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SUSCEPTIBILITY OF NON-CRYSTALLINE FERROMAGNETIC FeF_2 (*)

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Résumé. — On peut décrire la susceptibilité magnétique de FeF_2 non cristallin par une loi de Curie-Weiss entre 25 K et 150 K. On trouve une température de Curie paramagnétique $\theta = (22 \pm 1)$ K et un moment effectif $p_{\text{eff}} = (5,2 \pm 0,1) \mu_B$. Entre 15 K et 20,5 K l'aimantation varie avec la température et le champ, indiquant un comportement superparamagnétique. Aux températures inférieures, l'aimantation montre de l'hystérésis et une rémanence qui dépend faiblement du temps. Les moments approchant $4 \mu_B/\text{Fe}^{2+}$ impliquent que l'état ordonné est ferromagnétique.

Abstract. — In the temperature range $150 \text{ K} > T > 25 \text{ K}$ the magnetic susceptibility of non-crystalline FeF_2 can be described by a Curie-Weiss law. A paramagnetic Curie temperature of $\theta = (22 \pm 1) \text{ K}$ and an effective moment of $p_{\text{eff}} = (5.2 \pm 0.1) \mu_B$ are found. Temperature and field dependence of the magnetization between 15 K–20.5 K indicate superparamagnetic behaviour. At lower temperatures the magnetization shows hysteresis and a slightly time dependent remanence. The observation of moments which approach $4 \mu_B/\text{Fe}^{2+}$ implies that the ordered state is ferromagnetic.

Non-crystalline FeF_2 can be prepared by condensation of a molecular beam of FeF_2 on to a He-cooled substrate in a vacuum of $\sim 10^{-8}$ torr. We have shown previously by Mössbauer spectroscopy that non-crystalline FeF_2 becomes magnetically ordered below $\sim 21 \text{ K}$ [1]. This is in contrast to the Néel temperature $T_N = 78 \text{ K}$ found for crystalline antiferromagnetic FeF_2 [2]. The non-crystalline samples of FeF_2 are converted into the crystalline state only at temperatures above $\sim 800 \text{ K}$ [3]. It is thus possible to warm such samples to 300 K, carefully brush the amorphous material from the substrate, and then transfer the powder under an inert atmosphere into a magnetometer (Foner type, vibrating sample method) without any structural changes taking place. The measured susceptibility in a field of $H = 1250 \text{ Oe}$ and the temperature range $150 \text{ K} > T > 25 \text{ K}$ can be described by a Curie-Weiss law (Fig. 1). An extrapolated paramagnetic Curie temperature of $\theta = (22 \pm 1) \text{ K}$ was found together with $p_{\text{eff}} = (5.2 \pm 0.1) \mu_B$.

The derived value $g = 2.12 \pm 0.05$ of non-crystalline FeF_2 is only slightly larger than $g = 2.10 \pm 0.05$ for crystalline FeF_2 [4]. The magnitude and temperature dependence of the quadrupole splitting and the magnitude of the magnetic hyperfine interaction as derived from the Mössbauer spectra indicate a less complete quenching of the orbital momentum in non-crystalline FeF_2 compared to the crystalline phase [1, 3]. A simple

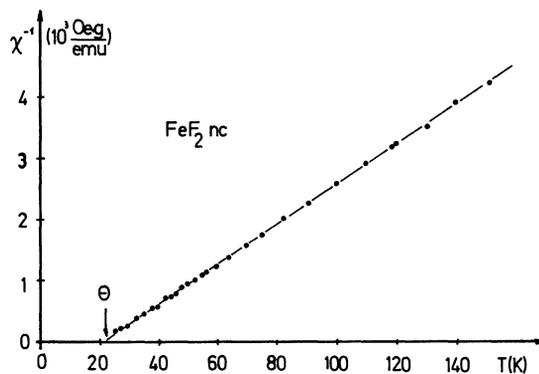


FIG. 1. — Inverse susceptibility of non-crystalline FeF_2 against temperature.

perturbational treatment for the crystal electric field levels shows that an increase of the rhombic distortion at Fe^{2+} in the non-crystalline phase leading to a decrease of the splitting between the ground state and the first excited orbital state from $\sim 700 \text{ cm}^{-1}$ (crystalline phase [5]) to $\sim 500 \text{ cm}^{-1}$ can explain the increase of orbital momentum. It would, however, only cause an increase of ~ 0.03 in g -factor which agrees well with the data found.

In figure 2 the magnetization curves between 15–20.5 K are plotted as $(M \times M_s(T = 0))/M_s(T)$ against $H \times M_s(T)/(T \times M_s(T = 0))$. The approximate ratios of the spontaneous magnetizations

$$M_s(T)/M_s(T = 0)$$

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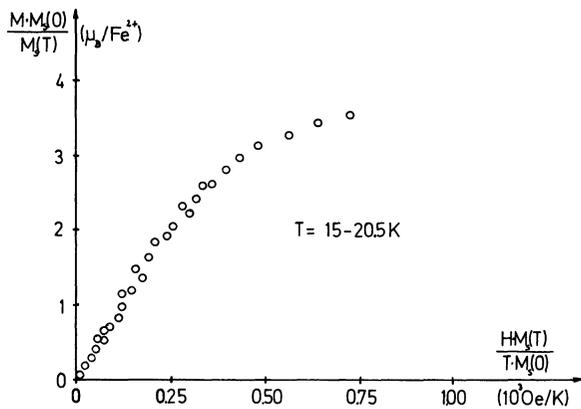


FIG. 2. — Plot of the magnetization $M \times M_s(T=0)/M_s(T)$ against $H \times M_s(T)/(T \times M_s(T=0))$.

were taken to be identical to the ratios

$$H_{\text{hf}}(T)/H_{\text{hf}}(T=0)$$

as determined by the hyperfine splitting of the Mössbauer resonance [1] (Fig. 3). The magnetization curves follow nearly superposing Langevin functions, a behaviour which is typical of superparamagnetism [6]. The large magnetic moments per Fe^{2+} ion (approaching $4 \mu_B$) indicate superparamagnetism of a ferromagnetic configuration rather than superparamagnetism in poorly compensated antiferromagnetic crystallites. If we attribute this magnetic behaviour to an ensemble of non-interacting particles, with all spins coupled ferromagnetically from the slopes of the Langevin functions we can derive a mean moment of $(115 \pm 40) \mu_B$ per saturated ferromagnetic particle corresponding to $\sim 30 \pm 10$ molecules and a volume of $\sim (1200 \pm 400) \text{ \AA}^3$ per particle. The interatomic distances are assumed to be identical to those of crystalline FeF_2 . The errors are mainly due to the inaccurate knowledge of $M_s(T)$ near T_c . The mean blocking temperature $T_B = 15 \pm 2 \text{ K}$ observed in these magnetization measurements (typical time of observation

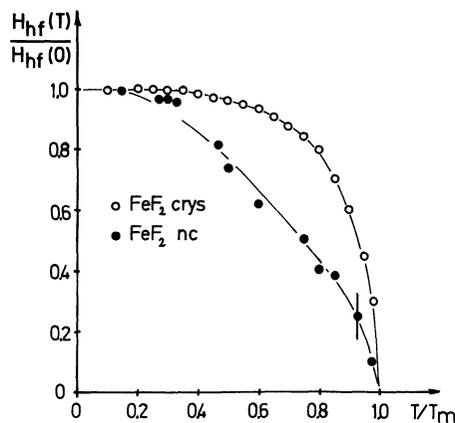


FIG. 3. — Normalized hyperfine magnetic field H_{hf} of non-crystalline FeF_2 [1] and of crystalline FeF_2 ([2] and own data) derived from hyperfine splitting of the Mössbauer resonance plotted against T/T_m . T_m is the Curie temperature $T_c = 21 \text{ K}$ for non-crystalline FeF_2 , and the Néel temperature $T_N = 78 \text{ K}$ for crystalline FeF_2 , respectively.

$\sim 1 \text{ s}$) allows an estimate of the anisotropy density K of the superparamagnetic particles. Using a simple model which applies only for non-interacting particles of uniaxial symmetry (certainly an oversimplification of the present case) [7] we may write :

$$\tau = \frac{\hat{M}_s}{\gamma K} \sqrt{\frac{kT_B}{K \cdot V}} \exp(K \cdot V/kT_B).$$

Here γ is the gyromagnetic ratio and \hat{M}_s is the saturation magnetization per unit volume. We then find $K \simeq (4.0 \pm 1.5) 10^7 \text{ erg/cm}^3$ which is about one third of the crystalline anisotropy of crystalline antiferromagnetic FeF_2 [8].

At even lower temperatures the magnetization curves show hysteresis and remanence. The remanence decreases slightly with time. The value found for the remanence at 4.2 K , $M_r = (1.5 \pm 0.5) \mu_B$ is somewhat less than $2 \mu_B$ which is expected for an ensemble of randomly oriented single domain particles of axial symmetry [9]. The magnitude as well as the time dependence of M_r indicate that due to a distribution of particle sizes (and probably of K , too) there is still a small amount of superparamagnetic, or at least nearly superparamagnetic, particles present at the lowest temperatures.

This observation of superparamagnetism is not contradictory to Mössbauer data which show an abrupt onset of magnetic hyperfine splitting below 21 K , since nuclear Larmor precession is still faster than the flipping of magnetization of a superparamagnetic particle. Since non-crystalline samples prepared by vapour quenching are likely to contain voids, a detailed discussion of the magnetization curves at low temperatures is precluded by the ill-defined demagnetization factor.

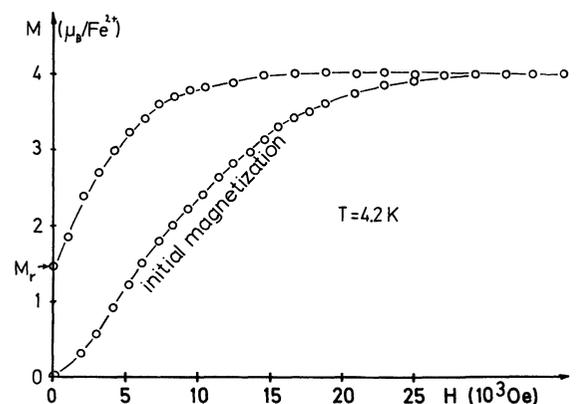


FIG. 4. — Magnetization of non-crystalline FeF_2 at 4.2 K .

If the molecular beam of FeF_2 is quenched on to a N_2 -cooled substrate, then the inverse high temperature susceptibility extrapolates to a Curie-Weiss temperature $\theta \simeq -120 \text{ K}$ which comes close to that found for crystalline FeF_2 [4]. Below 78 K , however, the susceptibility still increases. Values of about

2.5×10^{-3} emu/g \times Oe are found at 10 K which is more than ten times the corresponding value for crystalline antiferromagnetic FeF₂. At lower temperatures the susceptibility decreases. If the samples are cooled to 4.2 K in an applied field of 5×10^4 Oe a thermoremanence of $\sim 0.1 \mu_B$ per Fe²⁺ is found which vanishes upon heating to 18 K. The temperature dependence of the magnetization and the thermoremanence can be interpreted in terms of superparamagnetism of small antiferromagnetic particles [10] which are not totally compensated sublattices of crystalline FeF₂. The Mössbauer spectra further support the picture that in this case small particles of the usual crystalline structure of FeF₂ are formed. The samples are still «X-ray amorphous». The ferromagnetic properties of non-crystalline FeF₂ prepared by quenching to He-temperature, therefore, cannot be attributed to surface effects of fine particles alone. The breakdown of antiferromagnetism must be correlated with the distortion of the 135° bond angle between Fe²⁺-F⁻-Fe²⁺ connecting the corner Fe²⁺ with the central Fe²⁺ in the rutile cell of crystalline FeF₂. This

bond is responsible for the strong antiferromagnetic superexchange coupling in crystalline FeF₂. A suggested explanation of the ferromagnetic coupling is superexchange via nearly 90° Fe²⁺-Fe⁻-Fe²⁺ bonds similar to the exchange coupling between Fe²⁺ ions inside layers of crystalline FeCl₂ [11]. Although these magnetic data show that amorphous ferromagnetic FeF₂ has the same magnetic behaviour as an ensemble of ultra-fine particles, more independent evidence for the presence of these particles is desirable. Such behaviour could eventually be typical of some amorphous ferromagnets. The radial distribution function will be determined in order to decide whether an amorphous cluster model with particles of the proposed size or a random network model can give a better description of the non-crystalline structure. Resistivity measurements on freshly deposited non-crystalline samples will be performed to ascertain their insulating character.

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