

X-ray diffraction and magnetic susceptibility measurements for $\text{Fe}_x\text{Ni}_{1-x}\text{Ta}_2\text{O}_6$

S R de Oliveira Neto¹, E J Kinast², M A Gusmão¹, C A dos Santos²,
O Isnard³ and J B M da Cunha¹

¹ Instituto de Física, Universidade Federal do Rio Grande do Sul, CP 15051, 91501-970 Porto Alegre, RS, Brazil

² Universidade Estadual do Rio Grande do Sul, Rua 7 de Setembro, 1156, 90010-191 Porto Alegre, RS, Brazil

³ Institut Néel, CNRS, associé à l'Université J Fourier et à l'INPG, BP 166, 38042 Grenoble Cedex 9, France

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Abstract

The trirutile family of the tapiolite-like compound $\text{Fe}_x\text{Ni}_{1-x}\text{Ta}_2\text{O}_6$ was investigated by means of x-ray powder diffraction (XRD) and magnetic susceptibility measurements. From Rietveld refinement it is demonstrated that the family is a homogeneous solid solution obeying Vegard's law. Magnetic susceptibility curves exhibit typical signatures of low-dimensional systems, with broadened maxima due to short range correlations immediately above the antiferromagnetic transition temperature T_N . The T versus x phase diagram presents a minimum that suggests bicritical behaviour.

In the tetragonal tapiolite-like isomorphic compounds ATa_2O_6 ($A = \text{Fe}, \text{Co}, \text{Ni}$), the sublattice formed by the 3d transition-metal ions has the same symmetry as that of Ni in K_2NiF_4 , well known as a two-dimensional Heisenberg antiferromagnet [1]. This observation has motivated investigations to search for the existence of low-dimensional magnetic behaviour in tapiolite-like compounds. These compounds crystallize in the trirutile structure with space group $P4_2/mnm$, the A^{2+} and Ta^{5+} cations being surrounded by O^{2-} octahedra. From room temperature down to about 15 K, FeTa_2O_6 is clearly in the paramagnetic regime. The onset of long range order manifests itself near 10 K through an emerging hyperfine magnetic field, as measured by Mössbauer spectroscopy [2]. Magnetic susceptibility measurements show a Néel temperature, T_N , of about 9.5 K for FeTa_2O_6 , 7.1 K for CoTa_2O_6 and 10.3 K for NiTa_2O_6 [3–8]. Measurements of heat capacity have shown a sharp peak indicating a three-dimensional transition, with the specific heat curve reflecting a two-dimensional behaviour of short range correlations above the transition temperature [5]. A neutron diffraction study revealed magnetic structures with double propagation vectors: $(1/2, 0, 1/2)$ and $(0, 1/2, 1/2)$ for FeTa_2O_6 , and $(1/4, 1/4, 1/4)$ for CoTa_2O_6 [3]. The Néel temperature versus x phase diagram for the system $\text{Fe}_x\text{Co}_{1-x}\text{Ta}_2\text{O}_6$ exhibits a bicritical point at about $T = 4.9$ K and

Table 1. Unit-cell parameters and Bragg factors R_B . All the samples were indexed to the space group $P4_2/mnm$. Numbers in parentheses indicate $\pm\sigma$ on the last decimal given.

Sample	a (Å)	c (Å)	R_B (%)
NiTa ₂ O ₆	4.7175(1)	9.1205(4)	6.15
Fe _{0.15} Ni _{0.85} Ta ₂ O ₆	4.7229(1)	9.1326(3)	2.23
Fe _{0.40} Ni _{0.60} Ta ₂ O ₆	4.7355(2)	9.1554(5)	4.16
Fe _{0.60} Ni _{0.40} Ta ₂ O ₆	4.7427(1)	9.1705(3)	4.07
Fe _{0.85} Ni _{0.15} Ta ₂ O ₆	4.7506(1)	9.1862(3)	3.54
FeTa ₂ O ₆	4.7563(1)	9.1988(2)	3.40

Table 2. Crystal structure data and isotropic thermal parameters for Fe_{0.85}Ni_{0.15}Ta₂O₆.

Atom	x	y	z	B (Å ²)
Fe	0	0	0	1.1(1)
Ni	0	0	0	1.1(1)
Ta	0	0	0.330(5)	0.24(6)
O ₁	0.312(8)	0.312(8)	0	0.1(2)
O ₂	0.291(5)	0.291(5)	0.314(4)	0.1(2)

$x = 0.46$. That is to say, at this Fe concentration and lower temperatures the system shows coexistence of the two magnetic structures. This novel bicritical behaviour is interpreted as induced by competition between the different magnetic and crystallographic structures.

From neutron diffraction measurements for NiTa₂O₆, it was shown that the magnetic moments are collinear, aligned parallel to the $[1\ 1\ 0]$ direction. In the ab plane, ferromagnetic and antiferromagnetic chains exist which are perpendicular to each other along the $[1\ 1\ 0]$ and $[1\ \bar{1}\ 0]$ directions [9]. Thus, it would be interesting to replicate for the Fe _{x} Ni _{$1-x$} Ta₂O₆ system the investigation performed with Fe _{x} Co _{$1-x$} Ta₂O₆, in order to better understand the role played by the electronic structure of the 3d transition metal. In this paper we report crystal structure refinement and magnetic susceptibility measurements for this system.

Samples were prepared for $x = 0.00, 0.15, 0.40, 0.60, 0.85,$ and 1.00 . FeTa₂O₆ was prepared in vacuum, by the solid-state reaction of Fe, Fe₂O₃ and Ta₂O₅. Appropriate amounts of the powdered reagents were mixed, ground, pelleted, encapsulated in silica glass under vacuum (pressure $\approx 10^{-3}$ Pa), and heated at 1400 K for 24 h. After slow cooling, the sample was powdered to 320 mesh. NiTa₂O₆ was prepared in a similar way with NiO and Ta₂O₅, but in air, at 1600 K. For Fe _{x} Ni _{$1-x$} Ta₂O₆ samples, appropriate amounts of FeTa₂O₆ and NiTa₂O₆ were mixed and processed as for the FeTa₂O₆ preparation, but at 1600 K.

X-ray powder diffraction measurements were performed with a scan step of 0.05° for the range $10^\circ < 2\theta < 80^\circ$, with the fixed counting time of 1 s, through a Siemens diffractometer D500 using Cu $K\alpha_1$ and Cu $K\alpha_2$ radiations. The structure refinement of XRD patterns, carried out by the Rietveld method with the FULLPROF program [10], indicate that the samples are well crystallized and homogeneous due to the absence of spurious reflections and the small Bragg factor obtained. Table 1 shows unit-cell parameters and Bragg factors. All the samples are tetragonal, and have been indexed to the space group $P4_2/mnm$, as expected. A typical pattern is displayed in figure 1 for the sample Fe_{0.85}Ni_{0.15}Ta₂O₆. Atomic coordinates and isotropic thermal parameters for this sample are summarized in table 2. Figure 2 shows the unit-cell volume as a function of the iron concentration. The observed linear dependence for the whole range of substitution reflects the validity of Vegard's law for solid solubility.

Magnetic susceptibility measurements were carried out with a SQUID magnetometer, at temperatures ranging from 3.5 to 300 K, in an applied field of 1000 Oe. The results are shown in

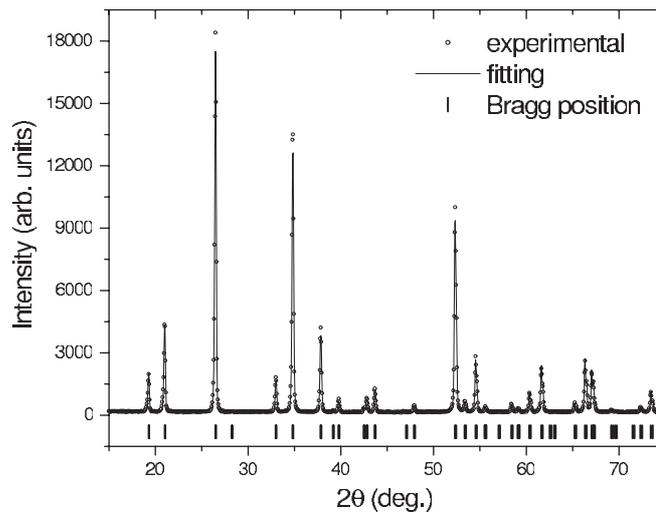


Figure 1. Room temperature x-ray powder diffraction pattern for $\text{Fe}_{0.85}\text{Ni}_{0.15}\text{Ta}_2\text{O}_6$. Points represent experimental data and the solid line the calculated pattern with Rietveld refinement. Vertical ticks show the $P4_2/mnm$ reflections.

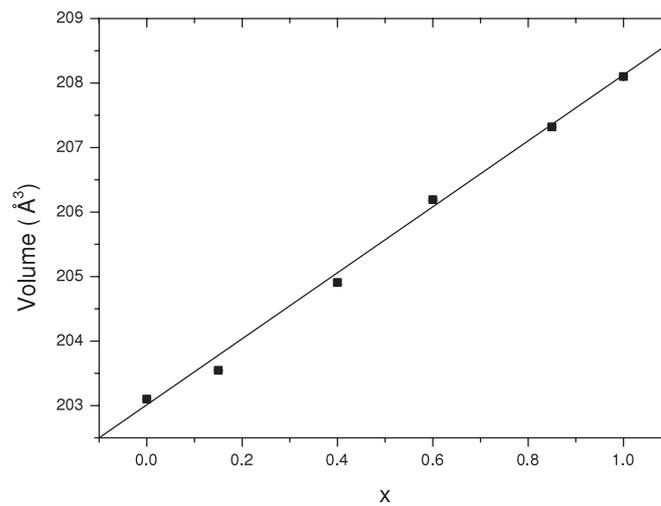


Figure 2. Variation in the unit-cell volume as a function of iron concentration. The solid line is a linear fit.

figure 3. Overall, the susceptibility increases with iron concentration, and presents a broadened maximum typical of two-dimensional systems. Below 6 K, the susceptibility of the sample with $x = 0.15$ rises again, while a sudden fall is observed for the samples with $x = 0.40$ and 0.60 . These strange behaviours suggest different regimes for magnetic structure evolution with temperature. From the susceptibility data, we obtained the long range order transition temperatures T_N by computing $\partial(\chi T)/\partial T$. This quantity follows the magnetic contribution to the specific heat [11], with a sharp peak at T_N . The plot of T_N versus x , shown in figure 4, indicates the presence of a minimum around $x = 0.60$. As in the case of the $\text{Fe}_x\text{Co}_{1-x}\text{Ta}_2\text{O}_6$,

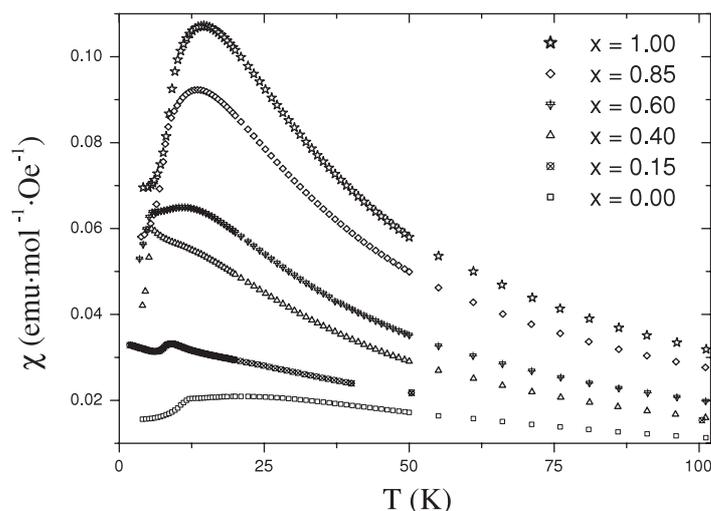


Figure 3. Magnetic susceptibility as a function of temperature for various samples from the system $\text{Fe}_x\text{Ni}_{1-x}\text{Ta}_2\text{O}_6$.

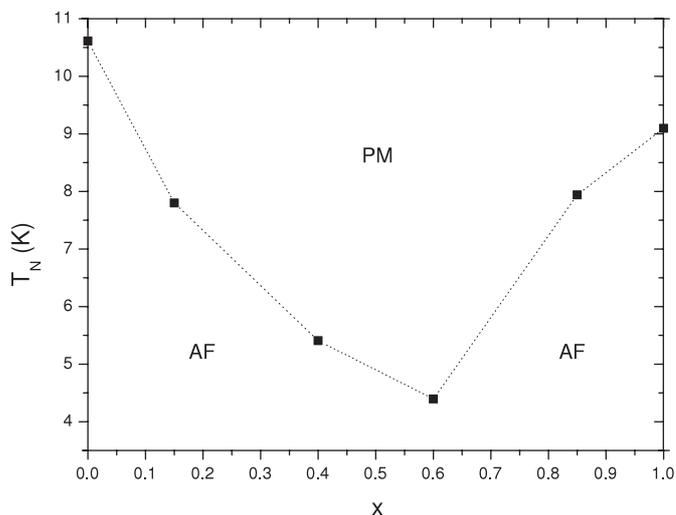


Figure 4. T_N versus x phase diagram, showing the paramagnetic (PM) phase and the regions of antiferromagnetic ordering (AF). Solid points are the T_N values obtained from magnetic susceptibility measurements. Broken lines are guides to the eyes.

this minimum can probably be associated with a bicritical point [3]. Detailed investigations in the range $0.15 < x < 0.60$ are in progress in order to address this specific question.

In conclusion, the tetragonal $\text{Fe}_x\text{Ni}_{1-x}\text{Ta}_2\text{O}_6$ system is a continuous solid solution, its volume obeying Vegard's law over the whole range of $\text{Fe} \leftrightarrow \text{Ni}$ substitution. Moreover, its magnetic behaviour is consistent with that of a layered system, as expected. However, particular features in the range $0.15 < x < 0.60$ suggest the existence of two regimes for the magnetic structure evolution with temperature in the ordered phase, indicating a possible coexistence of magnetic structures in this series.

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References

- [1] Jongh L J and Miedema A R 1974 *Adv. Phys.* **23** 1
- [2] Zawislak L I, da Cunha J B M, Vasquez A and dos Santos C A 1995 *Solid State Commun.* **94** 345
- [3] Kinast E J, Antonietti V, Schmitt D, Isnard O, da Cunha J B M, Gusmão M A and dos Santos C A 2003 *Phys. Rev. Lett.* **91** 19720
- [4] Eicher S M, Greedan J E and Lushington K J 1986 *J. Solid State Chem.* **62** 220
- [5] Kremer R K, Greedan J E, Gmelin E, Dai W, White M A, Eicher S M and Lushington K J 1988 *J. Phys. Coll.* **49** 1495
- [6] Reimers J N, Greedan J E, Stager C V and Kremer R 1989 *J. Solid State Chem.* **83** 20
- [7] Takano M and Takada T 1970 *Mater. Res. Bull.* **5** 449
- [8] Chung E M L, Lees M R, Balakrishnan G, Hague J P, Visser D, Paul D McK, McIntyre G J and Wilkinson C 2004 *J. Phys.: Condens. Matter* **16** 7837
- [9] Ehrenberg H, Wltschek G, Rodriguez-Carvajal J and Vogt T 1998 *J. Magn. Magn. Mater.* **184** 111
- [10] Rodriguez-Carvajal J 1993 *Physica B* **192** 55
- [11] Fisher M E 1962 *Phil. Mag.* **7** 1731