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Modulated non-resonant microwave power absorption of $FeNbO_4$ powders

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We report on the effects of temperature and DC magnetic field on the modulated non-resonant microwave power absorption measurements at 8.8-9.8 GHz, in powder samples of iron niobate, $FeNbO_4$ (FN), in the monoclinic phase (wolframite-structure). Two techniques recently implemented are used: magnetically modulated microwave absorption spectroscopy (MAMMAS) and low field non-resonant microwave absorption spectroscopy (LFNORMAS), the measurements were performed in the 90-450 K temperature range. MAMMAS response suggests that the dominant magnetic exchange is antiferromagnetic at low temperature, with a paramagnetic behavior for high temperature. The profiles obtained by plotting the slope vs. temperature of the LFNORMAS line, while cooling or heating, are similar to those detected by the MAMMAS technique, giving evidence that both types of measurement are due to the same processes of absorption. We conclude that both measurements are a manifestation of the same response to electromagnetic absorption, in which the same physical processes take place.

Keywords: Microwave absorption; Electron paramagnetic resonance; Magnetic transitions.

Reportamos sobre los efectos de la temperatura y campo magnético DC en mediciones de la absorción de potencia de microondas no-resonante modulada a 8.8-9.8 GHz, en muestras en polvo de niobato férrico, $FeNbO_4$ (FN), en la fase monoclínica (estructura wolframita). Se usan dos técnicas recientemente implementadas: la espectroscopia de absorción de microondas magnéticamente modulada (MAMMAS-Magnetically Modulated Microwave Absorption Spectroscopy-) y la espectroscopia de absorción no-resonante de microondas a campo magnético bajo (LFNORMAS- Low Field Non-Resonant Microwave Absorption Spectroscopy); las mediciones se realizaron en el rango de temperatura de 90-450 K. La respuesta MAMMAS sugiere que el intercambio magnético dominante es antiferromagnético a baja temperatura, con una conducta paramagnética para alta temperatura. Los perfiles obtenidos del gráfico de la pendiente vs. temperatura de la línea LFNORMAS, mientras enfriamos o calentamos, son similares a los detectado por la técnica de MAMMAS; dando evidencia que ambos tipos de mediciones son debidos a los mismos procesos de absorción. Concluimos que estas mediciones son una manifestación de la misma respuesta a la absorción electromagnética, en la que los mismos procesos físicos tienen lugar.

Descriptores: Absorción de microondas; resonancia paramagnética electrónica; transiciones magnéticas.

PACS: 78.70.Gq; 76.30.-v; 75.30.Kz

1. Introduction

In the last years, a considerable attention has been given to some types of ABO_4 oxides, which can be applied as gas sensor, or in catalytic and photodetector technologies. Among these materials, iron niobate, $FeNbO_4$ (FN), has recently gained particular importance [1-4]. This material is known as the key precursor for the successful preparation of a single-phase $Pb(Fe_{0.5}Nb_{0.5})O_3$ [5,6].

FN exhibits three different crystalline phases: monoclinic, orthorhombic and triclinic [7]. The wolframite-type structure of monoclinic symmetry (P2/c) has Fe^{3+} and Nb^{5+} ions completely ordered on two different crystalline sites. The Fe^{3+} ions are of primary importance for the magnetic properties of this compound. An antiferromagnetic ordering at low temperature is mentioned for FN with wolframite-type structure [2,8].

Additionally, of the several classes of compounds, the mixed valency oxides in which the transition metal ions are at identical lattice sites with different valence states have shown interesting properties. In a recent work [1], the high electrical conductivity of the monoclinic phase FN is associated to the mixed valence nature (Fe^{2+}/Fe^{3+}) of Fe ions in the Fe-O-Fe framework, and it is confirmed by magnetic susceptibility measurements as a function of temperature.

Recently, we have implemented two experiments to measure the modulated non-resonant microwave power absorption, as a function of temperature or DC applied magnetic field [9], which have been denominated as magnetically modulated microwave absorption spectroscopy (MAMMAS) and low field non-resonant microwave absorption spectroscopy (LFNORMAS), respectively. These techniques have recently been used to detect the magnetic transition in various materials [9-13] and provide high sensitive detection of magnetic order. More important, these techniques can distinguish between different dissipative dynamics of microwave absorbing centers [9,11,13-17].

2. Sample preparation and experimental details

The samples were prepared by the conventional ceramic method. In this method, stoichiometric Fe_2O_3 (99 % purity) and Nb_2O_5 (99.99% purity) were mixed by ball milling for 8 h and the calcination was done in air at 1200°C for 2 h. The X-ray diffraction powder analysis showed a single-monoclinic phase [5].

The microwave investigations used a JEOL JES-RES 3X spectrometer operating at X-band (8.8-9.8 GHz) adequately modified for the above-described techniques. In these techniques, the microwave response with modulation of a magnetic field is measured. The modulated non-resonant microwave power absorption spectra can be recorded either as the temperature of the sample is scanned in a constant magnetic field (MAMMAS measurements) or as the magnetic field is scanned at constant temperature (LFNORMAS measurements).

The MAMMAS signal was registered with an applied magnetic field (H_{dc}) of 600 G, an amplitude of the modulation field (H_{mod}) of 4 G, and an incident microwave power of 7 mW. A slow temperature sweep (˜1 K/min) was used.

LFNORMAS measures microwave absorption as a function of H_{dc} in symmetric field-sweeps in the -1000 G $< H_{dc}$ $<$ +1000 G range. In this technique the sample is zero-field cooled or heated to the desired temperature, and then it is maintained at a fixed temperature with a maximum deviation of $\pm$ 1 K during the whole LFNORMAS measurement (˜4 min. of sweep).

MAMMAS and LFNORMAS spectra were recorded in the 90-290 K and 295-450 K temperature regions. The complete scheme and details concerning the experimental setup for the MAMMAS and LFNORMAS measurements can be found elsewhere [9].

3. Results and discussion

The section (I) of Fig. 1 shows the MAMMAS response in the 90-290 K temperature range. This signal increases monotonically as temperature decreases from 290 K, reaching a maximum value at T_p=140 K. In this temperature range, the magnetic susceptibility studies reveal that FN is paramagnetic [1], and the paramagnetic microwave absorption increases with the decrease in temperature. Our MAMMAS measurement is in agreement with the interpretation that the absorbing process is due to paramagnetic dipoles [15,17]. As the temperature is decreased further, T<T_p, the MAMMAS response decreases and another magnetic process sets-in which suggests an antiferromagnetic exchange [9,15,17]; in this region the quantity of absorbing centers diminishes due to the start of the antiparallel spin alignment.

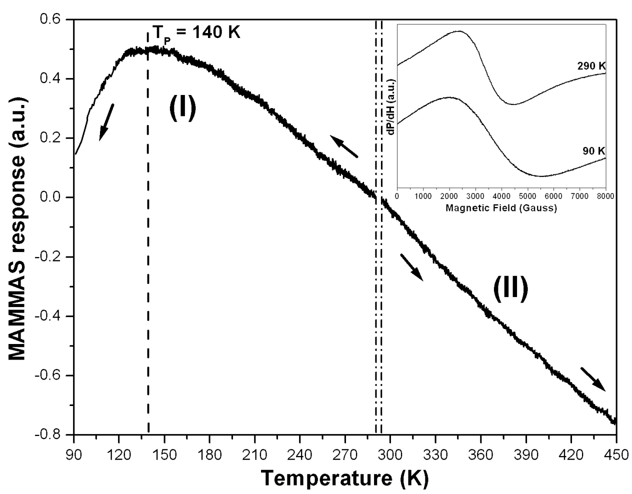

FIGURE 1. MAMMAS response (I) when decreasing the temperature, and (II) recorded in a heating run; no measurements were made between the central lines. The inset shows the EPR spectra of $FeNbO_4$ for 290 K and 90 K.

The MAMMAS profile in section (I) shows characteristics of a diffusive behavior over a wide temperature range. This characteristic can be ascribed to the presence of a small fraction of Fe^{2+} ions [1], which leads to fluctuations of the composition and produce the broaden of the MAMMAS response around its maximum.

The inset of Fig. 1 shows electron paramagnetic resonance (EPR) spectra at 290 K and 90 K. We observe that the EPR spectrum at 290 K shows a single broad Lorentzian line, attributable to Fe^{3+} ions. At 90 K, a contribution of Fe^{2+} ions in the spectrum is detected, which originates a broadened signal as compared with the spectrum at 290 K; *i.e.*, these Fe^{2+} ions give rise to a magnetic dipolar interaction with Fe^{3+} ions.

The section (II) of Fig. 1 shows the MAMMAS response recorded in the heating run for the 295-450 K temperature region. Starting from 295 K, as the temperature is increased, it shows a continuous decrease of the modulated microwave power absorption when increasing the temperature; *i.e.*, it is a continuation of the process due to paramagnetic dipoles to high temperatures [15,17].

On the other hand, Fig. 2(a) shows the LFNORMAS spectra (dP/dH vs. magnetic field, around zero field) recorded at selected temperatures for FN powders. We observe that the curves exhibit linear behavior with a positive slope and non-hysteretic traces. The positive slope implies that this modulated microwave absorption is a minimum around zero magnetic field and that it increases with applied magnetic field; in other words, this is a magnetic field-dependent absorption. The LFNORMAS line shows the absence of any irreversible microwave energy-absorption process. This behavior for FN, contrast strongly with that shown by high-Tc superconductors [9], ferrimagnetic [11] and ferromagnetic [16] materials.

The LFNORMAS line can be described by the experimental correlation:

$$dP/dH = S(T)H \tag{1}$$

where $S(T)$ depends only on temperature.

To find the nature of the MAMMAS response, we calculated the derivative of the LFNORMAS line, d^2P/dH^2, in the low magnetic field range (≤1000 G),

$$d^2P/dH^2 = S(T) \tag{2}$$

this value does not depend on the magnetic field.

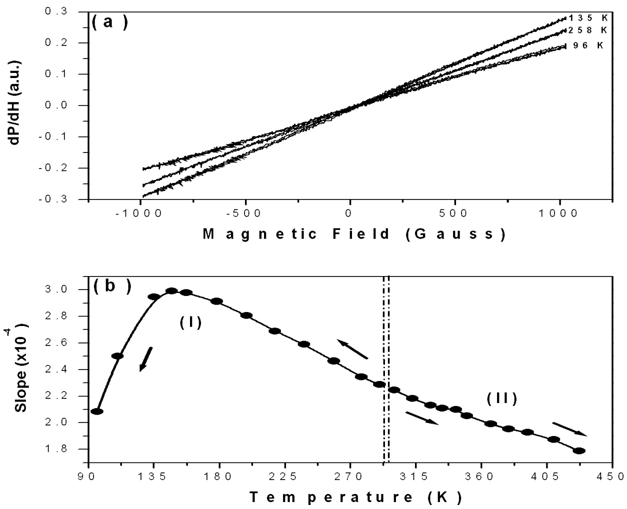

FIGURE 2. (a) LFNORMAS spectra for selected temperatures, with $H_{mod} = 0.63$ G and microwave power 1 mW. (b) The temperature dependence of the absorption line slope for temperature intervals of (I) 90-290 K and (II) 300-430 K; the solid lines are only guides for the eyes. No measurements were made between the central lines.

Figure 2(b) shows the behavior of the slope of the LFNORMAS line, $S(T)$, in the 90-290 K (section I) and 300-430 K (section II) temperature ranges. We observe that the profiles obtained are similar to the shapes of the corresponding MAMMAS responses. This clearly points to a common origin for both measurements, giving evidence that LFNORMAS spectra are generated by the same absorption processes above described, and which are due to the absorption dynamics of magnetic dipoles at all the temperatures. Also, as the MAMMAS responses are similar to the plot of the slope vs. temperature, we can establish an experimental correlation between the MAMMAS response and the second derivative microwave power absorption (d^2P/dH^2); *i.e.* for low magnetic field ($\leq$1000 G) the MAMMAS response is given as,

$$\text{MAMMAS response} \propto d^2P/dH^2 \tag{3}$$

which results similar to Eq. (2).

4. Conclusions

MAMMAS technique confirms that the dominant magnetic exchange is antiferromagnetic at low temperature (T<140 K), and has a paramagnetic behavior at high temperature. The LFNORMAS spectra showed straight lines with positive slope and non-hysteretic traces. The spectral changes for the plot of the slope vs. temperature, both during cooling and heating, showed features similar to MAMMAS profiles. We conclude that both experiments are therefore a manifestation of the sample response to electromagnetic excitation, in which the same fundamental physical processes take place; and the MAMMAS response has an experimental correlation with the derivative of the modulated microwave power absorption, d^2P/dH^2.

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