Magnetic properties of the covalent chain antiferromagnet RbFeSe₂

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Single crystals of the ternary iron selenide RbFeSe₂ have been investigated by means of x-ray diffraction, magnetic susceptibility, magnetization, and specific-heat measurements as well as by Mössbauer spectroscopy. Built up from linear chains of edge-sharing FeSe₄ tetrahedra, RbFeSe₂ represents a quasi-one-dimensional antiferromagnet. Below $T_N = 248$ K three-dimensional antiferromagnetic collinear magnetic order sets in, with the magnetic moments oriented perpendicularly to the chain direction. The hyperfine fields determined from our Mössbauer studies reveal strongly reduced magnetic moments. The high-temperature susceptibility data of RbFeSe₂ suggest a one-dimensional metallic character along the chains.

I. INTRODUCTION

The recent discovery of iron-based superconductors [1–4] has stimulated high interest and enormous scientific activities in the field of iron-pnictide and -chalcogenide materials. Notably, all iron-based superconductors exhibit some structural similarity. From the initially discovered LaFeAsO$_{1-x}$F$_x$ to recently reported K$_x$Fe$_{2-y}$Se₂ and (Tl,K)Fe$_{2-x}$Se₂, two-dimensional (2D) layers of FePn or FeCh (Pn = pnictogens, Ch = chalcogens) tetrahedra are the common structural units [5–9]. The mechanism of superconductivity and its relation to the crystal structure in these systems is still under debate. In particular, the question concerning localization or delocalization of the magnetic moments of iron deserves intense consideration. Therefore, in order to achieve deeper insight into the nature of superconductivity, the study of materials containing similar building blocks related to these systems is of significant interest. In this respect, it is important to note that currently pressure-induced superconductivity has been discovered even in the 1D spin-ladder compound BaFe₂S₃ consisting of FeS₄ tetrahedra as well [10].

Systematic structural investigations of ternary metal chalcogenides A_xFe$_y$X$_z$ (A = alkali metal, Tl; X = S, Se) have revealed a variety of distinct compositions with tetrahedral [FeX_4] structural units, i.e., A_5FeX_4, AFe₂X_2, AFe₂X_3, A_3FeX_3, AFeX_2, and A_3Fe₂X_4 [11–19]. The chalcogenide crystals Na₅FeS₄, A_3FeX_3 (A = Na, Cs; X = S, Se), and AFeX_2 (A = K, Cs; X = S, Se) consist of discrete tetrahedral [FeS₄]$^{5-}$ complexes [14], edge-linked double tetrahedral [Fe₂X_6]$^{6-}$ complexes [15,20,21], or one-dimensional $^1_\infty$[Fe$X_{4/2}$]$^-$ chains [15,22,23], respectively. Magnetic susceptibility measurements revealed a systematic reduction of the local iron-spin moment $S = 5/2$ of discrete tetrahedra down to $S = 3/2$ in double-tetrahedral complex and towards $S = 1/2$ in chain compounds [14,15,20–24].

In this work we concentrate on RbFeSe₂ chalcogenide, which belongs to the group of one-dimensional compounds AFeX_2 consisting of linear chains of edge-sharing [FeX_4] tetrahedra along the c direction separated by Rb atoms (see Fig. 1). Concerning the question about the relation of superconductivity and magnetism, these linear chain compounds serve as useful model systems, because the small Fe-Fe intrachain separation gives rise to strong covalence effects and is expected to promote spin reduction and charge-carrier delocalization on the verge to 1D metallic behavior.

The crystallographic and magnetic data for AFeX_2 (A = K, Rb, Cs, Tl; X = S, Se) are collected in Table I. In their magnetic properties, the iron compounds can be divided into three groups as follows (see references in Tiwary and Vasudevan [24], Seidov *et al.* [25], Asgerov *et al.* [26], Nishi and Ito [27,28], Welz *et al.*[29–32], and Bronger and Müller [15,22]):

(1) monoclinic TlFeS₂, TlFeSe₂, KFeSe₂, and RbFeSe₂ with the magnetic moments ordered perpendicular to the chains;

(2) orthorhombic CsFeS₂ with no magnetic order down to the structural transition at $T_{struc} = 70$ K (below T_{struc} with orientation of the magnetic moments approximately along the chain direction); and

(3) monoclinic KFeS₂, RbFeS₂ with the ordered moments slightly tilted from the chain axis.

All these compounds involve formally trivalent iron with a half-filled 3d electronic shell. The ordered magnetic moment, far below the ionic high-spin value of 5μ_B, indicates a considerable 3d delocalization, which has been attributed to intimate Fe contact resulting from the in-chain Fe distance, not much exceeding the Fe-Fe distance (2.48 Å) of metallic iron. Hence, a certain degree of itinerancy along the chains and concomitant one-dimensional metallic behavior can be expected.

In this article we present x-ray diffraction, magnetization, specific-heat, and Mössbauer experiments on single-crystalline RbFeSe₂. The comparison of our results with those of related 1D and 2D iron chalcogenides and pnictides is

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