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A Mössbauer Spectroscopy Study of the $\beta \leftrightarrow \gamma$ (Abma → $P4_2/ncm$) Structural Phase Transition of $(CH_3NH_3)_2FeCl_4$

CLAUDIO NICOLINI† and WILLIAM MICHAEL REIFF*

Department of Chemistry, Northeastern University, Boston, Mass. 02115, U.S.A.

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In this article the results of a zero field ^{57}Fe Mössbauer spectroscopy study of a polycrystalline and undiluted sample of $(CH_3NH_3)_2FeCl_4$ over the range 77 to 294 K are reported. There is clear evidence of the $\beta \rightarrow \gamma$ structural phase transition at 231 K that was previously observed by a variety of other physical techniques but curiously not observed in an earlier Mössbauer spectroscopy investigation The observation of the phase transformation is found to be highly dependent on the quality (crystallite size) within the polycrystalline sample and handling.

Introduction

In addition to being good examples of 2-D magnetic systems, the perovskite-like layer compounds, $(C_nH_{2n+1}NH_3)_2MCl_4$ (M = Mn, Fe, Cu), exhibit a number of structural phase transitions. These phase transitions are governed by the reorientation and ordering of the alkyl ammonium ions connected by different hydrogen bonding schemes and changes of the tilt systems of the corner sharing metal–halogen octahedra [1].

For the particular compound $(CH_3NH_3)_2FeCl_4$, Knorr *et al.* [2], using optical birefringence, x-ray and neutron diffraction techniques, found two structural phase transitions: 1) a continuous order–disorder transition from a high-temperature tetragonal (symmetry 14/mmm) to an orthorhombic phase (orthorhombic space group Abma) at 328 K and 2) a discontinuous transition to a low-temperature tetragonal modification at 231 K (space group $P4_2/ncm$). The latter is the so-called $\beta \leftrightarrow \gamma$ phase transition according to the nomenclature of Depmeier *et al.* [1]. Keller *et al.* [3], have studied the Mössbauer spectrum of a *powder* sample of $(CH_3NH_3)_2FeCl_4$ ground and diluted with plexiglass powder in order to obtain a random distribution of crystallites. Their study was a function of temperature in the range 100–300 K and they reported *no indication* of the $\beta \rightarrow \gamma$ phase transition at 231 K. In view of these two apparently contradictory results, we decided to study the Mössbauer spectra of a polycrystalline sample of $(CH_3NH_3)_2FeCl_4$ for which there was no pulverization, and over the range of 77 to 300 K.

Experimental

The title compound, $(CH_3NH_3)_2FeCl_4$ was prepared as described in the literature [4] under an atmosphere of N_2 or Ar. Chemical analysis of the product confirmed the expected stoichiometry. Typical sizes for crystallites of this sheet-like material used in this study were of ~0.5 mm^2. Special care was exercised when handling the crystallites such as to avoid further cleavage or fracture of this brittle material and to avoid any possible unnecessary stress when packing them in the Mössbauer sample holders.

Results

The Mössbauer spectra of $(CH_3NH_3)_2FeCl_4$ as a function of T over the range of 280.0 to 140.0 K are shown in Fig. 1. The Mössbauer spectrum at 294.2 K consists of a single quadrupole doublet (phase β). At 265 K, a new quadrupole doublet starts to appear (phase γ) indicating the beginning of the structural phase transition reported by Knorr *et al.* [2]. We find that the phase transition does not go to completion for temperatures as low as 100 K even after long periods (2–3 days) of thermal equilibration (see Fig. 1). The isomer shift, δ, and quadrupole splitting ΔE_Q, data of $(CH_3NH_3)_2FeCl_4$ at 294.2 K (phase β) and 231.1 K (phase β and γ) are given in Table I. The values of δ and ΔE_Q at 294.2 K agree well with those reported in the literature [4]. From the Lorentzian fit of the Mössbauer spectrum at 231.1 K, the intensity ratio I_β/I_γ can be calculated and is ~1.18. The smaller $\Delta E_Q^{(\gamma)}$ indicates higher symmetry for the local coordination

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†Present address: Center for Materials Research, Mass. Institute of Technology, Cambridge, Mass., USA.

*Author to whom correspondence should be addressed.

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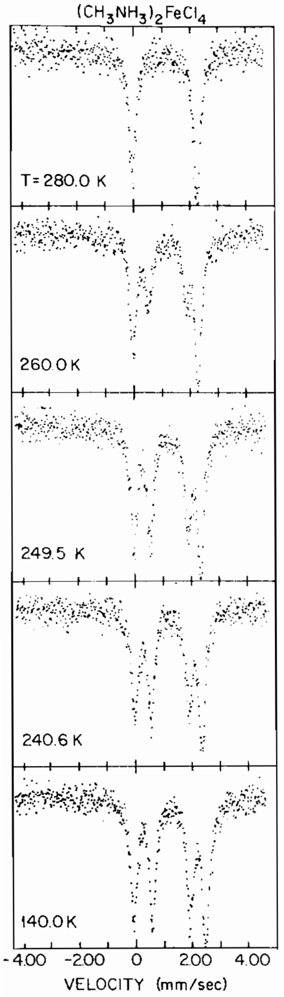

Fig. 1. Mössbauer spectra of a polycrystalline sample of $(CH_3NH_3)_2FeCl_4$ taken at various temperatures over the range of 280.0 to 140.0 K.

TABLE I. Mössbauer Spectra Parameters for $(CH_3NH_3)_2$-$FeCl_4$.

T(K)	δ^a (mm s^{-1})	ΔE_Q (mm s^{-1})
294.2 (phase β)	1.096	2.261
231.1 (phase β)	1.339	2.438
231.1 (phase γ)	1.196	1.343

^{a}Relative to Fe metal.

environment of Fe in the new phase. This is novel and quite the opposite of what is often observed for a variety of order–disorder and other types of structure transformations. The same polycrystalline and undiluted sample was finely ground in an inert atmosphere and a redetermination of the Mössbauer spectrum as a function of T showed *no evidence* of the phase transition. Apparently, sample grinding introduces defects such that no transition occurs. We believe that this is one of the reasons that the phase transition was not observed in the initial Mössbauer spectroscopy study [3]. Moreover, unground samples from chemical preparations which gave finely divided materials as products, likewise, did not show the structural phase transition at 231 K. We have also synthesized the analogous ethyl and propyl compounds in order to study the expected $\beta \leftrightarrow \gamma$ phase transition in the ethyl compound and the $\delta \leftrightarrow \epsilon$ and $\epsilon \leftrightarrow \zeta$ transitions [1] probably present in the Fe–propyl compound. These transitions have been observed for the Mn analogous compounds [1]. Unfortunately, after several attempts we have been unable to obtain 'good quality' crystalline materials of crystallite size $\geqslant 0.5$ mm^2 for these compounds. For the crystalline materials that we have obtained, no phase transition has been observed by ^{57}Fe Mössbauer spectroscopy. This is consistent with the behavior observed for finely divided, but carefully handled sample of $(CH_3NH_3)_2FeCl_4$.

We conclude by pointing out that the $\beta \rightarrow \gamma$ transition for the latter compound is slow but reversible. That is, with increasing temperature above $T_{Néel}$ the hyperfine split spectrum collapses to the β and γ doublets where the intensity of the latter γ only approaches zero after several days at high temperatures. A rapid decrease in temperature from ambient to just above $T_{Néel}$ results in the observation of *only* β forming an apparently metastable state.

Finally, we point out that the present work serves as a clear warning to avoid the common practice of sample pulverization and/or dilution so as to obtain isotropic absorbers presumably free of orientation-texture effects. In the present example this procedure results in non-observation of a phenomenon seen using a number of other techniques. It is preferable if possible to initially study neat, minimally handled samples prior to worrying about randomization.

Acknowledgements

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