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# DFT and Mössbauer spectroscopy study of $FeTe_{0.5}Se_{0.5}$ single crystal

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Iron chalcogenides attract significant attention of the scientific community after the discovery of superconductivity in iron based compounds [1]. Iron telluride is the parent compound for a substitutional series $FeTe_{1-x}Se_x$ of iron based superconductors. FeTe orders antiferromagnetically [2], whereas the substitution of Se at the Te site in FeTe introduces superconductivity and simultaneously suppress the antiferromagnetic ordering [3, 4]. The highest superconducting temperature for this Fe chalcogenide series is achieved at approximately 15 K for $FeSe_{0.5}Te_{0.5}$ at ambient conditions [3, 4]. It should be noted, that iron telluride has a strong tendency to off-stoichiometry of iron, and such off-stoichiometry is clearly detected by Mössbauer spectroscopy experiments [5]. In the FeTe iron atoms can occupy two different crystallographic positions. Iron atoms in the first position ($2a$) form in-plane Fe-Te layers with tellurium atoms while in the second position ($2c$) interstitial iron atoms are located in the interlayer space between the Fe-Te layers. It was shown that even a small amount of excess iron atoms leads to a modification of the electronic and magnetic properties of $Fe_{1+y}Te$ [5]. An iron off-stoichiometry is also typical for $Fe_{1+y}Te_{0.5}Se_{0.5}$ compounds [6]. In the present study we investigate the influence of iron off-stoichiometry on the magnetic state of $FeTe_{0.5}Se_{0.5}$ compound combining *ab initio* calculations and Mössbauer spectroscopy experiments. The refined stoichiometry for iron were 0.907(3) and 0.093(3) for Fe1 and Fe2 ions [6].

Mössbauer effect measurements were carried out at temperatures of 5 and 295 K using a conventional constant-acceleration spectrometer (WissEl, Germany) with $^{57}Co$ as $\gamma$-radiation source. Low-temperature measurements were carried out with a continuous flow cryostat (model CFICEV from ICE Oxford, UK).

The *ab initio* calculations were based on density functional theory (DFT) [7]. Exchange and correlation effects were accounted for by the generalized gradient approximation (GGA) as parametrised by Perdew, Burke, and Ernzerhof (PBE-sol) functional [8]. The Kohn–Sham equations were solved with projector-augmented wave (PAW) potentials and wave functions [9] as implemented in the Vienna Ab-Initio Simulation Package (VASP) [10], which is a part of the MedeA software of Materials Design [11].

The obtained from *ab initio* calculations hyperfine parameters for $FeTe_{0.5}Se_{0.5}$ with nine percent occupancy factor for Fe2 centers are similar to those of iron atoms presented for $Fe_{1.05}Te$ in [5]. Three groups of iron atoms with different hyperfine parameters can be identified. One of them (Fe2 group) is formed by only Fe2 interstitial iron atoms, whereas the other two are the first (Fe1/1 group) and the second (Fe1/2 group) coordination rings around the Fe2 consisting of four and eight Fe1 atoms, respectively.

The room-temperature Mössbauer spectrum is presented in Fig. 1. In accordance with the *ab inito* results, it is reasonable to model the Mössbauer spectrum with three doublets. Each of the doublets is characterized by isomer shift (IS), quadrupole splitting value, angle $\theta$, and partial area (A). Under the assumption that the Lamb–Mössbauer factor is the same for all iron atoms in the compound, the distribution of partial areas should represent the ratio between number of iron nuclei in different groups (one, four, and eight nuclei in Fe2, Fe1/1, and Fe1/2 groups, respectively). Initial values of quadrupole splitting (QS) and $\theta$ for the fitting procedure were taken from our *ab initio* calculations, whereas the initial value for the isomer shift was taken

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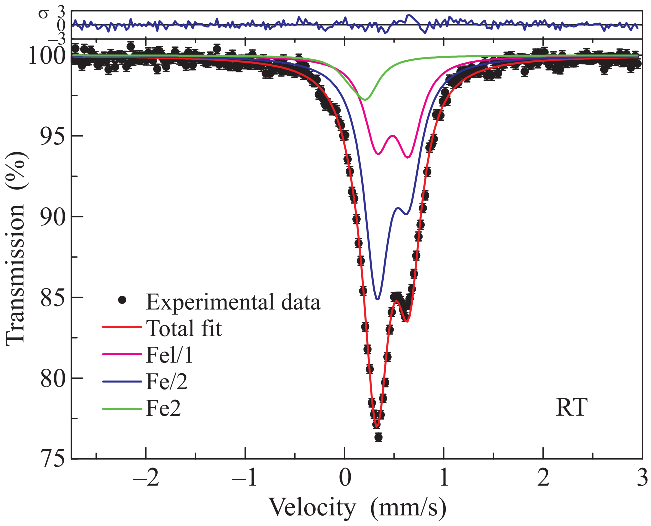


Fig. 1. (Color online) Room-temperature Mössbauer spectrum of single-crystalline $FeTe_{0.5}Se_{0.5}$ with nine percent occupancy factor of Fe2 centers (black symbols) and subspectra (colored) of the fitting (red line) corresponding to various groups of iron atoms

from [5]. During the fitting procedure the IS, QS and $\theta$-angle values were changed to reproduce the experimental spectrum by the proposed model. It could be seen from Fig. 1 that the model, based on *ab initio* calculations, describes well the experimental Mössbauer spectrum of $FeTe_{0.5}Se_{0.5}$ with nine percent occupancy factor of Fe2. Therefore we can conclude that the iron atoms in the this compound are divided into three groups.

The low-temperature Mössbauer spectrum of $FeTe_{0.5}Se_{0.5}$ with nine percent occupancy factor of Fe2 centers exhibits a complex shape. The combination of three magnetic sextets, an approach based on the presence of three different iron centers, was not able to reproduce the experimental spectrum. The shape of the spectrum is similar for that obtained for the spin density waves phases (SDW) [12].

The short-range ferromagnetic/antiferromagnetic correlations between nearest-neighbour spins in $Fe_{1+y}Te_{1-x}Se_x$ compounds were reported in [13]. It was proposed, that it could imply the coexistence and competition between SDW order and superconductivity in this system [13]. Because of the significant fraction of the excess interstitial iron atoms, it is reasonable to use a distribution of magnetic sextets with different values of hyperfine magnetic field on $^{57}Fe$ nuclei. The average value of the hyperfine field, corresponding to the distribution, was 110 kOe. This result is in a good agreement with the average hyperfine field value, $\langle H \rangle$, reported for $F_{1.1}Te$ compound in [14].

In conclusion, our results demonstrate that the iron atoms in $FeTe_{0.5}Se_{0.5}$ with nine percent occupancy factor for interstitial Fe2 centers are divided into three groups, and the excess iron atoms Fe2 affect the charge-density distribution up to a third coordination ring as it was observed in $Fe_{1.05}Te$ [5]. The low-temperature magnetic state could be characterized by a distribution of hyperfine fields on $^{57}Fe$ nuclei, which may indicate a distribution of magnetic moment values of iron atoms of different groups. The hyperfine field and magnetic moment distributions may also indicate an incommensurate spin-density waves phase, which coexists with superconductivity as it was observed in other iron-based superconductors [15].

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