

Magnetic properties of novel FeSe(Te) superconductors

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1. Introduction

The novel superconducting FeSe_{1-x}Te_x compounds have attracted extensive attention [1–4] due to the simplest crystal structure among the new families of iron-based layered compounds exhibiting superconductivity. This structural simplicity favors experimental and theoretical studies of chemical substitution and high pressure effects, which are aimed at promoting a better understanding of a mechanism of the superconductivity.

For the FeSe_{1-x}Te_x family, a noticeable increase of the superconducting transition temperature with x was found, from $T_C \sim 8$ K at $x=0$ to a maximum value of ~ 15 K at $x \simeq 0.5$. Additionally, a large enhancement of T_C up to 35–37 K was observed in FeSe under high pressures [5,6]. Similar pressure effects on T_C have been also reported for FeSe_{0.5}Te_{0.5} [7].

The FeTe compound is not superconducting but it exhibits peculiar magnetic properties. A drastic drop in the temperature dependence of its magnetic susceptibility $\chi(T)$ with decreasing temperature was observed at $T \simeq 70$ K, which is related to a first-order structural phase transition accompanied by the onset of antiferromagnetic (AFM) order [4,8]. At low temperatures a

monoclinic structure and a commensurate in-*ab*-plane AFM ordering were detected. The origin of the strong correlation between the structural and magnetic transitions in Fe_{1+x}Te is not yet clear.

There is a considerable controversy regarding an interplay between electronic structure, magnetism and superconductivity in FeSe_{1-x}Te_x compounds, and their magnetic properties are still neither well characterized, nor understood. The experimental data on magnetic susceptibility behavior of FeSe_{1-x}Te_x systems in the normal state are incomplete and contradicting [4,8,9]. Also, the magnetic behaviors of FeSe_{1-x}Te_x samples are presumably related to the presence of magnetic impurities and secondary phases. In order to elucidate the role of expected spin fluctuations in superconductivity, it is very important to obtain the intrinsic susceptibility of the Fe-based superconductors and investigate its evolution with doping, temperature, and pressure.

Here we report the experimental results on magnetic susceptibility studies for a series of FeSe_{1-x}Te_x compounds in the normal state. The experimental investigations were supplemented by *ab initio* calculations of the electronic structure and magnetic susceptibility of FeSe and FeTe within the density functional theory (DFT). The calculations strongly indicate that magnetic properties of the FeSe(Te) systems are closely correlated with crystal structure parameters. Therefore, the aim of this study was to shed more light on the relation between magnetic properties and

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the chemical and structural composition, and also on the interplay between the onset of superconductivity and magnetic instabilities in the $\text{FeSe}_{1-x}\text{Te}_x$ system.

2. Experimental details and results

Polycrystalline $\text{FeSe}_{1-x}\text{Te}_x$ samples were prepared by conventional solid-state synthesis. The starting chemicals were powder iron (Merck, 99.5%, 10 μm) and crystalline selenium and tellurium cleaned by the floating zone method. These chemicals were mixed in proportions consistent with the stoichiometry of reaction, sealed in an evacuated (10^{-4} bar) silica glass capsule, and annealed at 700 K for 14 days. The reacted mixture was ground in an agate mortar under acetone and then pressed into pellets of 6 mm in diameter at the load of 1–1.2 tons, followed by annealing in the evacuated silica glass capsule at 700 K for 20 days. The synthesized substances were examined by x-ray powder diffraction (XRD, $\text{Co K}\alpha$ radiation, Fe filter) and by electron microanalysis (CAMECA SX100, 15 kV). The single crystals were grown by a slow-cooling self-flux method [10]. One of the FeSe single crystalline samples was stabilized with a small amount of Co (about 1%). The phase content of the samples was checked by x-ray diffraction technique.

To examine the samples for the presence of ferromagnetic (FM) impurities, which are usually observed in $\text{FeSe}_{1-x}\text{Te}_x$ compounds and can mask their intrinsic magnetic properties, the measurements of DC magnetization M were carried out at $T=5$ K with magnetic field H up to 50 kOe using a SQUID magnetometer. The superconducting transitions are detected at 8 K and 13.6–14.2 K in $\text{FeSe}_{0.963}$ and $\text{FeSe}_{0.5}\text{Te}_{0.5}$ samples, respectively. The $M(H)$ dependencies for the majority of samples appeared to be quite linear, indicating that the concentration of FM impurities in these samples was negligibly small. For few $\text{FeSe}_{1-x}\text{Te}_x$ samples the magnetization data were corrected for ferromagnetic impurities by subtracting from the measured magnetic moment $M(T)$ the saturation moment m_s , which is assumed to be weakly dependent on T up to the room temperature [11]. As is seen in Fig. 1, the intrinsic magnetic susceptibility in the series of iron chalcogenides $\text{FeSe}_{1-x}\text{Te}_x$ was estimated to increase gradually with Te content by about ten times.

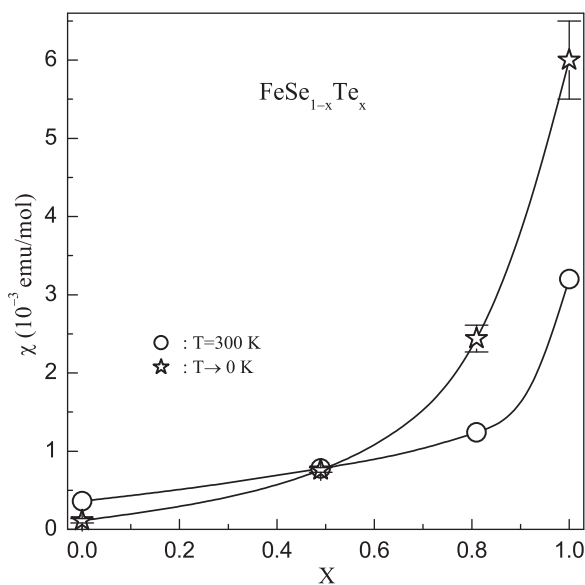


Fig. 1. Concentration dependencies of the magnetic susceptibility in the normal state for $\text{FeSe}_{1-x}\text{Te}_x$ alloys at $T=300$ K and $T\rightarrow 0$ K. Data for FeTe at $T\rightarrow 0$ K are estimated by extrapolation to zero temperature of the $\chi(T)$ dependence for the paramagnetic state. Solid lines are guides for the eye.

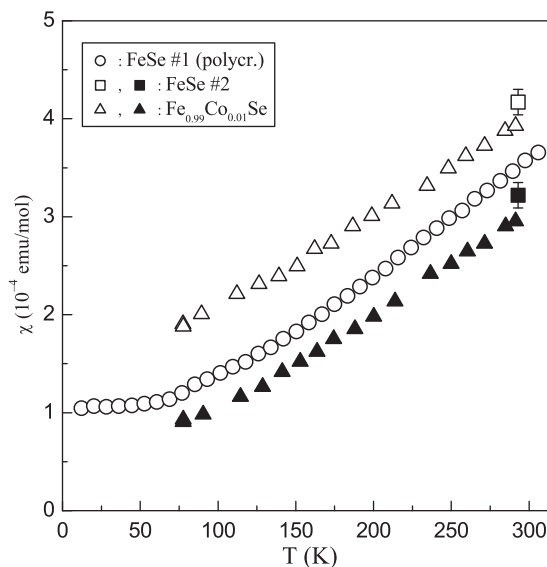


Fig. 2. Temperature dependencies of the magnetic susceptibility in the normal state for polycrystalline sample FeSe (#1) and single-crystalline samples FeSe (#2) and $\text{Fe}_{0.99}\text{Co}_{0.01}\text{Se}$. Data for single crystals corresponding to $H||ab$ plane and $H||c$ are denoted by the open and full symbols, respectively.

The measurements of temperature dependencies $\chi(T)$ for FeSe and the anisotropy of susceptibility of the single crystalline samples were carried out by a Faraday method in the temperature range 78–300 K and in magnetic field around $H \simeq 1$ T. The results of these measurements are presented in Fig. 2.

For FeTe $\chi(T)$ dependence exhibits an anomaly at $T \simeq 70$ K, which is apparently related to the magnetic and structural transitions [4,8,9,12]. In the paramagnetic state the $\chi(T)$ behavior is close to the Curie-Weiss law, and the values $\theta \simeq -240$ K and $\mu_{\text{eff}} \simeq 3.70\mu_B/\text{Fe}$ were estimated for FeTe. The study of the magnetic susceptibility under helium gas pressure P up to 2 kbar was performed at temperatures 55, 78 and 300 K using a pendulum-type magnetometer placed directly in the nonmagnetic pressure cell [13]. The measurements were carried out in the field $H=1.7$ T and their relative errors did not exceed 0.05%. The large positive values of the pressure effect, $d \ln \chi/dP \simeq 15 \div 30 \text{ Mbar}^{-1}$, were observed in the temperature range 78–300 K.

3. Computational details and results

To gain insight into the magnetic properties of FeSe(Te) compounds in the normal state, *ab initio* calculations of the electronic structure and paramagnetic susceptibility were performed for FeSe and FeTe. At ambient conditions FeSe(Te) possess the tetragonal PbO-type crystal structure, which is composed by alternating triple-layer slabs stacked along the c -axis. Each iron layer is sandwiched between two nearest-neighbor chalcogen layers, which form edge-shared tetrahedra around the iron sites. The positions of Se (or Te) sheets are fixed by the internal parameter Z , which represents the height of the chalcogen atoms above the iron square plane. The structure parameters of FeSe(Te) compounds were established by means of x-ray and neutron diffraction [3,4,8,9,14].

The aim of this work was to investigate the paramagnetic response in an external magnetic field and to elucidate the nature and features of paramagnetism in the parent FeSe and FeTe compounds. The dependencies of the magnetic susceptibility on volume, lattice parameters and temperature were addressed. *Ab initio* calculations of the electronic structures were carried

out by employing a full-potential all-electron relativistic linear muffin-tin orbital method (FP-LMTO, code RSPt [19]). The exchange-correlation potential was treated within the local spin density approximation [20] of the DFT. The calculated basic features of electronic structure for FeSe and FeTe are in a qualitative agreement with results of earlier calculations [15–18].

To evaluate the paramagnetic susceptibility of FeSe and FeTe, FP-LMTO-LSDA calculations of the field-induced spin and orbital (Van Vleck) magnetic moments were carried out within the approach described in Ref. [21]. The relativistic effects, including spin-orbit coupling, were incorporated, and the effect of an external magnetic field \mathbf{H} was taken into account self-consistently by means of the Zeeman term:

$$\mathcal{H}_Z = \mu_B \mathbf{H} \cdot (2\hat{\mathbf{s}} + \hat{\mathbf{l}}). \quad (1)$$

Here \mathbf{H} is the external magnetic field, μ_B the Bohr magneton, $\hat{\mathbf{s}}$ and $\hat{\mathbf{l}}$ the spin and orbital angular momentum operators, respectively. The field induced spin and orbital magnetic moments provide the related contributions to the magnetic susceptibility, χ_{spin} and χ_{orb} .

For the tetragonal crystal structure, the components of these contributions, $\chi_{i\parallel}$ and $\chi_{i\perp}$, are derived from the moments calculated in the external field of 10 T, which was applied parallel and perpendicular to the c axis, respectively. The evaluated anisotropy of the orbital contribution $\Delta\chi_{\text{orb}} = \chi_{\text{orb}\parallel} - \chi_{\text{orb}\perp}$ for FeSe and FeTe amounts to -0.3×10^{-4} and -0.35×10^{-4} emu/mol, respectively.

It is found that magnetic response to the external field is very sensitive to the unit cell volume, as well as to the internal parameter Z , related to the height of chalcogen species from the Fe plane. The calculated dependencies of susceptibility of FeTe as functions of the volume and parameter Z are given in Fig. 3. Similar dependencies were obtained for FeSe as well, but its susceptibility is scaled down about 10 times.

Finally, the thermal effects were taken into account to calculate the temperature dependence of susceptibility for FeSe compound via the Fermi-Dirac distribution function (see Fig. 4). It should be noted that the energy derivative of Fermi-Dirac distribution $-df/dE$ corresponds to a Dirac delta function at low temperatures, having a sharp positive peak at the Fermi energy E_F . This steep behavior of $-df/dE$ has introduced some instability in the numerical calculations of χ , which are clearly seen in Fig. 4.

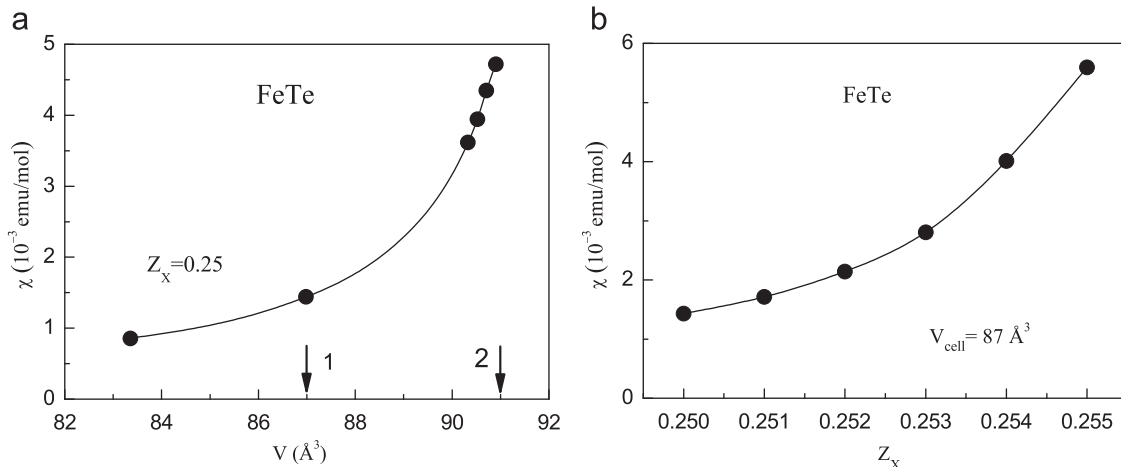


Fig. 3. Calculated paramagnetic susceptibility of FeTe. (a) As a function of unit cell volume. Z is taken to be 0.25. The arrows indicate the theoretical (1) and experimental (2) equilibrium volume values. (b) As a function of Z for the theoretical unit cell volume. The c/a ratio is fixed to the experimental ambient pressure value (1.64, [8]). Solid lines are guides for the eye.

4. Discussion

The experimental superconducting characteristics obtained for the studied $\text{FeSe}_{1-x}\text{Te}_x$ compounds agree with those reported in Refs. [8,9,12]. As seen in Fig. 1, our experimental data points to a gradual increase of the intrinsic magnetic susceptibility in $\text{FeSe}_{1-x}\text{Te}_x$ with increasing tellurium content of about ten times. For FeSe a substantial growth of susceptibility with temperature was revealed up to 300 K (Fig. 2), which indicates the itinerant nature of electronic states of Fe. In fact, this is confirmed by the calculated $\chi(T)$ for FeSe (see Fig. 4), which is in a qualitative agreement with the obtained experimental data.

The observed anisotropy of susceptibility $\Delta\chi$ is large in FeSe, and comparable with the averaged susceptibility itself at low temperatures. If one correlates the experimental data in Fig. 2 with the calculated $\chi(T)$ (Fig. 4) and $\Delta\chi_{\text{orb}} \simeq -0.3 \times 10^{-4}$ emu/mol, then the presence of a substantial and presumably anisotropic diamagnetic contribution can be assumed. In fact, the calculated χ_{spin} and χ_{orb} paramagnetic contributions have to be substantially compensated by a diamagnetic one in order to conform with the experimental

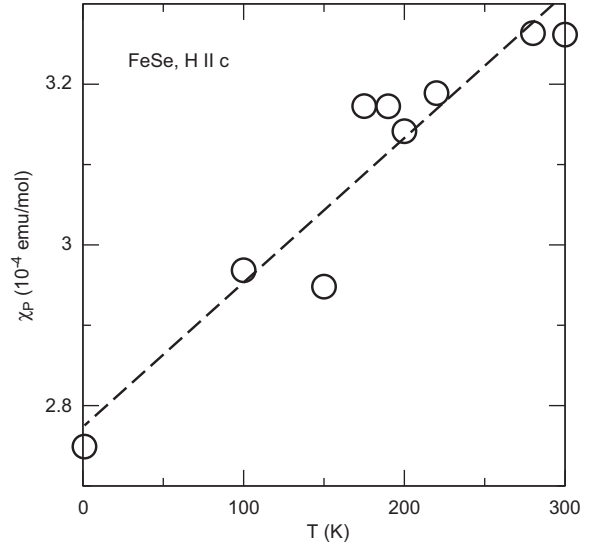


Fig. 4. Calculated temperature dependence of the paramagnetic susceptibility of FeSe. Z is taken to be 0.256, the unit cell volume and c/a ratio are fixed to their experimental ambient pressure values. The dashed line is a guide for the eye.

data in Fig. 2. Though the sign of calculated $\Delta\chi_{\text{orb}}$ is consistent with the observed $\Delta\chi$ for FeSe (Fig. 2), only the additional anisotropy could explain the experimental data on $\Delta\chi$. In this connection, it should be noted that a diamagnetism of conduction electrons χ_L can be many times larger than the free-electron Landau estimation χ_L^0 and such anomalous anisotropic diamagnetism is determined by a presence of quasi-degenerated states with small effective masses at E_F (see e.g. Ref. [22] and references therein).

As is seen in Fig. 3, the tetragonal FeTe compound is on the verge of magnetic instability. Due to this instability, our field-induced LSDA calculations for FeTe converged to the paramagnetic state only for reduced values of the lattice parameters. This is especially relevant to the parameter Z , which had to be reduced for about 10%. Nevertheless, these calculations have allowed to establish a trend for the effects of the structural parameters V and Z on χ , and to shed light on the nature of the observed pressure effect. Specifically, based on results of the *ab initio* calculations, presented in Fig. 3, it is found that the observed substantial pressure effect on χ for FeTe can be represented as a sum of two large in size and competing contributions, resulted from the pressure dependence of the structural parameters V and Z . Using the values of dV/dP (< 0) and dZ/dP (> 0), evaluated from Refs. [4,6,14], the large experimental value of the pressure effect, $d \ln \chi / dP \approx 20 \text{ Mbar}^{-1}$, can be described.

5. Conclusions

The intrinsic magnetic susceptibility in the series of iron chalcogenides $\text{FeSe}_{1-x}\text{Te}_x$ was found to increase gradually with Te content in about ten times. For FeSe a substantial growth of susceptibility with temperature was revealed up to 300 K, which points to the itinerant nature of the electronic states of Fe. The observed anisotropy of susceptibility $\Delta\chi$ is large in FeSe, and comparable with the averaged susceptibility at low temperatures.

Ab initio calculations of the paramagnetic susceptibility of FeSe and FeTe revealed that these systems are in close proximity to the quantum critical point, and this nearness can result in strong spin fluctuations. The calculated paramagnetic susceptibility of FeSe describes qualitatively the experimentally observed rise of χ with temperature. It is found, that the orbital contribution χ_{orb} in FeSe comes from d -electrons of Fe and provides the anisotropy $\Delta\chi_{\text{orb}} = -0.3 \times 10^{-4} \text{ emu/mol}$. The comparison of the experimental and calculated susceptibilities has revealed an additional anisotropic diamagnetic contribution about $-1 \times 10^{-4} \text{ emu/mol}$, which can originate from the diamagnetism of conduction electrons and has its origin in the quasi-degenerate electronic states close to E_F .

The calculated paramagnetic susceptibility of FeTe revealed a drastic sensitivity to the unit cell volume V and the height of Te species from the Fe plane. It is found that the observed large positive pressure effect on χ is related to considerable sensitivity

of the susceptibility to the structural parameters, particularly to the internal parameter Z , determining the dominant positive term. Our results point out that the itinerant magnetism approach is relevant to describe the paramagnetic state of FeSe. However, more rigorous calculations of χ are required for FeTe and the Te rich systems.

Acknowledgments

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