductive phases. Cuprate superconductors with puckered CuO$_2$ layers have generally lower $T_c$ values than those with flat ones, whereas for the Fe-based superconductors the highest $T_c$ values occur when the tetrahedra are closest to the regular shape [4]. In a recent work which incorporates also FeSe the distance between the X atom and the nearest Fe layer seems to be a crucial geometrical parameter for determining the $T_c$ value [5]. However, the actual mechanism behind the superconductivity transition is not known yet.

The presence of Fe has opened the possibility to perform $^{57}$Fe-Mössbauer-spectroscopy measurements and thereby to determine the spin and valence state of the Fe atoms. Various spectra from superconductive samples have established that the spin state of Fe is zero or close to zero [6,7]. This is true at least within the characteristic time-scale of $\sim 100$ ns of the $^{57}$Fe transition. However, the presence of antiferromagnetic fluctuations has been suggested [8,9] but may be difficult to detect by Mössbauer spectroscopy. A recent high-pressure experiment on the LaFeAsO phase showed that there is a strong connection between the spin-density-wave type magnetism of the non-superconducting state and the seemingly zero-Fe-spin spectra of the superconducting state [10].

In this work we report findings of the Mössbauer and Seebeck measurements performed on both sides of the critical temperature of FeSe$_{0.5}$Te$_{0.5}$ to record possible changes in the hyperfine parameters upon passing $T_c$.

2. Experimental

Samples of the FeSe$_{0.5}$Te$_{0.5}$ phase were synthesized from stoichiometric ratios of high-purity Se (99.99%), Fe (99.9%) and Te (99.8%) powders. The powders were sealed under vacuum in a quartz tube and fired for 20 h at 600 °C. After an intermediate grinding the samples were fired again at 650 °C for 20 h and furnace-cooled down to 300 K.

Bulk superconductivity was confirmed by measuring the diamagnetic signal from approximately 20 mg of the sample with a superconducting quantum interference device (SQUID: Quantum

* Corresponding author. Tel.: +358 22154239.
E-mail address: jilinden@abo.fi (J. Lindén).
Design, MPMS-XL) in both the zero-field-cooled and field-cooled (10 Oe) regimes.

X-ray diffraction patterns were measured in an ordinary $\theta$–$2\theta$ geometry using Cu Kα1 radiation (PanAnalytical X’Pert Pro MPD diffractometer) to check the sample purity. Rietveld analysis was done to confirm the tetragonal P4/nmm structure of the superconductive Fe$_{0.5}$Te$_{0.5}$ phase.

The Mössbauer measurements were carried out using a 25 mCi $^{57}$Co:Rh source (Cyclotron Co, purchased in April 2009) at fixed temperatures between 6.0 and 320 K, in transmission geometry with a maximum Doppler velocity of 3 mm/s. Additional measurements using maximum Doppler velocities of 8 and 10 mm/s were done to check the presence of magnetic impurities. Cooling of the sample was achieved with an Oxford CF506 continuous-flow cryostat with liq. N$_2$. Susceptibility measurements were done to confirm the tetragonal P4/nmm structure of Fe$_{0.5}$Te$_{0.5}$ with the fact that Te substitution is detrimental for the magnetic order in the Fe–Se system [11].

The Mössbauer transition [11] of Fe$_2$O$_4$ at ~120 K is also seen in the susceptibility data.

The Seebeck measurements were done (using self-made equipment) upon heating the sample from 4.0 to 300 K in steps of ~0.3 K. A sintered sample specimen was ground into the shape of a thin parallelepipeds of 2.0 $\times$ 1.5 $\times$ 0.3 mm$^3$ and inserted between two Cu sample holders using Ag paste. A resistor hidden inside one of the Cu holders was heated to achieve a temperature gradient up to ~1.5 K over the sample. Additional Seebeck data in applied fields of 0 and 8 T were collected using a physical-property measurement system (Quantum Design, PPMS) equipped with a self-made sample puck. The same sample as above was used.

### 3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern for the FeSe$_{0.5}$Te$_{0.5}$ sample. It is readily indexed by the PbO-type tetragonal structure of space group P4/nmm (isotransitional with $\beta$-FeSe). Impurity peaks assigned mainly to hexagonal Te-substituted $\delta$-FeSe [6] and/or Fe$_7$Se$_8$ are observed. Additionally, the presence of Fe$_2$O$_4$, confirmed by SQUID and Mössbauer spectroscopy measurements, is seen.

The magnetization versus temperature data obtained by SQUID measurements in the field-cooled and zero-field-cooled regimes confirm the onset of bulk superconductivity at 12.5 K for the Fe$_{0.5}$Te$_{0.5}$ sample, see the inset in Fig. 1. The positive background is due to the presence of magnetic impurity phases, i.e. Fe$_2$O$_4$. The Verwey transition [11] of Fe$_2$O$_4$ at ~120 K is also seen in the susceptibility data.

The Seebeck coefficient data are shown in Fig. 2. The negative sign indicates that the sample is an n-type conductor. Below the transition into the superconducting state the Seebeck coefficient becomes zero at 10.6 K. Above ~135 K positive values for the Seebeck coefficient are obtained. Using an external field of 8 T the low-temperature Seebeck data are clearly shifted by ~1 K towards lower temperatures. The shift is in accord with the rather high second critical field $H_c^2$. Similar results were reported in Ref. [12] for samples of Fe$_{1+y}$Te$_{1-y}$Se$_{y}$.

Mössbauer spectra obtained from Fe$_{0.5}$Te$_{0.5}$ at selected temperatures are shown in Fig. 3. Components due to two phases are readily observed. The paramagnetic main component covering 88% of the spectral intensity is due to Fe$_{0.5}$Te$_{0.5}$ (Component 1). It has an isomer shift of ~0.43 mm/s at 300 K and a quadrupole splitting of $eQV_{zz}/2 = 0.28$ mm/s, i.e. similar to the values obtained for $\beta$-FeSe [6], but $eQV_{zz}$ was somewhat larger, reflecting a higher deformation of the coordination tetrahedron around Fe upon introducing Te [13]. Another paramagnetic component (Component 2) with $\delta \approx 0.36$ mm/s covers ~9% of the spectral intensity. It has a quadrupole splitting of 0.16 mm/s. In the XRD pattern for a $\beta$-FeSe sample peak positions due to $\delta$-FeSe/Fe$_7$Se$_8$ impurities are observed [6]. When comparing the pattern with that of the present Fe$_{0.5}$Te$_{0.5}$ sample almost identical impurity peaks are observed, indicating that Component 2 is due to Te-substituted Fe$_7$Se$_8$ or $\delta$-FeSe. Fe$_7$Se$_8$ is magnetically ordered at room-temperature, but the absence of magnetic order is in accord with the fact that Te substitution is detrimental for the magnetic order in the Fe–Se system [14]. In a high-velocity spectrum (not shown) ~4% of Fe$_2$O$_4$ can be discerned. No other magnetic phases were observed.

As Component 2 interferes with Component 1 we tried the following three fitting schemes when analyzing the spectra of the most interesting region (6–100 K): (1) releasing all fit parameters
of Components 1 and 2, (ii) fixing the peak height and quadrupole coupling constant of Component 2 to an average of the $T < 100$ K region and (iii) fixing the isomer shift and quadrupole coupling constant of Component 2 to an average value of the $T < 100$ K region. The general features as presented below for Component 1 did not depend on the choice of scheme. Fitting scheme (iii) gave the “purest” behavior, as no specific temperature evolution was expected for the impurity component, except that its peak height should vary as a function of the temperature, which was violated by scheme (ii). In the end, we decided to present the results as obtained according to scheme (i), in order to avoid excessive fixing of fit parameters.

The isomer shift ($\delta$) of Component 1 in FeSe$_{0.5}$Te$_{0.5}$ is plotted against temperature in Fig. 4. The shift obtained from the fitting includes contributions from both the chemical shift and the second-order Doppler shift, which is known to increase convexly upon decreasing temperature, due to gradual depopulation of the excited phonon states [15]. However, it should be constant at low temperatures, because of the quantum mechanical zero-point motion. The chemical shift should not depend on temperature. An ordinary convex temperature evolution is indeed traced down to $T_c$ where a distinct drop is observed. The drop indicates that the Debye temperature ($\theta_D$) is decreasing, that is the lattice undergoes a softening. The actual size of the drop can only be estimated, as there is no leveling-off visible at 6 K. The temperature dependence for $\delta$ is given by [16]:

$$\delta(T) = \delta_0 + \frac{9k_BT}{16Mc} - \frac{9k_B}{2Mc} \left( \frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^3}{e^x - 1} \, dx,$$

where $c$ is the velocity of light, $k_B$ the Boltzmann constant, $M$ the mass of the $^{57}$Fe atom, and $\delta_0$ the temperature-independent part, i.e the chemical shift. A fit with Eq. (1) to the data of Fig. 4 yields $\theta_D = 460(5)$ K and $\delta_0 = 0.43$ mm/s. By fixing $\delta_0$ at the value 0.43 mm/s and setting $\theta_D = 400$ K the softening of the lattice is readily visualized: the drop in the second-order Doppler shift of at least $\Delta v_{SOD} = -0.013$ mm/s corresponds to a drop of $\Delta \theta_D = 60$ K in the Debye temperature (the lower curve in Fig. 4).

The drop in $\theta_D$ is also visible in the total absorption ($A$) for Component 1, given as the component intensity $I$ times the line width $\Gamma$, as shown in Fig. 5. The drop in absorption begins slightly above $T_c$. A softening of the lattice will decrease the recoil-free
fraction and hence the absorption will also decrease. A part of the leveling-off of the absorption could be due to the fact that the sample is rather thick, but that cannot explain the actual drop. Because of possible sample-thickness corrections the absorption data can only be used for qualitatively estimating $\theta_0$ and the drop at $T_c$. The standard expression for the recoil-free fraction $f$ is given by [17]:

$$f = \frac{\exp \left[ -\frac{3E_R}{2k_B\theta_0} \right]}{1 + \exp \left[ -\frac{\theta}{\theta_0} \right] \int_0^{\frac{\theta}{\theta_0}} \frac{\exp \left[ -x \right]}{x} \, dx}$$

where the recoil energy $E_R = 0.0019$ eV for the 14.4 keV $\gamma$ quantum of $^{57}$Fe. The absorption data of Fig. 5 should be proportional to the recoil-free fraction in the absorber, i.e. $A = C \theta$, where $C$ is a parameter depending on the sample thickness, signal-to-noise ratio for the detected $\gamma$ quanta, etc. Thus:

$$\ln A = \ln f - \ln C.$$  

Eq. (3) is plotted together with the experimental $\ln(A)$ data against temperature in Fig. 6. The data below 77 K where parameter $C$ is no longer constant are omitted in Fig. 6 because of the leveling-off of absorption data. The slope of the curve strongly depends on the Debye temperature. The best fit was obtained for $\theta_0 = 260(5)$ K, which is much lower than the estimate based on the second-order Doppler shift. In fact, due to possible "hidden" temperature-dependence in parameter $C$, the $\theta_0 = 460$ K is likely to be more reliable.

At low temperatures (Eq. (2)) for the recoil-free fraction can be approximated with:

$$f \approx \exp \left[ -\frac{3E_R}{2k_B\theta_0} \right].$$

Upon inserting the estimated $\theta_0 = 260$ K in Eq. (4) the recoil-free fraction before the drop is estimated at $f = 0.881$. About $T_c$ the absorption (shown in Fig. 5) drops from 5.63 to 5.45, which corresponds to a drop in $f$ from 0.881 to 0.853. Upon inserting the latter into Eq. (4) we get $\theta_0 = 208$ K, resulting in a drop of $\sim 50$ K in $\theta_0$. If the 460 K estimate is used the recoil-free factors before and after the drop are 0.93 and 0.90, respectively and the corresponding drop in $\theta_0$ is 140 K.

The quadrupole splitting of Component 1 (not shown) increases from $eQV_{zz}/2 = 0.28$ to 0.33 mm/s as temperature is decreased below 100 K. A leveling-off at 0.33 mm/s, possibly followed by a tiny drop of 0.01 mm/s around $T_c$, is observed. A small relaxation in the position of Fe or Se/Te atoms is all that is needed to cause a change in $eQV_{zz}$. The quantity $V_{zz}$ depends on the nearest-neighbor distance ($r$) as $V_{zz} \sim 1/r^2$. That is, it is extremely sensitive to movements of the atoms. The movements need not be commensurable, as the Mössbauer-resonant nuclei act as local probes.

We have also synthesized samples of the $\beta$-FeSe phase and observed a parallel drop in $\theta_0$ about its $T_c \approx 8.0$ K [18]. We recently reported drops in both the isomer shift and the absorption below $T_c = 15$ K for the superconducting Fe-based superconductors [19]. In this phase the drops were preceded by a lattice stiffening, giving the low-temperature absorption and isomer-shift curves concave shapes. Lattice softening in iron pnictides has also been observed using neutron scattering experiments and measurements on lattice stiffness constants [20–23]. However, in the conventional elemental superconductors Zn and Sn no changes in the Mössbauer isomer shift values of $^{65}$Zn and $^{119}$Sn, respectively, were observed upon passing $T_c$ [24,25]. This might suggest that some other mechanism than the BCS theory is behind the superconductivity transition in FeSe$_{0.5}$Te$_{0.5}$ and other new Fe-based superconductors. In particular, antiferromagnetic fluctuations about $T_c$ have been observed in some of the iron-based pnictides and chalcogenides phases by inelastic neutron scattering, cf. Refs. [8,26]. A possible connection between such fluctuations and the lattice softening was in fact suggested recently [27]. At the same time inelastic X-ray-scattering experiments point towards the importance of phonons in these phases [28,29].

4. Conclusions

$^{57}$Fe Mössbauer measurements of the FeSe$_{0.5}$Te$_{0.5}$ phase reveal a paramagnetic quadrupole doublet with an isomer shift compatible with zero spin Fe$^{2+}$. Upon decreasing the temperature below $T_c = 12.5$ K a softening of the lattice occurs. The softening corresponds to about 60 K decrease in the Debye temperature from its original value of $\sim 460$ K as determined by the isomer-shift vs. temperature data.

Acknowledgements

Mr. M. Lehtimäki and Mr. T. Tynell are acknowledged for their help with performing the XRD and Seebeck characterizations. Prof. P. Patuiri of Wihuri Research Center is acknowledged for her contribution to the in-field Seebeck measurements. Mr. S. Fröjdö is acknowledged for his assistance with the sample synthesis. This work was partially supported by Tekes (No. 1726/31/07) and Academy of Finland (No. 126528).

References