MÖSSBAUER SPECTROSCOPIC INVESTIGATIONS OF THE MAGNETIC PROPERTIES OF POTASSIUM THIOFERRATE-III

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Abstract—This paper deals with Mössbauer spectroscopic investigations on KFeS₂, especially in comparison with the linear antiferromagnet K_2 FeF₅, considering primarily the influence of an externally applied magnetic field. Above a transition temperature the application of an external magnetic field perpendicular to the *c*-axis results in a three-line spectrum. The angle α between the internal and external fields could be determined as $(101 \pm 4)^\circ$. A spin-flop field could not be observed up to an external field of 6 T.

Keywords: Alkali thioferrates-III, one-dimensional antiferromagnet, spin-flop field, combined magnetic and electric interaction, Mössbauer spectroscopy.

1. INTRODUCTION

Potassium thioferrate-III of the series of alkali thioferrate-III AFeS₂ (A = K, Rb, Cs) exhibits a special behaviour. Mössbauer spectroscopic magnetic studies [1-3] revealed a magnetic phase transformation at 245 K. Susceptibility measurements between 100 and 750 K [4] showed only a weak, nearly temperature-independent paramagnetism indicating an antiferromagnetic iron-iron interaction. Model calculations for linear antiferromagnets [5] yielded qualitative agreement with the measured KFeS₂ susceptibilitites. More precise measurements of susceptibility and heat capacity [6] showed an antiferromagnetic transition at 252 K, thus supporting the model of a quasi-one-dimensional antiferromagnet. Mössbauer spectroscopic studies on the linear antiferromagnet potassium fluoroferrate K₂FeF₅[7] in an externally applied magnetic field displayed novel phenomena, such as a reorientation of the spins at a certain external "spin-flop field" and a field dependence of the magnetic phase transition temperature. Similar measurements on KFeS₂ [8], however, did not show a behaviour analogous to that of K₂FeF₅.

2. SAMPLE

Potassium thioferrate-III crystals were prepared from a melt of potassium carbonate, powdered iron, and sulphur using sodium carbonate as a flux [9–11]. The resulting crystals are violet needles of semi-metallic gloss. KFeS₂ has a monoclinic [12] lattice structure with $C2/c(C_{2h}^6)$ symmetry. The iron-III ions are surrounded tetrahedrally by sulphide ions. The tetrahedra are edge-connected and arranged chain-like parallel to the *c*-axis of the lattice (see Fig. 1). The potassium ions are located between the chains. This results in a larger Fe–Fe distance between the chains than within the chains. The spins of the Fe³⁺ ions are coupled antiferromagnetically along the *c*-axis, forming ferromagnetic layers parallel to the plane of the a-b axes. All of the magnetic moments are located in planes parallel to the a-c plane. At a temperature of 4.2 K, the magnetic moments are inclined by an angle of 12.8° from the *c*-axis against the negative *a*-axis. Their value is 2.43 $\mu_{\rm B}$ [13]. To simulate a single crystal, KFeS₂ needles were arranged longitudinally and fixed to a Mylar foil.

3. RESULTS OF THE MEASUREMENTS

The measurements were performed in a Mössbauer cryostat equipped with a superconducting magnet with the magnetic field perpendicular to the c-axis of the crystals. The Mössbauer spectra of potassium thioferrate-III at room temperature showed a doublet which is due to the quadrupole splitting of the excited nuclear state. We measured two samples, one consisting of powdered KFeS₂ crystals [see Fig. 2(a)], the other representing crystals that had been ordered in the longitudinal direction [see Fig. 2(b)]. Considering the asymmetry of the line intensities the single crystal behaviour of the ordered crystals is clearly visible. While the powdered sample yields a doublet with equal line intensities, for the ordered crystals an experimental intensity ratio of A1/A2 = 0.71 results, which has to be compared with the theoretical value of 0.6 for a single crystal. From the asymmetry of the line intensities there follows a negative sign of the electric field gradient [14]. The ordered KFeS₂ crystals, simulating a single crystal, were measured between room temperature and 4.2 K. The result



Fig. 1. Structure of KFeS₂.

was a magnetic transition, below which occurs a combined electric and magnetic hyperfine interaction in the Mössbauer spectrum. At 4.2 K the six absorption lines of the asymmetric sextet of a single crystal exhibits the theoretical intensity ratios of A1:A2:A3 = 3:4:1. Experimentally, we obtained the ratios of 3:3.5:1.4. For the powdered sample one obtains instead A1:A2:A3 = 3:2:1. Hence, by using the ordered KFeS₂ needles, it is possible to simulate a single crystal as an approximation.

By extrapolation the saturation field strength $H_{hf}(T=0)$ was found to be $H_{hf}(T=0) = 23.7 \text{ T}$,

which is somewhat higher than the saturation field strengths measured on polycrystalline samples [15, 16]. Further we also recorded the Mössbauer spectra at 4.2 K applying various external magnetic fields from 1 to 6 (Fig. 3).

The resulting hyperfine field follows from the vector sum of the internal and external magnetic fields, thus supplying the angle α between the internal and external fields. α could be determined as $(101 \pm 4)^{\circ}$. If we had measured Mössbauer spectra of a pure single crystal we would have been able to determine the angle β between the *c*-axis and the direction of the internal magnetic field (direction of the magnetic moments). However, as we used ordered needles such a determination is not possible. We don't know exactly the orientation of the *a*- and *b*-axes.

Further dependence of the hyperfine field on an external magnetic field such as e.g. the existence of a "spin-flop field" [7] could not be observed up to an external field of 6 T. Moreover, measurements in the external magnetic field at the higher temperatures gave no hint towards a dependence of the transition temperature on an external magnetic field as observed with K_2FeF_5 . In the case of K_2FeF_5 , the transition temperature increases with increasing external field, if the field is perpendicular to the magnetic axis of the crystals. [7].



Fig. 2. Mössbauer spectrum of (a) powdered KFeS₂ crystals, (b) ordered KFeS₂ crystals.



Fig. 3. Mössbauer spectra of KFeS₂ at T = 4.2 K and various external fields.

At temperatures above the transition temperature, one finds with various external fields a threeline system in the Mössbauer spectrum (Fig. 4). This three-line system does not change anymore with increasing temperature. With both magnetic fields (2 T, 5 T) one obtains an isomer shift of (0.17 ± 0.2) mm s⁻¹, corresponding to the isomer shift of KFeS₂ at room temperature. Both external absorption lines show a smaller line width than the central line. With an applied magnetic field of 5 T the absorption of the inner line is somewhat smaller than that of the outer ones, however in the case of a field of 2 T it is somewhat larger. The splitting of the external lines depends on the strength of the magnetic field. As expected, the magnetic fields at the site of the nucleus, determinable there-from, are of approximately the same magnitude.



Fig. 4. Mössbauer spectra of $KFeS_2$ in an external magnetic field above the transition temperature.

4. DISCUSSION

In the KFeS₂ crystal the iron ions are arranged chain-like parallel to the *c*-axis of the crystal with the iron-iron distance within the chains being considerably smaller than the iron-iron distance between the chains. Within the chains the spins of the Fe³⁺ ions are coupled antiferromagnetically with the corresponding exchange integral J_1 . Between the chains the spins are coupled ferromagnetically, the corresponding exchange integral being J'. The ratio $\eta = |J'|/|J_1|$ characterizes the spacial dimensionality of the magnetic system. Up to now, quite different values were known, such as $\eta = 4 \cdot 10^{-4}$ [17], $4 \cdot 10^{-2}$ [18], $8.6 \cdot 10^{-3}$ [19].

Denoting by T_1 the temperature at which the short range one-dimensional antiferromagnetic order of the spins along the *c*-axis occurs, and by T_2 the temperature at which the long range three-dimensional antiferromagnetic order is observed these

temperatures are given, according to the molecular field approximation, by

$$T_1 = \frac{4S(S+1)}{3k_{\rm B}} (J_1 + J_2)$$

and

$$T_2 = \frac{4S(S+1)}{3k_{\rm B}}J',$$

where J_2 represents the exchange integral of the ferromagnetic interaction of next-nearest neighbours and S the spin of the iron atom.

Mauger *et al.* [20] in 1984 detected an anomaly of the susceptibility curve of KFeS₂ at 12.5 K. They postulated that this temperature at which by Mössbauer spectroscopy no change is observable, was the one at which three-dimensional antiferromagnetism occurs. This explanation seems to be reasonable in so far as a Néel temperature of 245 K which characterizes the three-dimensional antiferromagnetism, seems to be too high. As shown by Dingle *et al.* [21], such a behaviour has already been observed qualitatively with tetramethylammonium trichloromanganate (CH₃)₄NMnCl₃, where a transition of the one-dimensional towards a three-dimensional magnetic phase occurs at a Néel temperature of 0.84 K.

A transition from one-dimensional to three-dimensional antiferromagnetism, however, does not mean a decrease of the anisotropy η , in which case the interaction between the chains and within one chain would then be approximately of the same strength, as this would destroy the chain-like structure. In this case, its meaning is only that the ferromagnetic coupling between the chains proceeds to an antiferromagnetic one, thus producing a structure comparable with that of potassium pentafluoroferrate K_2FeF_5 (see Fig. 5).

 K_2 FeF₅ is also considered to be a quasi-onedimensional antiferromagnet with antiferromagnetic coupling within and between the chains and a Néel temperature for three-dimensional magnetic order of the same magnitude as the temperature T_2 for KFeS₂ $(T_N = 6.95 \text{ K} [7]).$

Introducing the temperature T_2 , the anisotropy η is estimated as being $\eta = T_2/T_1 = 0.05$ This value is of



Fig. 5. Schematic spin arrangement of K₂FeF₅ and KFeS₂.

the same order of magnitude as that determined by Tomkowics et al. [18]. As already mentioned, with KFeS₂ neither the effect of the "spin-flop field" nor the magnetic field dependence of the transition temperature, as observed with potassium pentafluoroferrate, could be detected. This difference in behaviour of the two substances may be explained by the different amounts of magnetic anisotropy. A larger anisotropy would produce a correspondingly higher "spin-flop field". Up to a field of 6 T (following [8] up to 10 T) no reorientation of the spins could be detected in the case of $KFeS_2$. According to [7], an external magnetic field causes a change of the effective magnetic anisotropy, thus influencing the appearance of spin waves. Now, a high anisotropy reduces the influence of spin waves and therefore causes a considerably smaller influence of an external magnetic field on the average spin value and therewith on the hyperfine field.

Above the transition temperature, with an applied external magnetic field of 2 or 5 T, the Mössbauer spectrum showed a three-line system (see Fig. 4).

There are two reasons why the spectra cannot be explained by a structural change of the crystals. First, there is a difference in splitting with various fields, which would mean an impossible dependence of the quadrupole splitting on a magnetic field. Secondly, a supplementary measurement of the KFeS₂ sample at room temperature did not show any change compared with that carried out before the low temperature measurements. Hence, there is no hint of a structural change.

We have to deal with a combined magnetic and electric interaction.

An internal magnetic field of 2 or 5 T at the site of the nucleus due to the spontaneous magnetization below the Néel temperature does not produce a three-line system Mössbauer spectrum. The difference between an external magnetic field and an internal one resulting from temperature lies in this case in the direction of the field. While the internal field forms an angle of 13.6° with the electric field gradient, the externally applied field is approximately perpendicular to the direction of the electric field gradient.

Mössbauer spectra calculated theoretically [22] (see Fig. 6) agree quite well with the measured results.

Two outer lines with the same intensity should appear theoretically with a magnetic field of 5 T, as well as two internal lines lying closely together and being of minor intensity, which appear in the measured Mössbauer spectrum as one slightly broadened absorption line with only slightly reduced intensity. Similar results are found with a magnetic field of 2 T, where the somewhat larger intensities of both internal lines cause a broadened line in the middle of the measured Mössbauer spectrum, which is more intense than the outer lines.

For a more exact investigation and support of our results measurements at even higher values of the



Fig. 6. Theoretically calculated location of the resonance line in the case of a superposition of electric and varying magnetic hyperfine interaction [22].

applied magnetic fields and at higher temperatures should be performed.

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