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Spin re-orientation in $FeCr_2S_4$

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Abstract The spinel $FeCr_2S_4$has been studied intensely for its peculiar magnetic and local structural changes which are sensitively influenced by the Jahn–Teller properties of Fe^{2+}in tetrahedral sulfur coordination. Recent muon spin rotation data give strong evidence that the commonly assumed collinear magnetic structure of this compound is only found between the Curie temperature $T_C = 165$ K and 50 K. For lower temperatures a helical structure has been proposed. We present new Mössbauer spectroscopic data taken on the same sample as used for muon spin rotation. Also the hyperfine spectra revealing non-equivalent iron sites support the appearance of a spin re-orientation around 50 K which may be related to the onset of short-range orbital order. Below 20 K severe dynamic broadenings are found which may indicate orbital fluctuations. Orbital order occurs around 11 K accompanied by severe changes in the crystalline electric field ground state as traced from quadrupole interaction.

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1 Introduction

The thiospinel $FeCr_2S_4$ has been studied since very early days of Mössbauer spectroscopy [1–3]. Magnetic order has been found below about 160 K [4]. Ferromagnetic coupling occurs between the B-site Cr. The A-site Fe^{2+} couples antiferromagnetically to the Cr sublattice resulting in ferrimagnetic order. $FeCr_2S_4$ has been reinvestigated several times via Mössbauer spectroscopy for its peculiar behavior of hyperfine interactions which appear to be highly sensitive to sample quality also giving reason for controversial discussion [5–11]. From a more modern point of view the reason for this sensitivity can be sought in the competition between spin and orbital degrees of freedom of the Jahn–Teller ion Fe^{2+} in tetrahedral sulfur coordination. This has recently caused new interest in this spinel. Structural, caloric and magnetic studies give ample evidence for orbital order occurring below about 10 K [12].

Muon spin rotation experiments [13] clearly pick up the magnetic ordering around 165 K, yet with some partial order extending up to about 175 K. A single spontaneous rotation signal is indicative for the collinear ferromagnetic regime. Below about 50 K, however, other rotation frequencies are found which have been attributed to the appearance of an incommensurate modulated spin structure, probably of helical type. Notably there occurs a drop in magnetization in the same temperature range [12], yet no significant change in entropy is derived from heat capacity [12]. There is some indication from TEM for a structural change [14] and an anomaly in ultrasound velocity both occurring around 60 K [15].

Here we report on Mössbauer data recorded on the same sample material as used for muon spin rotation and also heat capacity in order to preclude any problems with varying sample quality. Some preliminary data have been included in [13]. We will concentrate on a gross interpretation of the magnetic hyperfine interaction, a detailed discussion related to the behavior of the electric field gradients and the spin dynamics close to the magnetic and orbital transitions will be presented elsewhere.

2 Experimental

The sample material has been prepared via a solid state reaction. For details of preparation and analytical details, see [12]. The ^{57}Fe Mössbauer absorption experiments have been performed in a standard spectrometer with sinusoidal velocity sweep using a ^{57}Co in Rh source at room temperature. The absorbers were kept under a static Helium atmosphere in a flow cryostat (Cryovac). Absorber temperature was controlled with a stability of about ± 0.1 K.

Spectra were least-squares fitted using a general Hamiltonian allowing the treatment of electric quadrupole and magnetic hyperfine interactions of comparable strengths and variable Euler angles.

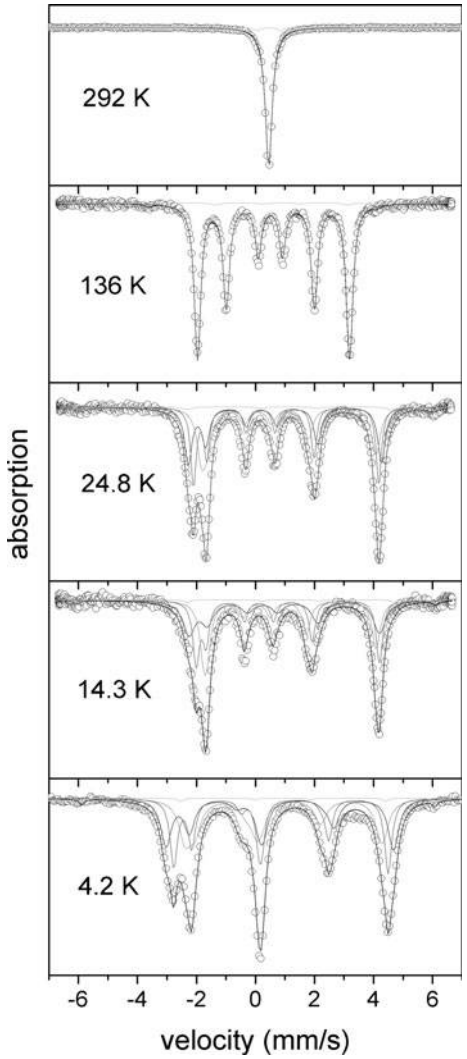

Fig. 1 ^{57}Fe absorption spectra of $FeCr_2S_4$ at various temperatures. Note that several sub-spectra are needed for the fit below about 50 K. The quadrupole doublet of very low intensity seen at room temperature and the corresponding weak magnetic pattern at low temperatures are related to a very small deviation from ideal stoichiometry

3 Results and discussion

In Fig. 1 we show a series of absorption spectra characteristic for the different temperature regimes. The spectra basically resemble in shape those reported earlier. Above $T_C = 165$ K we have a dominant single Lorentzian resonance line as expected for the ideal A-site tetrahedral sulfur coordination of Fe^{2+}, accompanied by a less than 5% of spectral area impurity signal, probably due to slight local deviations from stoichiometry [7]. In contrast to the results from muon spin rotation where partial long range order is found already above T_C, we find no indication for this from our Fe hyperfine spectra, i.e. this must rather be related to the Cr and not the Fe sublattice. Below T_C we find a 6-line pattern typical for the collinear ferromagnetic structure, yet a small quadrupole interaction due to an axially symmetric electric

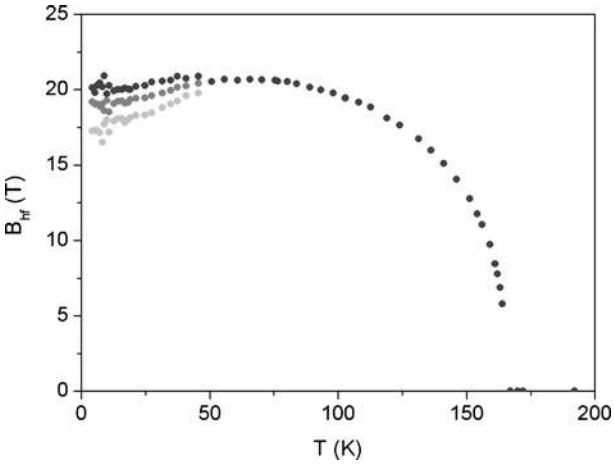

Fig. 2 Temperature dependence of hyperfine magnetic field B_{hf}

field gradient appears which is increasing with increasing magnetic hyperfine field as already described earlier [3]. The observation of a quadrupole interaction at iron below the Curie temperature despite neutron data prove cubic structure has been discussed controversially [1, 2, 5–11]. As first proposed by [2] this quadrupole interaction can be related to a magnetically induced electric field gradient. This may occur for the electronic ground state (E) of Fe^{2+} in tetrahedral crystalline electric field for certain orientations of the locally acting molecular magnetic field.

The variation of the magnetic hyperfine field B_{hf} with temperature is shown in Fig. 2. Its increase directly below T_C is typical for a second order magnetic phase transition and then follows a completely smooth sublattice magnetization curve down to about 50 K. A kink in B_{hf} around 130 K as indicated in [13] could not be reproduced.

Between about 50 K and 20 K the spectra can no more be described with a single magnetic site. We only could manage consistent fits using three sets of hyperfine interactions (see Fig. 2 for B_{hf}) having equal spectral weights standing for three magnetically and also structurally non-equivalent sites. The local symmetry is no more axially symmetric and an asymmetry parameter is necessary for describing the field gradient tensor which is in agreement with the TEM data of [14]. The non-equivalent magnetic sites found in our data give further support for the conclusions drawn from muon spin rotation regarding a change in spin structure from a collinear to a modulated one. Whether this is indeed helical with accompanying changes of the angles of B_{hf} vs. the electrical field gradient cannot reliably be resolved. We relate the spin re-orientation with the onset of short-range orbital ordering which is also indicated from X-ray data [12].

The gradual decrease of B_{hf} below 50 K is caused by continuous changes in the crystalline electric field. So there is no abrupt phase transition but a smooth change as also seen from heat capacity data [12].

Below 20 K we find strong line broadenings. This occurs in parallel to a maximum in mean-square displacement seen in X-ray data [12] and can be related to dynamical Jahn–Teller distortions. Finally below 10 K a dramatic change in quadrupole interaction becomes visible with a change of sign and re-orientation of the electric field gradient. Its major axis is now pointing perpendicular to the magnetic hyperfine field.

This has been described qualitatively already by [5]. We now managed quantitative fits of good quality, yet still three sub-spectra due to non-equivalent sites are necessary. The change of sign of electric field gradient indicates that the sequence of the lowest populated crystalline electric field states at Fe becomes modified upon orbital ordering.

From the temperature dependence of the turning of electrical field gradient we can define the orbital ordering transition for this sample with $T_{oo} = 10.6$ K in good agreement with specific heat data [12].

4 Conclusions

From our ^{57}Fe Mössbauer data we have found a sharp magnetic transition at $T_C = 165$ K indicating that the partial long-range order above T_C found by muon spin rotation [13] has to be related to Cr. A smooth variation of B_{hf} is traced from T_C down to about 50 K. There is a single magnetic Fe site consistent with a collinear ferrimagnetic structure. Below we find magnetically inequivalent Fe sites supporting spin re-orientation as proposed from muon data [13]. The sites are also structurally inequivalent which is in agreement with earlier TEM data [14]. This is interpreted with the onset of short-range Jahn–Teller distortions at Fe [12]. Orbital ordering occurs around 11 K accompanied by severe changes in the crystalline electric field ground state as traced from quadrupole interaction.

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