LOW TEMPERATURE PHASES OF MICROCRYSTALLINE FeCl_3 (*)

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Résumé. — Les spectres Mössbauer de FeCl_3 déposé à basse température à partir de la vapeur montrent deux doublets quadripolaires au-dessus de 6,5 K et des éclatements magnétiques hyperfins en dessous de 6,5 K. Par chauffage à 300 K, les échantillons peuvent être transformés irréversiblement en l'état cristallin normal. En dessous de leurs températures de transition magnétique, les spectres des phases trempées à partir de la vapeur ainsi que ceux de la phase cristalline normale montrent des effets de relaxation qui sont attribués à des fluctuations superparamagnétiques. Par opposition aux halogénures ferreux amorphes, les courbes d'aimantation des phases de FeCl_3 trempées à partir de la vapeur ont la même dépendance fonctionnelle que la phase cristalline. On suggère que la déposition de FeCl_3 à basse température conduit à des structures microcristallines plutôt qu'amorphes.

Abstract. — Mössbauer spectra of FeCl_3 , vapour deposited at low temperatures, show two quadrupole doublets above 6.5 K and magnetic hyperfine splittings below 6.5 K. Upon heating to 300 K the samples can be transformed irreversibly to the normal crystalline phase. Below their magnetic transition temperatures the spectra of both vapour quenched phases and of the normal crystalline phase exhibit relaxation effects which are interpreted as superparamagnetic fluctuations. In contrast to the amorphous ferrous halides, the magnetization curves of the vapour quenched phases of FeCl_3 show the same functional dependence as the crystalline phase. It is suggested that the low temperature deposition of FeCl_3 leads to microcrystalline rather than to amorphous structures.

1. Introduction. — It has been shown that the condensation of ferrous halides from a molecular beam onto a helium-cooled substrate leads to the formation of a non-crystalline phase [1]. The magnetic properties of these samples as studied with the Mössbauer effect [2], are markedly different from those of the crystalline compounds and have been discussed within the framework of published theories of amorphous magnetism [3, 4, 5]. The present paper discusses Mössbauer spectroscopic investigations of FeCl_3 samples prepared in a similar manner from a molecular beam. It will be shown that the behaviour of these FeCl_3 samples is very different from those of the ferrous halides.

2. Experimental. — Samples of anhydrous $^{57}\text{FeCl}_3$ were condensated from a molecular beam onto an Al-foil kept at temperatures < 10 K in a vacuum of $< 5 \times 10^{-8}$ torr. The deposition process was continuously monitored by the transmission of the 6 keV X-rays from a 30 mCi $^{57}\text{Co}(\text{Cu})$ source through the sample. Different samples were thus prepared with thicknesses between ~ 750 Å and 30 000 Å and served as the absorber in a Mössbauer transmission experiment. The sublimation temperature in the molecular

beam oven was usually kept at 360 K. It is known [6] from electron diffraction measurements that at this temperature the vapour consists totally of dimer molecules Fe_2Cl_6 . Higher temperatures which should lead to the sublimation of monomer FeCl_3 could not be applied because of the onset of decomposition into FeCl_2 and Cl_2 . Mössbauer spectra were taken between 2.6-300 K without removing the samples from the cryostat. Details of the apparatus will be described elsewhere [7].

3. Results. — At temperatures $\gtrsim 6.5$ K spectra consisting of four partially resolved resonance lines were observed. They are interpreted as the quadrupole pattern of two non-identical Fe sites, labeled A and B in figure 1. The splittings are $\Delta E_Q(\text{A}) = 1.74$ mm/s and $\Delta E_Q(\text{B}) = 0.86$ mm/s, the isomer shifts are $\text{IS}(\text{A}) = 0.37$ mm/s and $\text{IS}(\text{B}) = 0.47$ mm/s at 20 K against an absorber of Fe metal at 300 K. These values are in marked contrast to the well-known hyperfine (hf) parameters of crystalline FeCl_3 which, above its Néel temperature $T_N = 8.9$ K, shows a slightly broadened, single line ($\Delta E_Q \lesssim 0.05$ mm/s) with $\text{IS} = 0.57$ mm/s. The relative intensities of the two quadrupole spectra (area under the lines) is dependent on conditions during sample preparation. Sublimation with higher deposition rates than ~ 50 Å/min favours formation of the doublet B which has the smaller

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FIG. 1. — Spectra of two samples of FeCl_3 , deposited from a molecular beam onto $a < 10$ K Al foil for $T > T_m$. Sample a) (thickness $\sim 5\,000$ Å) was deposited at a rate of 25 Å/min, sample b) (thickness $30\,000$ Å) at a rate of 300 Å/min.

quadrupole splitting. Below about 6.5 K a magnetic hf pattern with rather broad resonance lines is observed (Fig. 2). The temperature (T_m) at which the magnetic pattern begins to appear is again dependent on the preparation condition and sample thickness. Values range from 4 K (for a sample with ~ 750 Å thickness and a deposition rate of ~ 10 Å/min) to 6.5 K (for samples thicker than $\sim 13\,000$ Å and deposition rates of 60 – 300 Å/min). In general, magnetic spectra seem to appear for the vapour quenched samples only well

FIG. 2. — Spectra of FeCl_3 (absorber thickness $13\,000$ Å) deposited from a molecular beam onto $a < 10$ K Al foil at a rate of 80 Å/min for $T < T_m$.

below the Néel temperature of crystalline FeCl_3 . The magnetic spectra can be interpreted as two 6-line patterns with identical magnetic hf fields and the quadrupole splittings and isomer shifts found at higher temperatures for the sites A and B. However, a rather substantial line broadening ($\text{FWHM} \gtrsim 0.5$ mm/s) has to be assumed for such a fit. This broadening, together with the strong enhancement of the $m_e = \frac{1}{2} \rightarrow m_g = -\frac{1}{2}$ and $m_e = -\frac{1}{2} \rightarrow m_g = \frac{1}{2}$ hf transitions is taken as evidence for spin fluctuations with correlation frequencies comparable to the nuclear Larmor frequency. For least squares curve fitting procedures a relaxation model given by van der Woude and Dekker [8, 9] was used. This model is considered to be especially appropriate in the vicinity of a magnetic transition point where the Weiss molecular field theory is a good approximation. The electronic spins are thought to flip stochastically between discrete Zeeman levels due to the interaction with fluctuating local fields. The relaxation frequencies calculated from the curves fitted to the observed hf spectra are strongly temperature dependent. They are best interpreted in terms of a fluctuation of the magnetization of superparamagnetic particles. Such fluctuations of magnetization in particles with volume V and anisotropy energy density K occur according to Jacobs and Bean [10] with a characteristic flipping time given by

$$\tau_F = \tau_0 \cdot \exp(K \cdot V / kT). \quad (1)$$

The time τ_0 can be understood as the reciprocal of the Larmor frequency of the magnetization M in an effective molecular field $H_m \propto KV/M$. If $\tau_F \ll \tau_L$, the Larmor precession period of the nuclear magnetic moment in the effective hyperfine field, the nuclear Zeeman splitting will disappear and a non-magnetic spectrum will be observed. This will occur if the energy barrier $K \cdot V$ becomes small enough which occurs usually for particles below 100 Å diameter. The value of τ_0 may be estimated to be on the order of 10^{-10} – 10^{-12} s. Its exact magnitude is not a stringent condition for the occurrence of superparamagnetic behaviour, since the exponential term dominates τ_F . Superparamagnetism has been studied by Mössbauer spectroscopy in considerable detail for fine particles of different iron oxides by various authors [11, 12, 13]. It could be shown that the above relaxation theories lead to a good understanding of the Mössbauer spectra. For our samples we find a nearly constant value of $K \cdot V = 6 \times 10^{-15}$ erg for absorbers thicker than $13\,000$ Å in the temperature regime $T \lesssim 0.9 T_m$ under the assumption of $\tau_0 \approx 10^{-11}$ s. Near T_m the observed decrease of $K \cdot V$ reflects the expected lowering of anisotropy constant. Thinner absorbers give in general a somewhat lower value of $K \cdot V$. Figure 3a gives the temperature dependence of the mean hf field as returned from the relaxation fits. It should be noticed that the saturation value ($T \rightarrow 0$) of the hf field is only 420 kOe and thus much smaller than the value of 495 kOe reported [14] for crystalline FeCl_3 .

FIG. 3. — Temperature dependence of hf magnetic field for FeCl_3 deposited from a molecular beam onto a $a < 10 \text{ K}$ Al foil a) and for FeCl_3 converted into the normal crystalline phase b).

Upon heating to about 100 K, phase A gradually converts irreversibly into phase B. At the same temperature a partial formation of the normal crystalline phase is also observed (Fig. 4). Complete crystallization can be achieved only for absorbers thicker than $\sim 10\,000 \text{ \AA}$ while thinner samples show only partial crystallization even after annealing at 330 K for several days. The resonance spectra as a function of temperature for such recrystallized absorbers is plotted in figure 5. They show the expected single resonance line (unresolved quadrupole splitting) above T_N . The value of the Néel temperature $T_N = 8.90 \pm 0.05 \text{ K}$ was determined by thermal scanning [15] and is in excellent agreement with the results of Stampfel *et al.* [14] for single crystals of FeCl_3 . In the course of this work we have also investigated the Mössbauer spectra of the polycrystalline FeCl_3 which was used in generating the molecular beam. The spectra of the polycrystalline

FIG. 4. — Spectra of FeCl_3 (absorber thickness $30\,000 \text{ \AA}$) deposited from a molecular beam onto a $a < 10 \text{ K}$ Al foil at a rate of $300 \text{ \AA/min}$, for various temperatures above 100 K.

FIG. 5. — Low temperature spectra of vapour deposited FeCl_3 (see Fig. 2) after annealing at 330 K.

material are similar to those shown in figure 5 and exhibit also relaxational broadening below T_N . Especially thin absorbers show a pronounced *paramagnetic* single line in the middle of the spectrum. Those spectra could be fitted with the same superparamagnetic relaxation procedure described above. A Gaussian distribution of particle sizes $0.5 \leq V/\bar{V} \leq 1.5$ around the mean volume $\bar{V}$ was required to obtain a good fit. The temperature dependence of the hf field obtained from this fit is given in figure 3*b*. It shows the same functional behaviour as that of the vapour quenched sample, but gives the expected higher saturation value of the hf field. The energy barriers $K.V$ for the flipping of the particle magnetization are $6.5\text{--}7.5 \times 10^{-15}$ erg for samples thicker than $\sim 10\,000$ Å in the temperature range up to $\sim 0.9 T_N$.

4. Discussion. — The well-known crystalline phase of FeCl_3 forms a rhombohedral bimolecular lattice where Fe^{3+} ions possess a nearly octahedral surrounding [16]. The quadrupole splitting is thus very small and cannot be resolved. The isomer shifts of the low temperature vapour quenched phases A and B are lower than that found for the crystalline phase indicating a higher contact electron density. This may arise from a lower Cl^- coordination of the Fe^{3+} ion when compared to that of the octahedral surrounding in the crystalline FeCl_3 . From geometrical reasons a tetrahedral coordination appears favourable for a ratio of the ionic radii $r_{\text{Fe}^{3+}}/r_{\text{Cl}^-} \simeq 0.35$ [17]. Since FeCl_3 vapour below 1 000 K is formed from Fe_2Cl_6 molecules [6] (see Fig. 6), we assume that the tetrahedral coordination of the Cl^- ions around Fe^{3+} as present

FIG. 6. — Fe_2Cl_6 molecule (see ref. [6]). Bond lengths : $l = 2.11 \pm 0.03$ Å ; $m = 2.28 \pm 0.03$ Å. Bond angles : $\alpha = (128 \pm 3)^\circ$, $\beta = (92 \pm 3)^\circ$. Ions 1, 2, 3, 4, 5, 6 form a plane perpendicular to 1, 2, 7, 8.

in this dimer molecule is frozen during the rapid condensation. Direct formation of the known crystalline phase from the dimer molecules could not be observed. The electric field gradient at the Fe^{3+} site of the dimer molecule can be estimated using a simple point charge model [18] with the parameters given in figure 6. Higher than nearest neighbour influences were neglected. A splitting $\Delta E_Q \simeq 1.6 \pm 0.2$ mm/s was calculated. This value is in agreement with that found for phase A : $\Delta E_Q(\text{A}) = 1.74$ mm/s. The splitting of the doublet B with $\Delta E_Q(\text{B}) = 0.86$ mm/s is obviously caused by a slightly higher symmetrical coordination around the Fe^{3+} . This could come about if the angle α in figure 6 were reduced. Such a deformation is expected if long chains are formed by Fe_2Cl_6 molecules linked together end by end. The observed gradual transformation to phase B upon annealing may be regarded as an indication for the formation of such chains. The reduced value for the saturation hf field for both condensed molecular phases when compared to crystalline FeCl_3 — which itself is already rather small with respect to most ionic ferric ions — is in agreement with the increased population of the 4s shell deduced above from the increase in contact density (decrease of IS). It had been mentioned earlier, that Mössbauer effect studies of the magnetic properties of the dihalides FeF_2 , FeCl_2 and FeBr_2 proved the existence of non-crystalline phases if these materials were prepared with the same method used here. These ferrous halides [2] and other non-crystalline magnets [15] exhibit a distribution of hf fields of 10–20 % around its mean value. In contrast the magnetically split spectra of the condensed phases of FeCl_3 set an upper limit of ~ 5 % for the distribution of the hf field around its mean value. The comparison of the normalized magnetization curve (Fig. 3*a*) of the condensed phases of FeCl_3 with those of the non-crystalline ferrous halides [2] again show a significant difference : Due to fluctuations in the local exchange integrals [3, 4] resp. in the anisotropy fields [5] a considerably less steep rise of the hf field below the magnetic ordering temperature is characteristic for amorphous magnets. The mean magnetization curve of the low temperature vapour quenched phases of FeCl_3 , however, still has the same functional dependence as that of crystalline FeCl_3 (Fig. 3*b*). From the apparent absence of fluctuations in exchange integrals we conclude that the low temperature phases cannot be interpreted as being amorphous in the sense of a random network amorphicity [20] which is the basis of the magnetic theories of references [3–5]. It is our opinion that we have here an example of a *cluster type* or *microcrystalline* material with particles on the order of 20–100 Å diameter. Such a microcrystalline structure is sometimes also called non-crystalline [20]. Evidence for microcrystalline structural units comes from the observed superparamagnetic relaxation. Although the calculated values of the flipping barriers $K.V$ should be taken with care because of the very simple model applied,

they can be used for a rough estimate of the average particle size. Taking $K = 5 \times 10^4 - 1 \times 10^5 \text{ erg/cm}^3$ which is the appropriate range of values [21] for small particles of FeF_3 we find particle diameters of the order of 40-60 Å.

The apparent decrease of T_m with sample thickness is connected with a decrease of flipping barriers and thus represents the expected decrease in blocking temperature of the superparamagnetic fluctuations.

The samples transformed to the normal crystalline state still exhibit superparamagnetic behaviour. Probably large crystals cannot be formed upon annealing

due to the small dimensions of our samples. This is reflected also by the apparent reluctance of thin absorbers to transform to the normal crystalline state at all. Furthermore, it appears that even the usual chemical procedure for the preparation of FeCl_3 leads to rather small crystallites. Superparamagnetism in crystalline FeCl_3 can only be avoided if care is taken to grow large crystals.

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