

Magnetic studies of ordered and disordered NbFeO₄ phases

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Abstract

A.c. susceptibility measurements of ordered and disordered NbFeO₄ of α -PbO₂ structure are reported. The order temperature of 50 K for the ordered phase of wolframite structure decreases when defects in the magnetic layers are introduced. Moreover, a net magnetic moment is observed below the order temperature for the less disordered NbFeO₄, associated with a positive Weiss temperature. The interpretation is given on the basis of different signs for intrachain (through an edge) and interchain (through an apex) Fe–Fe exchange interactions.

1. Introduction

NbFeO₄ is reported to have three structures, rutile (quadratic; space group, $P4_2/mnm$) above 1380 °C, α -PbO₂ type (orthorhombic; space group, $Pbcn$) between 1085 and 1380 °C, and wolframite (monoclinic; space group, $P2/c$) below 1085 °C [1, 2]. The rutile structure is characterized by strings of edge-sharing octahedra along the c axis, while the octahedra are staggered along the c axis in the other two arrangements. The wolframite form is an ordered and slightly distorted variant of the α -PbO₂ structure in which every zigzag chain contains either iron or niobium atoms (Fig. 1).

A low temperature route has recently been developed in order to obtain pure NbFeO₄ by avoiding the reduction of iron, although annealings are performed under air [3]. Owing to the thermal treatments, the samples present either the orthorhombic or the wolframite structures, *i.e.* different levels of order between niobium and iron. These different metallic arrangements have few effects on the diffraction patterns, since only the X-ray diffraction lines 100, 011 and 021 forbidden in the α -PbO₂ type structure occur in the wolframite arrangement. However, they affect the magnetic behaviour. We report here an a.c. magnetic study of this series in the temperature range 4.2–100 K.

2. Experimental details

NbFeO₄ is synthesized according to the coprecipitation method described previously [3]. The precipitate is submitted to different thermal treatments described in Table 1. The a.c. magnetic measurements were carried

out in the temperature range 4.2–100 K using a Lake Shore Cryotronics Inc. model 7000 AC instrument. The frequency was 333 Hz and the exciting field amplitude 1 Oe.

3. Results

Three representative samples presenting either the orthorhombic structure of α -PbO₂ type (samples A and B) or the wolframite structure (sample C) were examined. Cell parameters are in agreement with those given by Roth and Waring [1]. Magnetic susceptibility data are reported in the temperature range 4.2–100 K through a plot of χ^{-1} vs. T (Fig. 2). Above a temperature of about 60 K all these compounds exhibit a Curie–Weiss behaviour ($\chi = C/(T - \theta)$) with negative Weiss constants for samples A and C and a positive constant for sample B (see Table 1). These results indicate that, while in the former two compounds the predominant exchange interactions are antiferromagnetic, in the B compound these are ferromagnetic. On the contrary, the low temperature magnetic data reveal a sharp peak in χ at temperatures $T_c = 35$ K (sample B) and 50 K (sample C), which indicate the occurrence of magnetic order in these two compounds. Furthermore, in sample B, an out-of-phase signal is detected at T_c which indicates the presence of a net magnetic moment in the ordered state. In turn, for sample A, no magnetic order has been found down to $T = 4.2$ K, in agreement with previous studies [4]; only a rounded maximum is observed at about 15 K.

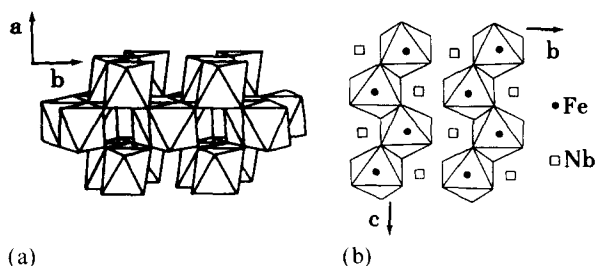


Fig. 1. (a) Schematic representation of the α -PbO₂ structure. (b) Arrangement between iron and niobium in NbFeO₄.

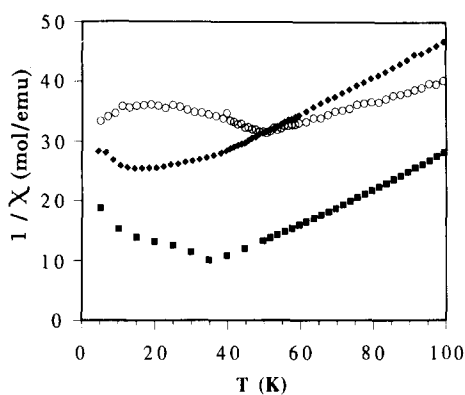


Fig. 2. Thermal variation in inverse susceptibility of the various NbFeO₄ samples A (◆), B (■) and C (○).

4. Discussion

The magnetic behaviour of this series has been shown to be dependent on the thermal treatment of the samples. In the following discussion, we will try to correlate these behaviours with the structural features of the samples, in particular with the presence of a cationic disorder due to the type of distribution of Nb⁵⁺ and Fe³⁺ ions on the metallic sites.

Let us first discuss the structural features of this series. The structure exhibits zigzag chains directed along the *c* axis. In these chains the metal niobium and iron occupy octahedral sites sharing edges (see

Fig. 1(a)). Furthermore, the octahedral sites share an apex with octahedra belonging to the four neighbouring chains. When NbFeO₄ is submitted to a thermal treatment at 1000 °C for a long time (sample C), cationic order is to be expected according to the wolframite structure. In this structure, every chain contains either iron or niobium atoms, and thus in the *a* + *b* direction the iron and niobium chains alternate (see Fig. 1(b)). From a magnetic point of view, this arrangement gives rise to magnetic layers of iron alternating with layers of niobium [5]. Then, the observed critical temperature at *T* = 50 K in compound C is in agreement with such a type of cationic distribution, and is to be associated with the occurrence of an antiferromagnetic three-dimensional ordering as a consequence of both strong ferromagnetic intralayer exchange interactions and weak antiferromagnetic interlayer interactions.

When the thermal treatment is performed at either lower or higher temperatures, disordered phases with the α -PbO₂ structure result (samples A and B respectively). In such cases, some of the niobium ions are expected to substitute iron ions, but depending on the amount of disorder different magnetic behaviours can be observed.

Thus, when the cationic disorder is sufficiently small the result would be to create defects in the two-dimensional magnetic lattice, favouring, at the same time, exchange interactions between neighbouring magnetic layers through the iron atoms located in the niobium layers. This seems to be the case for compound B. The decrease in the ordering temperature, from 50 K to 35 K, may be a consequence of the presence of defects in the magnetic layers. On the contrary, the presence of some Fe³⁺ ions between two magnetic layers would determine a parallel alignment of the four nearest-neighbour Fe³⁺ ions located in these layers. This could contribute to the explanation of the net magnetic moment observed in the ordered state. The presence of a magnetically ordered state below 40 K seems to rule out the effect of ferromagnetic impurities such as Fe₃O₄. Moreover, bearing in mind that the synthesis is carried

TABLE 1. Thermal treatments performed on the NbFeO₄ precipitate dried at 700 °C, crystallographic structures, susceptibility maxima and Weiss temperatures

Sample	Annealings		Quenching	Structure	<i>T_c</i> (K)	θ (± 2 K)
	Temperature (°C)	Time (h)				
A	700	3	No	α -PbO ₂ type		-50
B	1100	1/2	Yes	α -PbO ₂ type	35	40
C	1000	16	No	Wolframite	50	-90

out in air at low temperatures, the presence of Fe²⁺ is not reasonable. The dominant ferromagnetic exchange interactions could result from the different exchange pathways. Thus, if we assume different signs for intrachain (through an edge) and interchain (through an apex) Fe–Fe exchange interactions, the effect of a cationic disorder will be to decrease the number of intrachain interactions, increasing the number of interchain interactions.

When the incidence of cationic disorder increases, the number of diamagnetic defects in the magnetic layer will increase, preventing the occurrence of a long-range magnetic ordering. Thus, the lack of magnetic ordering in compound A can be correlated with the larger cationic disorder of this compound as compared with compound B.

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