MAGNETIC ORDERING IN $\alpha$- AND $\beta$-FeF$_3$.3H$_2$O

I. Dézsi, S. Sankar, L. Mulay, J. Houlihan, T. Pannaparayil

To cite this version:
I. Dézsi, S. Sankar, L. Mulay, J. Houlihan, T. Pannaparayil. MAGNETIC ORDERING IN $\alpha$- AND $\beta$-FeF$_3$.3H$_2$O. Journal de Physique Colloques, 1988, 49 (C8), pp.C8-1463-C8-1464. <10.1051/jphyscol:19888672>. <jpa-00228904>

HAL Id: jpa-00228904
https://hal.archives-ouvertes.fr/jpa-00228904
Submitted on 1 Jan 1988

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
MAGNETIC ORDERING IN $\alpha$- AND $\beta$-$\text{FeF}_3\cdot3\text{H}_2\text{O}$

I. Dézsi (1), S. G. Sankar (2), L. N. Mulay (3), J. F. Houlihan (3) and T. Pannaparayil (3)

1) Ingenieurwissenschaften, Universität des Saarlandes, 6600 Saarbrücken, F.R.G.
2) Carnegie Mellon University, Pittsburgh, PA 15213-2683, U.S.A.
3) Pennsylvania State University, University Park, PA 16802, U.S.A.

Abstract. – The two crystallographic modifications of ferric fluoride trihydrate ($\alpha$- and $\beta$-$\text{FeF}_3\cdot3\text{H}_2\text{O}$) were synthesized and characterized. Magnetic susceptibility and Mössbauer effect measurements suggest that the $\alpha$- and $\beta$-phases are low dimensional antiferromagnets at higher temperatures and become three dimensionally ordered below 6.5 and 14.7 K respectively.

1. Introduction

Ferric fluoride trihydrate, $\text{FeF}_3\cdot3\text{H}_2\text{O}$, is known to exist in two different crystallographic forms [1]. In a previous study, Dézsi et al. [2] synthesized and characterized the $\alpha$- and $\beta$-$\text{FeF}_3\cdot3\text{H}_2\text{O}$. The present work was undertaken to elucidate the magnetic structures of these two phases.

2. Experimental

The $\alpha$ and $\beta$ forms of $\text{FeF}_3\cdot3\text{H}_2\text{O}$ were prepared by known techniques [2] and characterized by susceptibility measurements, Mössbauer and ESR spectroscopy. The Mössbauer spectra of the samples were obtained in the temperature range 300 to 4.2 K. The molar susceptibility ($\chi_M$) was deduced from SQUID magnetometer measurements in a fixed field of 10 kOe from 8 to 300 K.

3. Results and discussion

At 300 K the Mössbauer spectra of $\text{FeF}_3\cdot3\text{H}_2\text{O}$ revealed a doublet with a quadrupole splitting ($\Delta E$) of 0.37 and 0.60 mm/s for the $\alpha$- and $\beta$-phases respectively (Fig. 1). The $\Delta E$ value for the $\alpha$-phase gradually increased with time and reached exactly the value for the $\beta$-phase is metastable. On lowering the temperature, the doublet in the Mössbauer spectrum transformed to a magnetically split six-line pattern at 14.7 K for the $\beta$-phase, in agreement with the observation made by Imbert et al. [3]. At 4.2 K the spectrum of this phase (Fig. 2E) corresponded to a single hyperfine field of 434.8 kOe. The spectrum of the $\alpha$-phase in the range 10 to 6.5 K consisted of a quadrupole doublet and magnetically split six lines. The spectra obtained at 7.5 and 6.5 K are shown in figures 2B and 2C respectively. The magnetically split parts of these spectra correspond to hyperfine fields of 418.6 and 417.9 kOe respectively and therefore are not due to any $\beta$-phase present in the sample. The quadrupole doublet in the spectrum disappeared between 6.0 and 6.5 K. At 4.2 K the $\alpha$-phase showed two superposed magnetic spectra (Fig. 2D) with hyperfine fields of 446.7 and 421.1 kOe. Therefore, there are at least two magnetic sublattices in the $\alpha$-phase. The hyperfine parameters obtained from the 4.2 K spectra are listed in table I.

The results of the susceptibility ($\chi_M$) measurements (Fig. 3) showed two different magnetic structures for the $\alpha$ and $\beta$ phases. The susceptibility decreased smoothly and monotonically with temperature ($T$) for the $\alpha$-$\text{FeF}_3\cdot3\text{H}_2\text{O}$. For the $\beta$-form $\chi_M$ vs. $T$ curve first decreased rapidly with increasing temperature, reached a minimum at 30 K and then showed a broad

---

1) On leave from Central Research Institute for Physics, Budapest.
Table I. - The isomershift ($\delta$), quadrupole splitting ($\Delta E$), hyperfine field ($H_h$), line width ($\tau$), and intensity ratio ($R$) of the ferric fluoride trihydrate samples at 4.2 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta E$ (mm/s)</th>
<th>$\tau$ (mm/s)</th>
<th>$R$</th>
<th>$H_h$ (kG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$ - FeF$_3$-3H$_2$O</td>
<td>0.347</td>
<td>0.228</td>
<td>0.317</td>
<td>434.79</td>
<td></td>
</tr>
<tr>
<td>$\alpha$ - FeF$_3$-3H$_2$O</td>
<td>0.356</td>
<td>0.125</td>
<td>0.236</td>
<td>446.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.373</td>
<td>0.172</td>
<td>0.270</td>
<td>421.13</td>
<td></td>
</tr>
</tbody>
</table>

The shape of the $\chi_m$ vs. $T$ curve with a broad maximum around 130 K. The effective magnetic moment per Fe-ion ($\mu_{Fe}$) was calculated from the $\chi_m$ data using the spin only formula. These results are also shown in figure 3. For both $\alpha$- and $\beta$ - FeF$_3$-3H$_2$O, $\mu_{Fe}$ decreased gradually as the temperature was lowered from 300 to 8 K. For the $\alpha$-form $\mu_{Fe}$ varied from 4.73 to 2.0 $\mu_B$ (Bohr Magnetons). The $\beta$-form showed a smaller range of values (4.1 to 0.86 BM) for $\mu_{Fe}$ than that observed for the $\alpha$-form. These ranges of values for $\mu_{Fe}$ fall well below that for a free Fe$^{3+}$ ion (5.96 $\mu_B$). ESR measurements showed significantly different room temperature $g$-values for the two phases ($g_{\alpha}$ = 2.0083, $g_{\beta}$ = 2.0024).

A description of the crystal structure of $\beta$ - FeF$_3$-3H$_2$O has been reported by Teufer [4]. In $\beta$ - FeF$_3$-3H$_2$O each iron atom is surrounded by six ligands in the form of a nearly regular octahedron. Adjacent octahedra share apices in the direction of the $C$ axis and fluorine atoms are assumed to form the bridges between iron atoms. The four other ligands of each octahedron are two fluorine atoms and two water molecules which occupy statistically the four positions of a square around the iron atom. Water molecules outside of the octahedra are in lattice positions; they are tetrahedrally surrounded by the 4F/H$_2$O ligands of four neighboring octahedra.

The isomershift observed for the $\beta$-phase cannot be explained by cooperative exchange interaction between a large number of paramagnetic cations, which otherwise would have shown a relatively sharp maximum in the $\chi_m$ vs. $T$ curve. The $\chi_m$ data from 130 to 300 K are described fairly well by the Curie-Weiss law with a Weiss constant $\theta$ approximately -700 K. Considering the positions occupied by the Fe$^{3+}$ ions and the ligands (F$^-$, H$_2$O) as described by Teufer [4] and making use of a generalized equation [5] for the exchange integral $J$ in terms of the coordination number ($Z$), $S = 5/2$ and $g = 2.0024$ an approximate value $J = 41.7 \text{cm}^{-1}$ has been estimated. This estimated value for $J$ is consistent with the observed Fe$^{3+}$-Fe$^{3+}$ distance $(3.902 \AA)$ reported by Teufer [4]. This small value of $J$ is reminiscent of the interactions encountered in metal cluster compounds [6]. The subnormal values for the magnetic moment (0.86 to 4.1 $\mu_B$) and the large Weiss constant indicate that some of the Fe$^{3+}$ ions in the $\beta$-phase are coupled antiferromagnetically with super-exchange via the F$^-$ ions.

On the basis of the susceptibility data we postulate the following structure for $\beta$ - FeF$_3$-3H$_2$O. The water molecules are located in every second apex of the octahedron between the Fe$^{3+}$ ions forming Fe$^{3+}$-F$^-$-Fe$^{3+}$-$\text{H}_2\text{O}$-$\text{Fe}^{3+}$ type chains. This suggests that the chains of Fe$^{3+}$ ions could be broken by the intervening H$_2$O molecules, thus forming even smaller dimer clusters of Fe$^{3+}$ antiferromagnetically coupled leaving some of the Fe$^{3+}$ ions uncoupled. The formation of such clusters is known to give a broad maximum in the $\chi_m$ vs. $T$ curve [7]. The uncoupled ions would show the initial decrease in $\chi_m$ up to 30 K.

4. Conclusion

Based on the results, we suggest that both the $\alpha$- and $\beta$ - FeF$_3$-3H$_2$O are low (one) dimensional antiferromagnets at higher temperatures and become three dimensional antiferromagnets below 14.7 K and 6.5 K respectively. There exist at least two magnetic sublattices in the $\alpha$-phase at lower temperatures.