Magnetic and vibrational properties of the covalent chain antiferromagnet RbFeS$_2$

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Ternary rubidium-iron sulfide, RbFeS$_2$, belongs to a family of quasi-one-dimensional compounds with the general chemical composition AFeCh_2 (where A – K, Rb, Cs, Tl; Ch – S, Se). Understanding the magnetic properties of these compounds is a challenge. The controversy concerning the spin-state of the iron ion needs to be resolved to build the proper model of magnetism. Single crystals of RbFeS$_2$ were grown and characterized by powder x-ray diffraction. QD MPMS-5 SQUID magnetometry was used to measure the magnetic susceptibility, and specific heat was measured utilizing QD PPMS-9 setup. Above the transition to three-dimensional antiferromagnetic order at the Néel temperature of T_N = 188 K, the susceptibility exhibits unusual quasi-linear increase up to the highest measured temperature of 500 K. The specific heat was measured in the temperature range 1.8 – 300 K. *Ab initio* phonon dispersion and density-of-states calculations were performed by means of density functional theory (DFT), and the calculated lattice specific heat was subtracted from the measured one giving the magnetic contribution to the specific heat. Our results suggest that the features of the magnetic specific heat are general for the whole family of the covalent chain ternary iron chalcogenides of the AFeCh_2 structure and indicate an intermediate S = 3/2 spin state of the iron ion.

1. Introduction

Ternary rubidium-iron sulfide, RbFeS$_2$, is a representative of a family of quasi-one-dimensional compounds with the chemical composition AFe$Ch2$ (where A – K, Rb, Cs, Tl; Ch – S, Se) [1]. Understanding the magnetic properties of these compounds meets with a controversy concerning the spin-state of the iron ion important for building the proper model of magnetism [3]. RbFeS$_2$ consists of linear chains of edge-sharing [FeS4] tetrahedra along the crystallographic c direction, separated by Rb atoms (see Fig. 1a). These chains are cross-linked by alkali atoms to form a three-dimensional structure. Concerning the question about the relation of superconductivity and magnetism in iron-based superconductors, these linear chain compounds serve as a useful model system, because the small Fe-Fe intra-chain separation (2.71 Å [2]) gives rise to strong covalence

effects and is expected to promote spin reduction and charge-carrier delocalization on the verge to 1D metallic behavior [2].

In the present study, we focus on the magnetic properties of $RbFeS_2$. The aim of the present report is to obtain the temperature dependence of the specific heat of the magnetic subsystem of the compound under study. The temperature behavior of the magnetic specific heat can shed light on the magnetic intra-chain and inter-chain interaction between iron ions in $RbFeS_2$. While the magnetic interactions in $RbFeS_2$ are essential to build the correct model of the magnetic subsystem of $RbFeS_2$. We assume that the total specific heat originates from two contributions, a lattice specific heat due to acoustic and optical phonon, and a magnetic one determined by the thermal population of excited magnetic states. We estimate the magnetic specific heat as a difference between the total experimentally measured heat capacity and the calculated lattice specific heat. The lattice specific heat we use in the present study was obtained within the quasi-harmonic approach by using *ab initio* calculated phonon density of states obtained in our previous study [4].
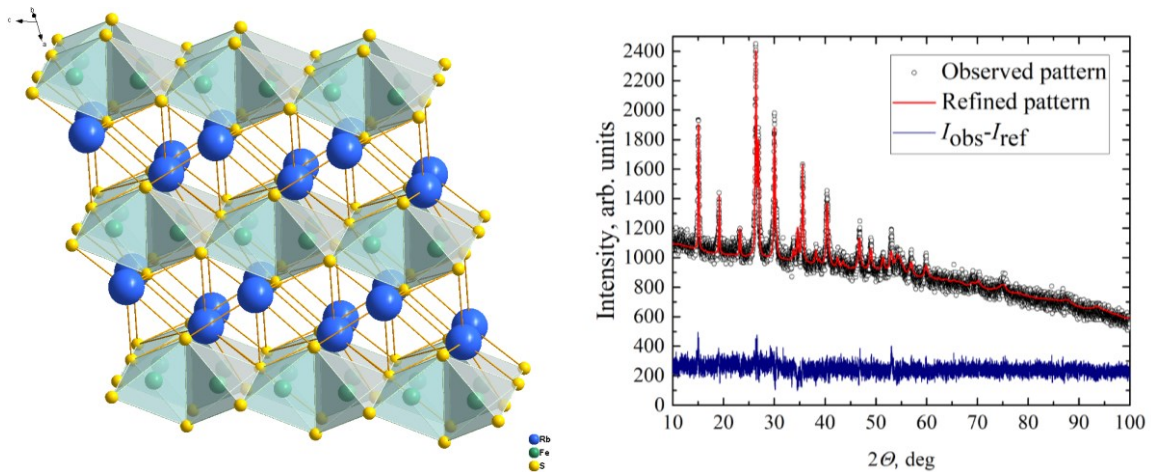

FIG. 1. *Left(a):* crystal structure of RbFeS2. The FeS4 tetrahedra, with Fe drawn as the green sphere in the center and S as the yellow sphere at the corners, are highlighted in transparent green color. Large blue spheres denote Rb ions. *Right(b):* Powder-diffraction pattern of $RbFeS_2$. The empty circles represent the measured intensities. The red solid line shows the refined pattern. The difference pattern $I_{obs.} - I_{cal}$ is indicated by the solid blue line.

2. Sample preparation and methods

Single crystals of $RbFeS_2$ were grown by the Bridgman method. The structural details of the crystals were investigated by conventional x-ray diffraction on powdered single crystals at room temperature using a STOE STADI P diffractometer with CuKα radiation. The data were analyzed by standard Rietveld refinement using the program FULLPROF [5] (Fig. 1b).

We could not detect any impurity phases above the background. The structural analysis confirmed the C2/c monoclinic structure for $RbFeS_2$ with lattice parameters $a = 7.234$ Å, $b = 11.739$ Å, $c = 5.441$ Å, and $\beta = 112.005°$[6]. The specific heat was measured by a relaxation method using a PPMS (Quantum Design) in the temperature range 1.8-300 K indicating an anomaly is at $T_N = 188$ K evidencing long-range AFM order[7].

3. Magnetic specific heat

We assume that the total specific heat consists of two contributions, a lattice specific heat due to acoustic and optical phonon, and a magnetic one determined by the thermal population of excited

magnetic states. We estimate the magnetic specific heat as a difference between the total experimental heat capacity and the calculated vibrational part. The phonon density of states enables to calculate directly the lattice contribution to the specific heat by using the harmonic approximation [8]. In the harmonic approximation the lattice heat capacity can be determined as follows [9]:

$$C_V(T) = DNk_B \int \left[\frac{\hbar\omega / 2k_B T}{\sinh\left(\hbar\omega / 2k_B T\right)} \right]^2 g_T(\omega) d\omega ,$$

where D is the number of degrees of freedom in the unit cell (3 in our case), and $g_T(\omega)$ is the total phonon density of states. In the present study, we use *ab initio* calculated phonon density of states [4]. We obtained the magnetic specific heat as a difference between the experimentally measured total specific heat and the calculated lattice contribution. The magnetic specific heat is presented in Fig. 2.
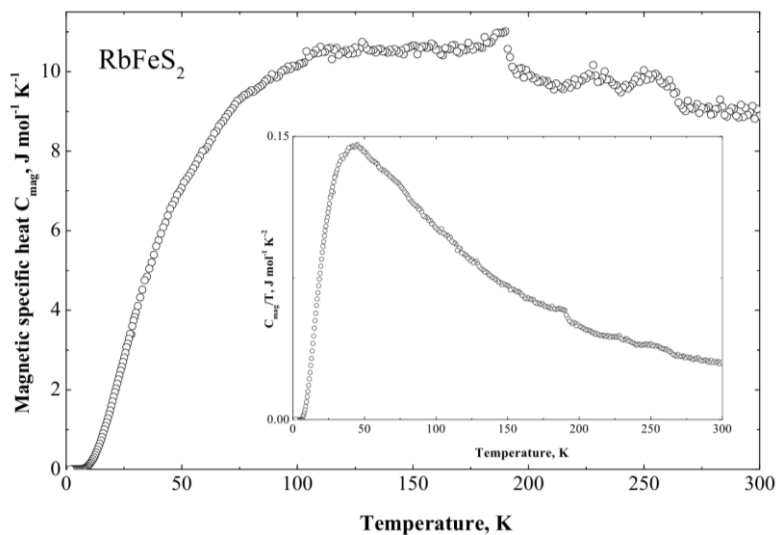

FIG. 2. The temperature dependence of the magnetic heat capacity of $RbFeS_2$ was obtained as a difference between the experimentally measured specific heat and the calculated lattice contribution. Inset represents the magnetic specific heat drawn as $C(T)/T$.

Despite the fact of the structural similarity of the $RbFeS_2$ with a related $RbFeSe_2$ compound, the temperature dependencies of their magnetic specific heats are not similar to each other. While magnetic specific heat of $RbFeSe_2$ shows complicated temperature dependence which could not be described within existing models of spin chains, the temperature behavior of magnetic specific heat of $RbFeS_2$ corresponds to the coupled dimer model [10]. Both compounds have a similar structure, the linear dimensions are only the feature that is different [2]. In the $RbFeSe_2$, d_{Fe-Fe} distance between iron ions is 2.85 Å, while in $RbFeS_2$ Å it is 2.71 [2]. It is notable that a 3-4 percent difference in the iron ions interaction range dramatically changes the magnetic properties of the compound. It should be noted, that the current results should be considered preliminary because the used *ab initio* phonon density of states was calculated within the density functional theory without taking into account DFT+U approach [4]. It could be necessary for the compounds with d-electrons and electronic delocalization.

4. Conclusion

To summarize, the crystalline $RbFeS_2$ samples were grown by the Bridgman method. The powder X-ray diffraction pattern was analyzed by the standard Rietveld refinement using the FULLPROF program [5]. Crystal structure parameters were calculated using the Rietveld refinement technique. The total specific heat was measured by a relaxation method using a PPMS (Quantum Design) in the temperature range 1.8-300 K. The lattice specific heat we use in the present study was obtained within the quasi-harmonic approach by using the *ab initio* calculated phonon density of states realized in our previous study. The magnetic specific heat was obtained as a difference between the experimentally measured total specific heat and the calculated lattice contribution. The temperature dependence of the magnetic specific heat of $RbFeS_2$ shows behavior similar to the coupled dimer spin chains.

5. Acknowledgment

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