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Magnetic behaviour of the antiferromagnet $FeTa_2O_6$

L I Zawislak†, G L F Fraga†, J B Marimon da Cunha†, D Schmitt‡, A S Carriço§ and C A dos Santos†‖

† Instituto de Física, UFRGS, CP 15051, 91501-970 Porto Alegre, RS, Brazil
‡ Laboratoire Louis Néel, CNRS, 166X, 38042 Grenoble Cédex, France
§ Departamento de Física, UFRN, 59072-970 Natal, RN, Brazil

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Abstract. The magnetic behaviour of the antiferromagnet $FeTa_2O_6$ was investigated through heat capacity, magnetic susceptibility and magnetization measurements. The broad magnetic susceptibility curve (peaked at 15 K) presents an inflection typical of two-dimensional systems. This inflection is observed near 10 K, the temperature at which early reported Mössbauer measurements indicate the onset of magnetic order. The heat capacity measurements have shown a clear transition at 8.7 K, where Mössbauer measurements show complete ordering. Magnetization curves, for temperatures between 1.4 K and 5 K, display a noticeable change in slope, suggesting a spin-flop transition induced by a field higher than 10 T. It is argued that this transition, which disappears for $T > 6$ K, is evidence of two-dimensional behaviour.

1. Introduction

Low-dimensional systems have attracted a great deal of both experimental and theoretical research effort. In this context the antiferromagnets of the K_2NiF_4 family have been the subject of a colossal number of publications in the late 1960s and early 1970s [1]. These body-centred-tetragonal compounds present magnetic properties considered as signatures of two-dimensional systems. For instance, the susceptibility curve shows a broad maximum and falls off slowly in the paramagnetic region. Below this maximum a subtle inflection is observed [2–4]. The broad maximum is indicative of short-range correlations, while the inflection point is associated with long-range order, as indicated by specific heat measurements. The difference between the susceptibility maximum and the inflection point is small in 3D systems and large in 2D ones [5].

The magnetic susceptibility results for $FeTa_2O_6$ have suggested an antiferromagnetic ordering with a broad maximum at about 15 K, while the heat capacity experiments show a clear transition at 8.5 K [6]. These data indicate short-range correlations at about 15 K and long-range ordering at 8.5 K. Similar results have been obtained for the isomorphous compounds $CoTa_2O_6$, $NiTa_2O_6$ and $CoSb_2O_6$ [2, 3]. Therefore, the magnetic behaviour of the $FeTa_2O_6$ family is analogous to that of the K_2NiF_4 group.

The general features of the above-described magnetic behaviour have been supported by recent Mössbauer spectroscopy (MS) measurements on $FeTa_2O_6$ [7]. Results from reference [7] show that from room temperature (RT) to about 15 K the compound is clearly in the paramagnetic regime. Below 15 K short-range correlations dominate, as indicated by the increasing asymmetry of the quadrupolar doublet. The onset of long-range order is

‖ E-mail: cas@if.ufrgs.br; fax: ++55 51 319 1762.

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Table 1. Fractional atomic coordinates and lattice parameters for $FeTa_2O_6$ at room temperature, as obtained from Rietveld refinement.

Atom	x	y	z
Fe	0	0	0
Ta	0	0	0.331(1)
O_1	0.287(8)	0.287(8)	0
O_2	0.296(1)	0.296(1)	0.313(2)
a (Å)	4.754(6)		
c (Å)	9.197(5)		
R_p [a]	6.15		
R_{wp} [b]	7.91		

[a] Profile $R_p = 100 \times \sum |Y_{obs} - Y_{calc}| / \sum Y_{obs}$.
[b] Weighted profile $R_{wp} = 100 \times [\sum w(Y_{obs} - Y_{calc})^2 / \sum w(Y_{obs})^2]^{1/2}$.

manifested near 10 K by the emerging hyperfine magnetic field. Decreasing the temperature, the local magnetization at the iron site jumps, at about 8.5 K, to the saturation value, with very modest further increase for temperatures down to 4.2 K. A plot of the hyperfine magnetic field as a function of the temperature shows a curve qualitatively similar to the one calculated using the two-dimensional Ising model.

In the present work, confirming the results of reference [7], we report, for the first time, magnetization measurements supporting the low-dimensional character of $FeTa_2O_6$.

2. Experimental procedures

The magnetic measurements were performed, at the Laboratoire Louis Néel, on the same sample as was used in an MS study previously reported [7]. The sample quality was examined through x-ray powder diffraction (XRPD) patterns, obtained with a Siemens diffractometer with monochromated Cu Kα radiation ($\lambda = 1.5418$ Å). Structural refinement of spectra obtained with a scan step of 0.05° 2θ in the 2θ-range from 5° to 100°, with a fixed counting time of 4 s, were performed using the FULLPROF program [8].

The magnetization measurements were made by using the extraction method at temperatures ranging from 1.4 K to 300 K, in magnetic fields up to 10 T (up and down cycles), produced by a superconducting coil. The heat capacity was measured by using the AC calorimetry technique [9] at temperatures ranging from 1.2 K to 60 K.

3. Results and discussion

The XRPD pattern shown in figure 1 was indexed to the space group $P4_2/mnm$, with crystallographic parameters (table 1) similar to those previously reported [6]. The small goodness of fit ($\chi^2 = 3.26$) obtained for the Rietveld refinement and the absence of spurious reflections on the XRPD diagram are strong indications that we have prepared a well crystallized single-phase sample. Further evidence of the good quality of the sample comes from the Mössbauer spectroscopy results [7]. All of the spectra were fitted with a linewidth at half-height (Γ) fixed at 0.27 mm s^{-1}. As the iron foil (99.999%) calibration gave the value $\Gamma = 0.26$ mm s^{-1}, this early result is indicative of there being no significant impurity effect on the Mössbauer spectra.

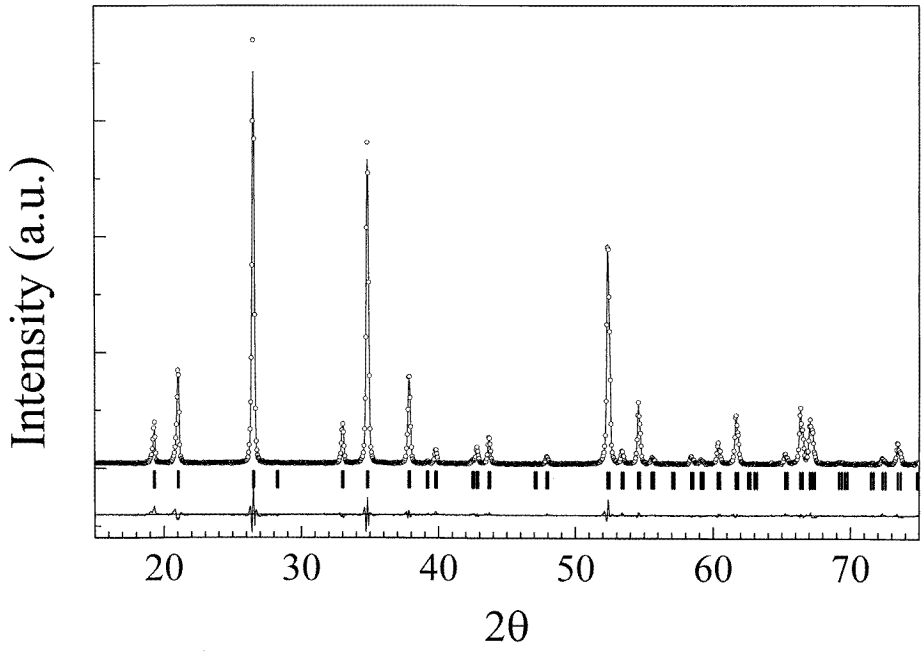

Figure 1. The room temperature x-ray powder diffraction pattern for $FeTa_2O_6$.

From the crystallographical properties of the space group $P4_2/mnm$ and from the atomic coordinates displayed in table 1, it becomes evident that Fe^{2+} and Ta^{5+} cations are surrounded by O^{2-} octahedra, and that Fe–O planes are well defined in the trirutile structure of $FeTa_2O_6$. Successive Fe–O planes are separated by two Ta–O planes, so the intraplane coupling is expected to be stronger than the interplane coupling, which favours low-dimensional magnetic behaviour.

Our susceptibility and heat capacity results are similar to those previously reported [6]. The susceptibility measurements, displayed in figure 2, show a broad maximum at 15 K and an inflection at about 10 K. The Curie–Weiss law gives $\mu_{\text{eff}} = 5.06\mu_B$/Fe and $\theta = -8.7$ K. As can be seen in figure 3, the heat capacity measurements show a very sharp spike at 8.7 K. The inset of figure 3 shows the function $\partial(\chi T)/\partial T$, plotted against T, which represents the magnetic component of the heat capacity [5]. The slow decay from 10 K to 20 K suggests that a large amount of the entropy gain on warming up the sample occurs above $T_N \simeq 8.7$ K. This λ-profile of the magnetic component of the heat capacity is typical of two-dimensional systems, as it strongly suggests that significant short-range correlations are taking place above T_N [1].

The linear relationship between the magnetization and applied field, displayed in the inset of figure 4, is clear evidence that the paramagnetic state occurs above 15 K. Furthermore, there is a noticeable feature at intermediate-field values for measurements below 6 K. The measurements made between 1.4 K and 5 K show a clear change in slope at about 6 T, with a ratio, R, between high-field and low-field slopes very close to three. This functional change, shown in figure 4 for the measurement at 1.4 K, is an indication of a spin-flop transition. A small hysteresis, barely noticeable between 6 T and 10 T, supports this hypothesis.

In order to interpret the magnetization curves at low temperatures, we have adopted

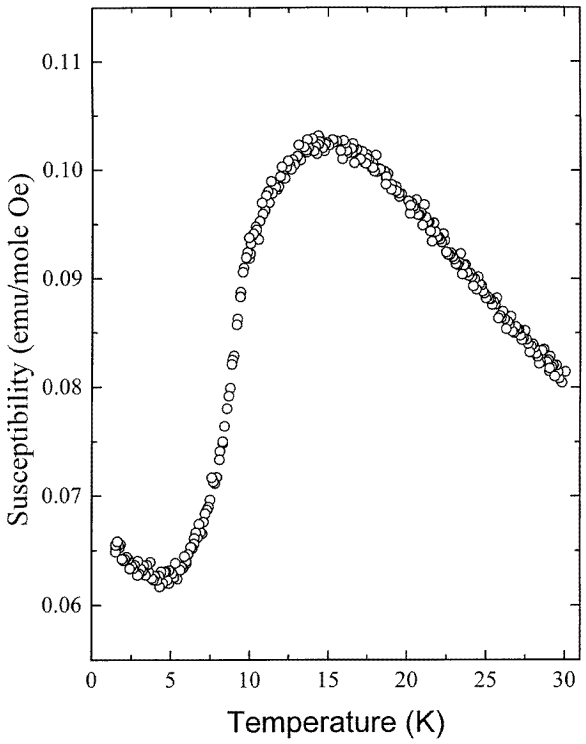

Figure 2. The magnetic susceptibility of $FeTa_2O_6$.

Eicher's model for the magnetic structure [6], taking into account the random orientation of grains in our sample, as indicated by the Mössbauer data [7]. Each grain consists of two families of antiferromagnetic (AF) planes. The uniaxial anisotropy of one family is rotated by 90° with respect to that of the other. The 3D lattice is a stacking of alternating planes from each family. The anisotropy-field direction correlates with the symmetry of the local field originating from the oxygen coordination of the Fe atoms in the lattice. The total magnetization is calculated by adding up the contributions from the two 2D antiferromagnetic lattices, and neglecting the interaction between moments in different planes. We also neglect possible differences in the AF coupling within a single plane. The evolution of the magnetic phase under an external magnetic field is obtained by a numerical procedure which consists in keeping the moments in the direction of the local effective field. The orientation of spins with respect to the uniaxial axis is adjusted self-consistently in such a way that each magnetic moment is directed along the local effective field produced by its neighbours, with anisotropy and external field included. This procedure allows the incorporation of temperature and magnetic field effects [10].

If an external field is applied along the anisotropy direction of one family of AF planes, it will induce transverse canting of spins belonging to the other family of planes. Therefore, unlike in the case of usual AF structures, there is no threshold for the build-up of magnetization along the field direction. Calling the effective exchange and anisotropy fields H_e and H_a, it can be shown that starting from $M = 0$ at zero applied field, the magnetization initially increases linearly with a slope proportional to $2/(H_e + H_a)$ until the spin flop is reached. At the critical field, H_{sf}, the transition to the spin-flop phase produces

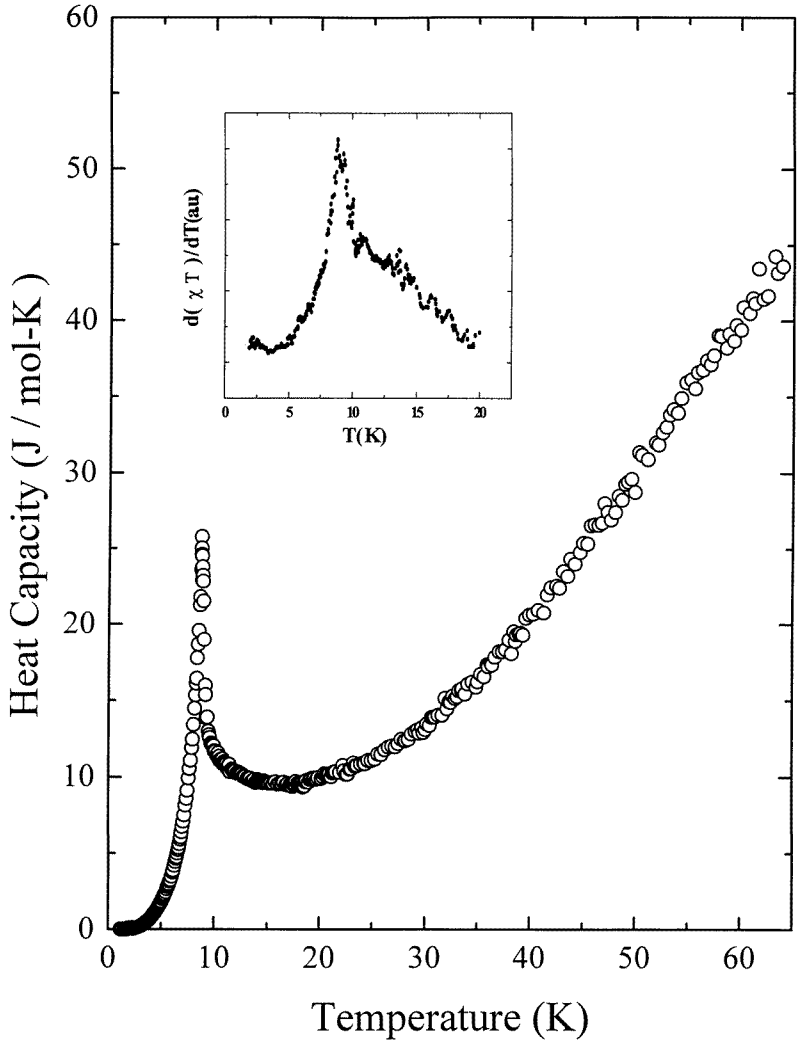

Figure 3. The heat capacity of $FeTa_2O_6$. The inset shows the function $\partial(\chi T)/\partial T$.

a discontinuity in M. The family of planes in the spin-flop phase generates a term in the magnetization, which would by itself lead to a slope of $M(H)$ proportional to $2/(H_e - H_a)$.

At this point it is instructive to consider the limiting case of very weak anisotropy. If $H_a/H_e \ll 1$ then the static transverse susceptibility is equal to the static susceptibility in the spin-flop phase. Therefore, apart from the discontinuity at H_{sf}, the total magnetization displays a change in slope beyond this field. For low-field values only the family of planes with anisotropy perpendicular to the applied field participate in the magnetization, which grows linearly with the field strength. For applied fields larger than H_{sf}, both families of planes contribute to the magnetization along the field direction. Thus, if the anisotropy is small, the total static susceptibility should increase by a factor of two just after H_{sf}.

A random orientation of grains tends to decrease the ratio between the average high-field static susceptibility and the average low-field static susceptibility. The fraction of the

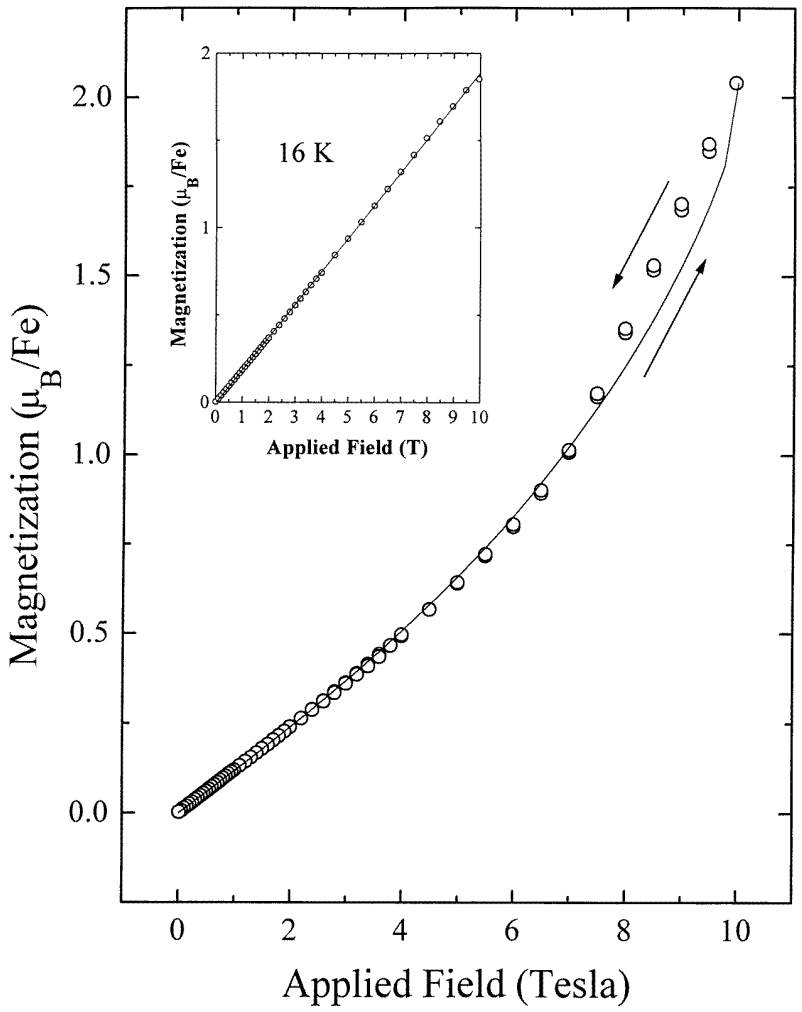

Figure 4. The magnetization versus applied field at $T = 1.4$ K. The continuous curve represents the calculated average magnetization. The inset shows the magnetization curve for $T = 16$ K.

sample volume contributing to the static susceptibility at low-field values increases, due to transverse canting of spins. Therefore, the ratio R is expected to be less than two. However, the value observed in this work is close to three. This result could suggest that the anisotropy field would be comparable to the effective exchange field. Increasing the anisotropy field favours a relative increase in the high-field static susceptibility, as compared to the low-field static susceptibility. Even for extremely large values of the anisotropy field with respect to the exchange field (e.g., $H_a/H_e = 0.34$), R is around 2.5. Hence, the maximum field shown in figure 4, 10 T, is probably below the spin-flop field for $FeTa_2O_6$. In addition, as our sample consists of grains oriented at random, one should not expect to see the discontinuity in magnetization at the spin-flop transition. In fact, the magnetization jump is not seen in figure 4. Instead, for temperatures below 6 K, only a clear change in the slope of $M(H)$ is displayed.

The random orientation of grains is modelled by averaging the $M(H)$ curves for a uniform distribution of angles between the applied field and the uniaxial axis. We expect this should reproduce the measured $M(H)$, except in the immediate neighbourhood of the spin-flop field. Even a small biasing in the orientation of grains with the applied field may affect the magnetization for these field strengths. Averaging over grains is admissible if each grain behaves like the bulk material. This is valid provided that surface effects, in the grains, are not significant. In the past it has been shown that surface effects are strong for low-anisotropy antiferromagnets, leading in some cases to surface-induced low-field instability of the antiferromagnetic phase. However, for materials with relatively high anisotropies, surface effects are restricted to the surface region [10]. To reproduce the experimental data we estimate H_a to be of the order of $0.04H_e$. For anisotropy-field values of this order, grain size effects should not be relevant.

We expected $FeTa_2O_6$ to have magnetic properties similar to those of K_2NiF_4, for which H_a/H_e is of the order of 10^{-3} and the measured value of the spin-flop field is 19 T [11, 12]. For K_2NiF_4, the anisotropy field is largely due to the crystal field produced at the magnetic sites by the fluorine octahedra, and the large value of the Néel temperature, T_N (around 100 K), is due to the exchange field. Therefore, as T_N for $FeTa_2O_6$ is about 10 K, the anisotropy field is very likely to be of the order of 1 T, while the exchange field should be smaller by a factor of ten compared to those of the K_2NiF_4. We were able to fit the low-temperature magnetization curve assuming $H_{sf} = 10$ T and $H_a = 1.4$ T. The change of slope at around 6 T (figure 4) results from the increase in $M(H)$ produced, below H_{sf}, by the random distribution in grain orientation. The total magnetization, $M(H)$, calculated along the field direction, assuming $T = 0$ K, is shown by the full line in figure 4. This curve was scaled so as to fit the measured magnetization at 10 T. The small discrepancy, of around 10%, near 10 T is expected, since just below the spin-flop field any minor biasing in the grain orientation distribution might affect $M(H)$.

The change in the slope of the $M(H)$ curve for $T = 1.4$ K around 6 T could suggest a spin-flop field of 6 T. This, however, is not consistent with the observed hysteresis at larger values of applied field. The hysteresis shown in figure 4 is weak because only a small fraction of the sample—just those grains whose anisotropies are at fairly small angles to the applied field—contribute to it. Thus, as predicted by our model, $H_{sf} > 10$ T.

4. Conclusion

So far the discussion of low-dimensional magnetism of the MTa_2O_6 family (M = transition metal atom) has focused primarily on results for thermodynamic quantities such as the specific heat and magnetic susceptibility. Our measurements of these properties, in addition to the x-ray diffraction results, strongly indicate a two-dimensional character for the magnetic behaviour of $FeTa_2O_6$.

In a complementary way, our magnetization measurements represent the first attempt to draw conclusions as regards the magnetic order of the low-dimensional $FeTa_2O_6$ antiferromagnet arising from field effects. Furthermore, they confirm the early proposed model for the magnetic structure [6]. Eicher's original work (Mössbauer spectroscopy and neutron scattering) does not focus on the effect of the interplane coupling on the magnetic order. We extended his investigation by examining the nature of the coupling between planes explicitly. The existence of a field-induced first-order transition strongly indicates very weak magnetic interaction between the two families of AF planes composing the $FeTa_2O_6$. Since the anisotropies are perpendicular, any exchange interaction that couples magnetic moments in neighbouring planes would produce in each an effective field perpendicular to

the anisotropy. In this case there would be no first-order transition from the AF to the spin-flop phase. Instead, the magnetization in both families would grow continuously with the field.

In conclusion, two-dimensional magnetic behaviour has been observed in a powder single-phase $FeTa_2O_6$ sample. Our heat capacity and magnetic susceptibility results are similar to those previously published [6]. In addition, we have obtained, for the first time, magnetization curves over a large range of temperatures. The low-temperature measurements are consistent with a spin-flop transition induced by a field higher than 10 T. The ratio of almost 1/3 between the susceptibilities below and above the spin-flop field is indicative of a strong anisotropy field, as compared to the case for K_2NiF_4 [11].

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