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MAGNETIC PROPERTIES OF THORIUM FERRICYANIDE

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The magnetic properties of $\text{Th}_3[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ were investigated. It was shown that this compound is antiferromagnetically ordered in the low temperature region. The observed antiferromagnetic ordering is stable only in the low field.

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1. Introduction

In the last few years, there has been great interest in the preparation of molecular magnets and in the study of their magnetic properties [1-3]. Recent studies by several groups [4, 5] have shown that e.g. classic Prussian blue analogues are very attractive for applications to novel magnetic and optical materials. In our previous papers, we have studied the magnetic properties of some Prussian-blue-like compounds containing $4f$ and $5f$ ions, respectively [6, 7]. The results for the $\text{Th}_3[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ described in this paper are the continuation of our previous investigations. Thorium ferricyanide is of particular interest since four-valent Th^{4+} ion has no occupied $5f$ -levels, no occupied $6d-7s$ states and therefore has no net magnetic moment. The system is very simple, with only one type of magnetic ion (Fe^{3+}).

2. Experimental

The investigated compound was prepared by reacting mixtures of ThCl_4 aqueous solution with $\text{K}_3[\text{Fe}(\text{CN})_6]$ aqueous solution. The dirty-green precipitate was filtered, washed with water and ethanol, and dried at room temperature. Purity of the used ingredients were of p.a. grade. The powdered samples were placed in thin walled plastic capsules for magnetization measurements. Magnetic measurements were carried out using a vibrating sample magnetometer and SQUID magnetometer in the temperature range 4.2–100 K. X-ray powder patterns were taken by HZG-4/A diffractometer using $\text{Co } K_{\alpha_{1,2}}$ radiation.

3. Results and discussion

A manual examination of JCPDS-ICDD database by the Hanawalt method (using a classification according to the three most intense diffraction peaks) gave a possible identification nickel iron cyanide hydrate (card No. 46-0906). The cell

of the phase (space group $F\bar{4}3m$, $a = 1.0229(5)$ nm) was used as initial model for the Rietveld refinement procedure with Le Bail strategy of structure factors extracting [1] to determine the lattice constraints for the investigated phase. The procedure enabled refining the cell dimension even in the absence of an atomic structural model. The resulting fit is shown in Fig. 1, where the short vertical lines represent the refined peak positions for the lattice parameter a equal to $1.00959(10)$ nm.

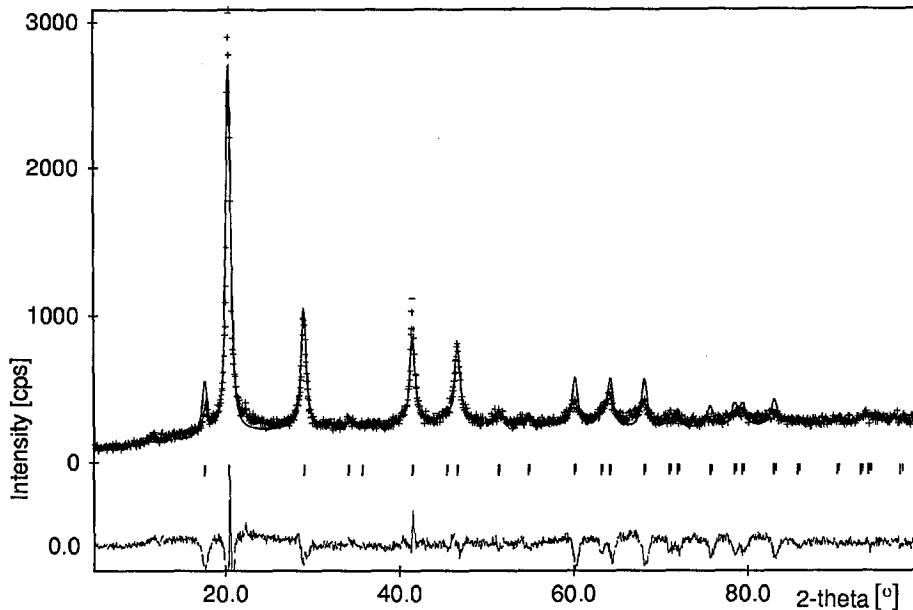


Fig. 1. Diffraction pattern of $\text{Th}_3[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$, points represent experimental values, full lines are calculated.

The temperature dependence of inverse susceptibility $\chi_m^{-1}(T)$ (see Fig. 2) suggests the antiferromagnetic ground state, with the negative paramagnetic Curie temperatures. It is evident from this figure that the $\chi_m^{-1}(T)$ curve is apparently convex at low temperatures, however a slight curvature has been observed in the whole temperature range.

The non-linearity of χ_m^{-1} vs. T curve is more evident from Fig. 3, where $\chi_m T$ vs. T is displayed. From the figure one can see that the paramagnetic moment p_{eff} is temperature dependent. In our case its value increases from $3 \mu_B$ (low temperature region) up to $3.58 \mu_B$ at around 100 K. Since the octahedral (CN) surrounding induces a low spin state of the d -electrons localized on the Fe^{3+} cation, the five d -electrons of ion, which occupy the t_{2g} triplet, lead to an $S = 1/2$ state with the expected theoretical value of $p_{\text{eff}} = 1.73 \mu_B$. Even the observed high temperature paramagnetic moment is lower than the theoretical value for $\text{Th}_3[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ molecule ($p_{\text{eff}} = 6.92 \mu_B/\text{f.u.}$), suggesting that crystal field effect may be responsible for the low experimental values.

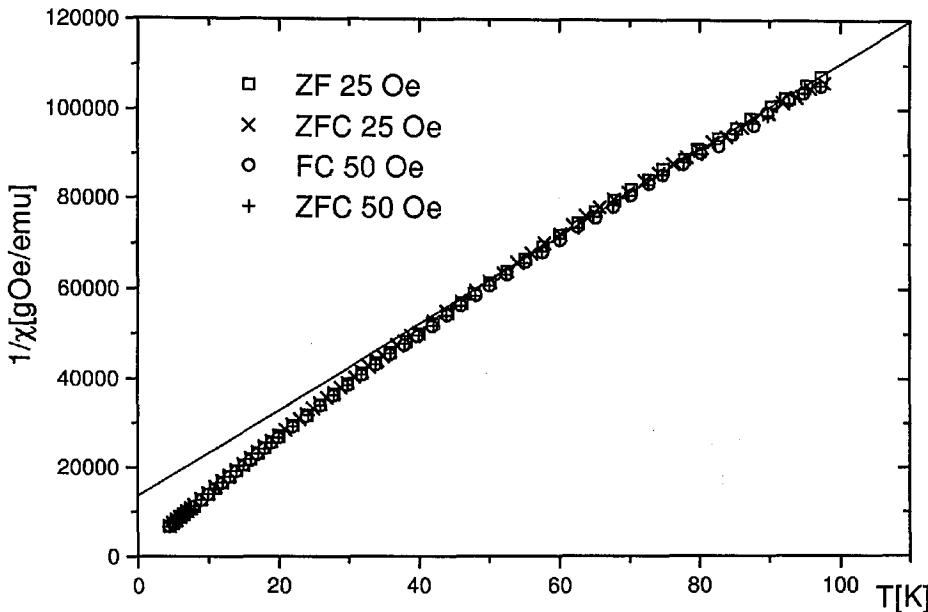


Fig. 2. Inverse susceptibility vs. temperature dependence for investigated compound.

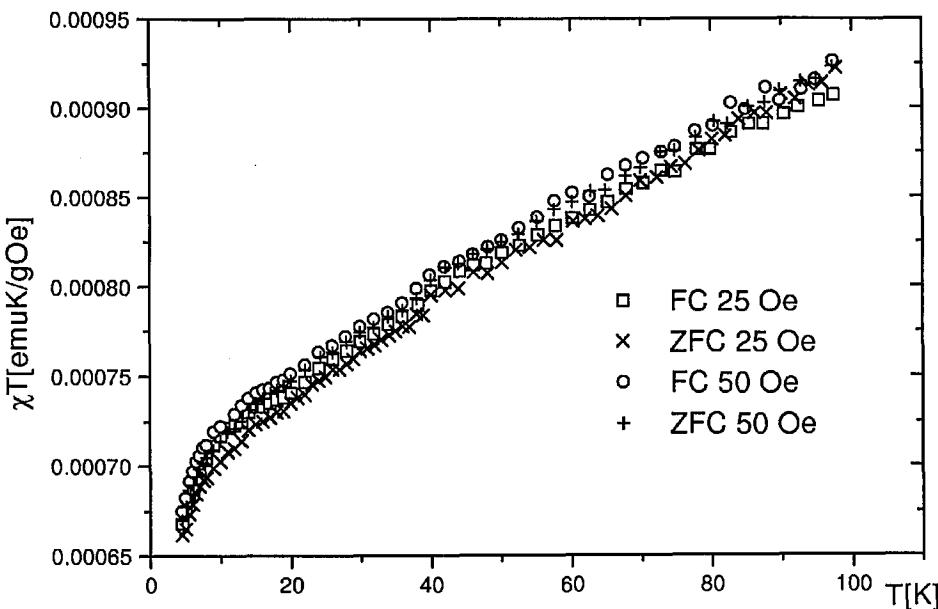


Fig. 3. χT vs. T dependence of $\text{Th}_3[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$.

The antiferromagnetic ordering in $\text{Th}_3[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ can only be observed in low fields. In higher fields the downward curvature of magnetization

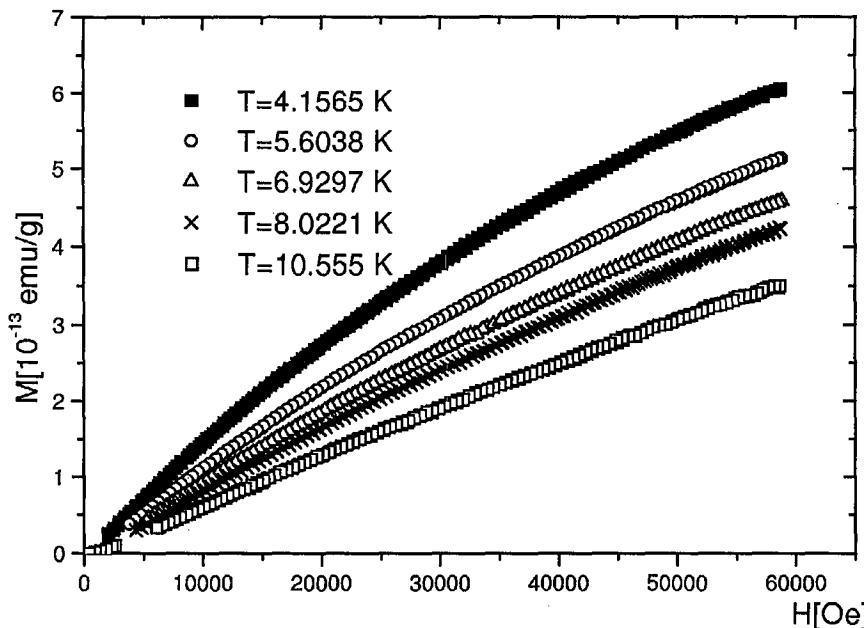


Fig. 4. Magnetization curves of $\text{Th}_3[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ for different temperatures.

curves has been observed between 4.2 and 10 K, as can be seen from Fig. 4. However, saturation is difficult to reach even for liquid helium temperature. Therefore, we have extrapolated the M vs. $1/H$ dependence to $1/H = 0$ for obtaining the saturation value. The obtained $\mu_s = 2.94 \mu_B/\text{f.u.}$, which corresponds to 0.7 μ_B per Fe^{3+} ion.

Acknowledgments

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