Magnetic Properties of Chain Antiferromagnets $RbFeSe_2$, $TlFeSe_2$, and $TlFeS_2$

Z. Seidov[a, b], H.-A. Krug von Nidda[a], V. Tsurkan[a, c], I. Filippova[c], A. Günther[a], A. Najafov[b],
M. N. Aliyev[d], F. G. Vagizov[e], A. G. Kiiamov[e], L. R. Tagirov[e, f, g], *, T. Gavrilova[f], and A. Loidl[a]

[a]Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, 86135 Augsburg, Germany
[b]Institute of Physics, Azerbaijan National Academy of Sciences, Baku, AZ-1143 Azerbaijan
[c]Institute of Applied Physics, Moldova Academy of Sciences, Chisinau, MD-20208 Moldova
[d]Faculty of Solid State Physics, Baku State University, Baku, AZ-1148 Azerbaijan
[e]Institute of Physics, Kazan Federal University, Kazan, 420008 Russia
[f]Zavoisky Physicotechnical Institute, Russian Academy of Sciences, Kazan, 420029 Russia
[g]Institute of Advanced Studies, Tatarstan Academy of Sciences, Kazan, 420111 Russia
*e-mail: ltagirov@mail.ru

Abstract—Single crystals of ternary ion chalcogenides $RbFeSe_2$, $TlFeSe_2$, and $TlFeS_2$ are studied by X-ray diffraction, SQUID magnetometry, and Mössbauer spectroscopy. Common structural units of these chalcogenides are tetrahedra of $FeCh_4$ (chalcogen Ch = Se, S), arranged in chains by sharing an edge. It is found that $RbFeSe_2$, $TlFeSe_2$, and $TlFeS_2$ undergo transition to a collinear antiferromagnetic state below temperatures T_N = 248, 290, and 196 K, respectively. Their magnetic moments are oriented perpendicular to the axes of the chains of $FeCh_4$ tetrahedra.

INTRODUCTION

The recent discovery of superconductors based on iron [1, 2] has stimulated great interest in studies of iron chalcogenides and pnictides. The main structural feature of iron superconductors is the presence of two-dimensional layers [2, 3] or one-dimensional chains [4] containing tetrahedra of $FePn_4$ or $FeCh_4$, where Pn and Ch are pnictogens and chalcogens. The interconnection of superconductivity and structure, and the degree of magnetic moment localization on iron ions, has therefore drawn much attention.

Ternary iron-containing chalcogenides $RbFeSe_2$, $TlFeSe_2$, and $TlFeS_2$ belong to the family of quasi-one-dimensional compounds of the class $AFeCh_2$ (A = K, Rb, Cs, Tl; Ch = S, Se), in which $[FeCh_4]$ tetrahedra are ordered along crystallographic axis c of lattices with shared edges [5–8]. The tetrahedra chains are connected to each other by rubidium or thallium atoms, forming a three-dimensional lattice (see Fig. 1 in [5] and Fig. 9 in [6]) with weak mechanical strength. The minimum distances between iron atoms in the chains (2.83 Å for $RbFeSe_2$; 2.74 Å for $TlFeSe_2$; 2.65 Å for $TlFeS_2$) are close to that of interatomic spacing in metallic iron (2.48 Å) [10]. Such short distances produce strong covalence effects that usually reduce the local spin on magnetic ions and delocalize charge carriers at the Fermi level. This in turn ensures quasi-one-dimensional conductivity along the chains. Ternary iron chalcogenides with $AFeCh_2$ structure (A =

K, Rb, Cs, Tl; Ch = S, Se) are thus quite interesting and promising objects for investigating the correlation between the structural features of iron chalcogenides and the cooperative phenomena that occur in them (including magnetism and superconductivity).

EXPERIMENTAL

Single crystals of $RbFeSe_2$, $TlFeSe_2$, and $TlFeS_2$ were grown using the Bridgman technique. They had the acicular shape typical for quasi-one-dimensional compounds. Their elemental composition was determined via wavelength-dispersive X-ray microanalysis (WDS EPMA) and showed no deviations from stoichiometry at the 2% level of the measurement error. The phase composition was determined from X-ray diffraction measurements of powder samples at room temperature on a STOE STADI P diffractometer equipped with an X-ray source that had a copper electrode. Rietveld analysis of the diffraction patterns using the FULLPROF software [11] revealed no foreign phases (at least at the sensitivity level of the instrument).

Magnetic measurements were made on a SQUID MPMS5 QUANTUM DESIGN magnetometer in the temperature range of 1.8 to 720 K and magnetic fields of up to 50 kOe. Mössbauer measurements were made on a WissEl constant acceleration spectrometer in the temperature range of 10–300 K; our source of gamma radiation was ^{57}Co in a rhodium matrix. The spec-
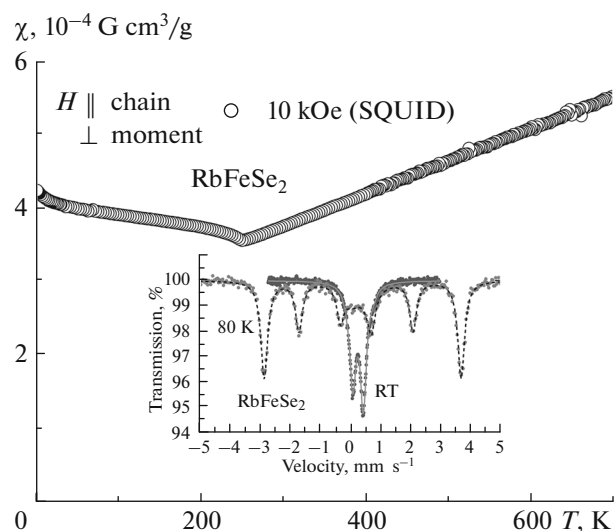
Fig. 1. Temperature dependence of the susceptibility of RbFeSe$_2$ single crystals. The insert shows the Mössbauer spectra of RbFeSe$_2$ at room temperature (RT) and at 80 K.

Fig. 2. Temperature dependence of the susceptibility of TlFeSe$_2$ single crystals.

trometer was calibrated at room temperature using metallic α-Fe. The grinding of the single crystals and all preliniary procedures for X-ray, magnetic, and Mössbauer studies were performed in a high-purity argon atmosphere. The conditions during our measurements ensured the maximum protection from interaction with the environment: the samples were either encapsulated in silicone sealant or put into an airtight container transparent to ionizing radiation.

RESULTS AND DISCUSSION

RbFeSe$_2$

Figure 1 shows dependence $\chi(T)$ with a magnetic field applied parallel to crystallographic axis c (i.e., parallel to the chains of FeSe$_4$ tetrahedra). The temperature dependence of the magnetic susceptibility is typical for one-dimensional magnetic systems subject to antiferromagnetic transitions. There is a characteristic kink in the $\chi(T)$ dependence at $T_N = 248$ K. The linear dependence of the magnetic moment on the field applied parallel to the chains at the temperatures above and below the kink temperature is evidence of an antiferromagnetic state with Néel temperature $T_N = 248$ K and the magnetic moment of iron atoms ordered perpendicular to the chains [12].

When $T > T_N$, susceptibility grows linearly with temperature up to the highest temperature of measurement, 720 K. The linear growth of the susceptibility is atypical for one-dimensional chain systems with antiferromagnetic Heisenberg exchange, which display a maximum on the susceptibility curve at a temperature comparable to the energy of intrachain iron–iron exchange (in the same units of measurement). For instance, susceptibility maxima were observed in
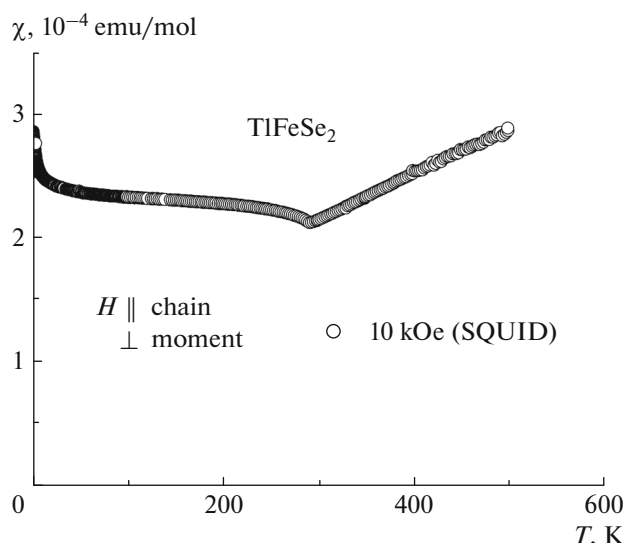
potassium and cesium iron sulfides at $T_{max} = 565$ K (for KFeS$_2$) and $T_{max} = 800$ K (for CsFeS$_2$) [13].

The observed behavior of the susceptibility with maxima was explained by a model of $S = 1/2$ spins with antiferromagnetic exchange between nearest neighbors [14]. This could, however, be evidence of a substantial reduction of the spin moment on an iron site, compared to expected spin $S = 5/2$ for electron configuration $3d^64s^2$ of the Fe atom. Our Mössbauer measurements (see the insert in Fig. 1) yield a hyperfine field of ~202 kOe at 80 K; along with the magnetic moment of 2.66μ_B obtained from the neutronographic studies in [12], this could correspond to an intermediate spin of $S = 3/2$ on an iron ion instead of the high-spin state $S = 5/2$, which follows from the electron configuration of the iron atom. At the same time, low-spin state $S = 1/2$ is obviously incompatible with the results from our magnetic and Mössbauer measurements.

TlFeSe$_2$

The results from studies of $\chi(T)$ with magnetic fields applied parallel to crystallographic axis c are presented in Fig. 2. The shape of the curve is generally similar to that of RbFeSe$_2$, but the kink here corresponds to $T_N = 290$ K. Above this point, the dependence $\chi(T)$ is linear up to the highest temperature of measurement. The magnetic moment of 2.1μ_B [15] means that neither the high-spin $S = 5/2$ nor the low-spin $S = 1/2$ pure states of the iron ions can describe the magnetic properties of thallium iron selenide.
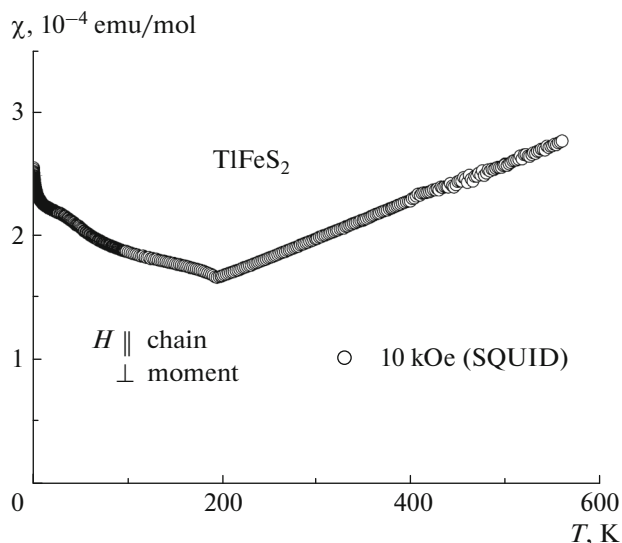
Fig. 3. Temperature dependence of the susceptibility of $TlFeS_2$ single crystals.

that will block the metallic conductivity along the chain. Means of local detection (e.g., nuclear magnetic resonance) are needed to confirm one-dimensional conductivity.

TlFeS2

The results from studies of $\chi(T)$ with magnetic fields applied parallel to crystallographic axis c are presented in Fig. 3. The shape of the curve resembles that of $RbFeSe_2$ and $TlFeSe_2$, but the kink here is at $T_N = 196$ K. Above 196 K, the dependence $\chi(T)$ is linear up to the highest temperature of measurement. The values of the magnetic moment ($1.85\mu_B$ [16]) and the hyperfine field (163 kOe [17]) are also inconsistent with the high- or low-spin states of the iron ions in thallium iron sulfide.

CONCLUSIONS

Quasi-one-dimensional ternary iron chalcogenides $RbFeSe_2$, $TlFeSe_2$, and $TlFeS_2$ display similar temperature behaviors of their magnetic susceptibility that are characterized by linear temperature dependences in the paramagnetic region above T_N. The temperature dependence of the susceptibility reveals no signs of saturation up to the highest temperatures at which measurements are still possible and the crystal chemistry of a sample remains intact. The strictly linear dependence of the susceptibility up to the highest temperatures of measurement and the considerable drops in the magnetic moment and hyperfine field suggest conductivity of a metallic character along the structural chains. Our earlier measurements of the temperature dependences of the resistivity of thallium iron chalcogenides [18] and preliminary measurements of the resistivity of rubidium compounds revealed no metallic conductivity along the c axes of single crystals. This was because if the one-dimensional character is retained strictly, there will inevitably be defects or kinks on the millimeter scale of length

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