Magnetic ordering in TlFe$_{1.3}$Se$_2$ studied by Mössbauer spectroscopy

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**Abstract**

We report the results of $^{57}$Fe Mössbauer spectroscopy measurements of the new nonsuperconducting compound TlFe$_{1.3}$Se$_2$ in the temperature range 4.4–373.2 K and in an external magnetic field of 90 kOe. We provide evidence for a possible phase separation into magnetic majority and minority phases. We show that these magnetic phases order antiferromagnetically with two different magnetic moments at 5.0 K of 2.00(1) and 1.40(2) $\mu_B$, and with the Néel temperature $T_N$ = 324.5(6.3) K. We find that the Debye temperature of the studied compound is 221(2) K.

1. Introduction

Recently, there has been renewed interest in the family of Fe-deficient compounds TlFe$_{2-y}$Se$_2$ that had been synthesized and studied a long time ago [1–4]. This interest has been triggered by the discovery of superconductivity in iron-based superconductors [5–7]. In particular, the recent discovery of superconductivity in iron-selenide compounds A$_x$Fe$_2$$_{1-y}$Se$_2$ and (A,Tl)$_x$Fe$_{2-y}$Se$_2$ (A = K, Rb, Cs) [8–14], with critical temperatures up to about 32 K, has resulted in a renewed interest in iron-based chalogenide compounds.

Initially, these new superconductors were believed to have the crystal structure of the ThCr$_2$Si$_2$ type (space group $I4/mmm$) [15], but it was soon realized that there is a well-defined $\sqrt{5} \times \sqrt{5} \times 1$ ordering of Fe vacancies, similarly to what had been proposed by Hägglström et al. [2] for TiFe$_{2-y}$Se$_2$ compounds, which reduces the symmetry to the space group $I4/m$ [16–18]. A remarkable characteristic of these new superconductors is that they are very strong antiferromagnets, with unprecedentedly high values of Néel temperature, $T_N$, of 475–559 K (Refs. [17,19–23]) and of Fe magnetic moment of 2.0–3.3 $\mu_B$ [17,22,24–26]. Although it is still under debate how superconductivity can coexist with such strong antiferromagnetism in these superconductors, there is an increasing body of experimental evidence [27] suggesting that the antiferromagnetic phase is spatially separated from the superconducting phase.

In view of this renewed interest in the TiFe$_{2-y}$Se$_2$ compounds [28–31], we have carried out a detailed study of the recently synthesized new compound TlFe$_{1.3}$Se$_2$ (Ref. [14]) with Mössbauer spectroscopy. We provide evidence for a possible separation into magnetic majority and minority phases. We show that the compound studied is an antiferromagnet with $T_N$ = 324.5(6.3) K.

2. Experimental methods

The single crystals of the studied compound TlFe$_{1.3}$Se$_2$ were grown by the Bridgman method [14]. Powder X-ray powder diffraction measurements were performed at 298 K in Bragg-Brentano geometry with a PANalytical X'Pert scanning diffractometer using Cu Kα radiation.

The $^{57}$Fe Mössbauer measurements were conducted using standard Mössbauer spectrometers operating in sine mode and a 100-mCi $^{57}$Co(Rh) source, which was kept at the same temperature as that of the absorber in-field measurements and at room temperature for zero-field measurements. The spectrometers used for zero-field and in-field measurements were calibrated, respectively, with a 6.35-μm-thick $^5$Fe foil [32] and a Michelson interferometer [33], and the spectra were folded.

The Mössbauer absorber for low-temperature (<300 K) measurements was made in a glove box from several pulverized single crystals. The powder material was mixed with boron nitride and placed into a boron-nitride container. The surface densities of the Mössbauer absorbers for low-temperature and high-temperature measurements were 24.3 mg/cm$^2$ and 17.5 mg/cm$^2$, respectively. Both Mössbauer absorbers were exposed to air for about 60 s when they were transported from the glove box to the Mössbauer cryostat and the Mössbauer oven. The high atomic absorption of the 14.4-keV γ-rays by Ti and Se, and a relatively small concentration of Fe in the compound studied, necessitated an acquisition time of about 3–7 days for a single Mössbauer spectrum.
The surface densities of the Mössbauer absorbers for low-temperature and high-temperature measurements correspond to an effective thickness parameter $T$ of 2.6 Å and 1.3 Å, respectively, where $T$ is the Lamb-Mössbauer factor of the absorber. Since $T > 1$, the resonance line shape of the Mössbauer spectrum was described using a transmission integral formula [35]. In addition to the hyperfine parameters, only the absorber Debye-Waller factor $f_a$ and the absorber linewidth $\Gamma_a$ were fitted as independent parameters. The source linewidth $\Gamma_s = 0.130$ mm/s and the background-corrected Debye-Waller factor of the source $f_s = -0.30$ were used in the fits [35]. The $^{57}$Fe Mössbauer spectra were analyzed by means of a least-squares fitting procedure which entailed calculations of the positions and relative intensities of the absorption lines by numerical diagonalization of the full hyperfine interaction Hamiltonian [34].

3. Experimental results and discussion

The room-temperature powder x-ray diffraction pattern of TlFe$_{1.3}$Se$_2$ is shown in Fig. 1. It reveals that the studied compound is single phase as there are no extrinsic Bragg peaks present in the measured pattern. The structural parameters of TlFe$_{1.3}$Se$_2$ obtained from the Rietveld refinement (Fig. 1) in the $I4/mmm$ space group are listed in Table 1. Rietveld analysis of the powder x-ray diffraction pattern of TlFe$_{1.3}$Se$_2$, with a freely refined occupancy (Table 1) of Fe [0.727(23)], yields the formula TlFe$_{1.43}$Se$_2$ for the compound of nominal composition TlFe$_{1.3}$Se$_2$.

The $^{57}$Fe Mössbauer spectra of TlFe$_{1.3}$Se$_2$ at 5.0 K measured in the external magnetic fields $H_{ext} = 0$ and 90 kOe applied parallel to the γ-ray propagation direction are shown in Fig. 2. One can see that the zero-field spectrum (Fig. 2) results from the superposition of at least two Zeeman patterns. The fit of this spectrum with two Zeeman patterns yields the following parameters: the absorber linewidth $\Gamma_a$, the centre shift $\delta$ (relative to Fe at 298 K), the hyperfine magnetic fields $H$, the quadrupole splitting $\delta q = \frac{1}{2}eQV_{zz}$, the asymmetry parameter $\eta$, the angle $\beta$ between $V_{zz}$ and $H$, and the spectral area $A$ [34]. The values of these parameters corresponding to these two-component Zeeman patterns are $\Gamma_a = 0.179(13)$ mm/s, $\Gamma_{zz} = 0.207(40)$ mm/s, $\delta_1 = 0.541(4)$ mm/s, $\delta_2 = 0.445(19)$ mm/s, $H_1 = 268.3(1.8)$ kOe, $H_2 = 187.4(2.5)$ kOe, $\delta q_1 = 0.946(179)$ mm/s, $\delta q_2 = 1.837(94)$ mm/s, $\eta_1 = 0.1(2)$, $\eta_2 = 0.0(2)$, $\beta_1 = 44(6)^{\circ}$, $\beta_2 = 48(1)^{\circ}$, $A_1 = 75.7(7)^{\%}$, $A_2 = 24.3(9)^{\%}$.

As the Fe atoms are located at the 4d sites in the space group $I4/mmm$ (Table 1), one would expect to observe at temperatures below the magnetic ordering temperature one Zeeman pattern, and the measured pattern. The structural parameters of TlFe$_{1.3}$Se$_2$ obtained is single phase as there are no extrinsic Bragg peaks present in the

### Table 1

Refined structural parameters of TlFe$_{1.3}$Se$_2$ at 298 K. Space group: $I4/mmm$ (No. 139), lattice constants $a = 3.9047(3)$ Å, $c = 13.8634(6)$ Å.

<table>
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<tr>
<th>Atom</th>
<th>Site</th>
<th>Point symmetry</th>
<th>Occupancy</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_{iso}$ ($\AA^2$)</th>
</tr>
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<tbody>
<tr>
<td>Ti</td>
<td>2a</td>
<td>4/mmm</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.6(1)</td>
</tr>
<tr>
<td>Fe</td>
<td>4d</td>
<td>4m2</td>
<td>0.727(23)</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0.5(1)</td>
</tr>
<tr>
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<td>4e</td>
<td>4mm</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.353(3)</td>
</tr>
</tbody>
</table>

$R_{p} = 11.9\%$, $R_{wp} = 15.3\%$, $\chi^2 = 18.4\%$

![Fig. 1](image1.png)

**Fig. 1.** The powder x-ray diffraction pattern of TlFe$_{1.3}$Se$_2$ at 298 K. The experimental data are denoted by open circles, while the line through the circles represents the result of the Rietveld refinement. The row of vertical bars shows the Bragg peak positions for the $I4/mmm$ space group. The lower solid line represents the difference curve between experimental and calculated patterns.

![Fig. 2](image2.png)

**Fig. 2.** The $^{57}$Fe Mössbauer spectra of TlFe$_{1.3}$Se$_2$ at 5.0 K in zero and 90 kOe external magnetic field $H_{ext}$ applied parallel to the direction of the γ-rays, fitted (blue solid lines) with two Zeeman patterns (brown and green lines), as described in the text. The zero-velocity origin is relative to the source. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The relatively large values of $\delta$ indicate that Fe atoms in both the main and separated magnetic phases are in the divalent oxidation state [34]. One can estimate the on-site magnetic moment $\mu$ of iron atoms from the measured $H$ since, to a first approximation, $H$...
is proportional to $\mu$ via the relation $H = a\mu$, where the value of the proportionality constant $a$ is compound specific [40]. To convert $H$ to $\mu$, $a = 134$ kOe/$\mu_B$ was used. This value of $a$ was obtained from $H(4.2\text{ K}) = 201(4)$ kOe and $\mu(16\text{ K}) = 1.5(2)\mu_B$ determined from a Mössbauer and neutron diffraction study of orthorhombic Tl$_4$Fe$_2$S$_4$ [41]. Thus, the values of the iron magnetic moments at 5.0 K of the majority and the minority phases are $2.00(1)$ and $1.40(2)\mu_B$, respectively.

The $^{57}$Fe Mössbauer spectra of a magnetically ordered compound measured in zero external magnetic field give information on the magnitude and direction of the hyperfine magnetic field, and thus of the Fe magnetic moment, but not on the type of magnetic ordering of these moments. Information on the type of magnetic ordering can be obtained from Mössbauer spectra measured in a strong enough external magnetic field $H_{ext}$ [42]. It can be observed in the Mössbauer spectrum of TlFe$_{1.3}$Se$_2$ measured in $H_{ext} = 90$ kOe (Fig. 2) that each component Zeeman pattern in the zero-field spectrum is split into two components of equal intensity. Furthermore, the fitted hyperfine magnetic fields $H_i(H_{ext})$ ($i = 1,2$) obey, within experimental error, the relation $H_i(H_{ext}) = H_i \pm H_{ext}$ ($i = 1,2$). This clearly demonstrates [42,43] the antiferromagnetic ordering of the Fe magnetic moments in the compound studied. In addition, obeying this relation means that the spin-flop field [42,43] for the studied antiferromagnet is larger than 90 kOe.

Fig. 3 shows the $^{57}$Fe Mössbauer spectra of TlFe$_{1.3}$Se$_2$ measured in the temperature range 4.4–373.2 K. The spectra at 4.4 and 34.9 K can be fitted with two Zeeman patterns, similarly to the zero-field spectrum at 5.0 K in Fig. 2. However, the fits of the spectra at 48.4 K and at higher temperatures (Fig. 3) require the inclusion of an additional quadrupole doublet pattern. The spectral area of this quadrupole doublet pattern increases with temperature at the expense of the spectral area of the two Zeeman patterns. What is also evident from visual inspection of the spectra in Fig. 3 is that the hyperfine magnetic fields $H_1$ and $H_2$ corresponding to the two Zeeman patterns decrease with temperature, as expected, but that this decrease is unusually small. This can be clearly seen in Fig. 4 which shows the temperature dependence of $H_1$ and $H_2$ derived from the fits of the Mössbauer spectra in Figs. 2 and 3.

![Fig. 3. The $^{57}$Fe Mössbauer spectra of TlFe$_{1.3}$Se$_2$ at the indicated temperatures fitted (blue solid lines) with two Zeeman patterns (brown and green solid lines) and a quadrupole doublet pattern (pink solid lines), as described in the text. The zero-velocity origin is relative to $\alpha$-Fe at room temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
One observes a sudden drop of the hyperfine magnetic field (Fig. 4) at \( T_N = 324.5(6.3) \) K. At 318.2 K \( H_1 \neq 0 \) and \( H_2 \neq 0 \), but at 330.7 K \( H_1 = H_2 = 0 \). Clearly, the transition at \( T_N = 324.5(6.3) \) K is a first order magnetic transition. A similar abrupt drop of the hyperfine magnetic field around \( T_N \) was observed for the nonsuperconducting compounds TlFe\(_2\)Se\(_2\) at 0 K and \( B = 90 \) kOe are reported. Evidence is provided for a possible phase separation into majority and minority magnetic phases. It is shown there in.

4. Conclusions

The results of a \(^{57}\text{Fe}\) Mössbauer spectroscopy study of the new nonsuperconducting compound TlFe\(_1.64\)Se\(_2\) for temperatures between 4.4 and 373.2 K and in an external magnetic field of 90 kOe are reported. Evidence is provided for a possible phase separation into majority and minority magnetic phases. It is shown that these phases order antiferromagnetically with two different magnetic moments at 5.0 K of 2.00(1) and 1.40(2) \( \mu_B \), and with the Néel temperature \( T_N = 324.5(6.3) \) K. The Debye temperature of the studied compound is found to be 221(2) K.

Acknowledgments

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References