

Mössbauer Spectroscopic Characterization of Fe Occupation of Columns in the Nb₂₈O₇₀ Structure

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Abstract

In search of an experimental route to produce linear arrays of spins without the use of nanotechnological tools, we have doped Nb₂₈O₇₀ with small amounts of transition metal oxides (TM; in this case Fe₂O₃) or rare-earth oxides, and investigated the location of the alien metal (Fe in this case) in the structure. Previous AC magnetic susceptibility measurements at low temperatures have been consistent with the formation of arrays of TM magnetic moments along the widely spaced columns parallel to the crystallographic *b*-axis in the Nb₂₈O₇₀ structure. To obtain further details about the TM distribution, the previous investigation has been extended now to include a room-temperature Mössbauer spectroscopic analysis of the Fe-doped material. The data are consistent with the presence of low-spin Fe³⁺ ions in both octahedral and tetrahedral coordinations of oxygens, and confirm (as suggested in the previous work) that Fe also interchanges positions with Nb ions located at tetrahedrally coordinated sites in the columns of the structure.

Keywords

Mössbauer Spectroscopy, Niobium Oxides, Spin Arrays

1. Introduction

Two-dimensional magnetic structures are well known for their influence on several technologically important effects, like giant magnetoresistance [1], high-temperature superconductivity in the cuprates [2], and magnetocaloric effects [3], just to mention the most widely investigated.

Investigations on one-dimensional spin arrays have also recently been published [4] [5]. This subject has been of our interest for some time. In previous

work we undertook an investigation on how to build one-dimensional magnetic “lines”, by exploiting a suitable crystal structure that might serve as a framework for lines of spins added by alien ions [6] [7]. Materials like those employed as solid electrolytes contain wide channels along one of the crystallographic directions (Vanadium bronzes, for instance [8]) and the objective in that case is achieving large directional conductivity.

In our case we look for channels in which alien ions support localized magnetic moments. The compound $\text{Nb}_{28}\text{O}_{70}$ (also called $\text{H-Nb}_2\text{O}_5$, or simply the “niobate”, for short) indeed displays a suitable structure, since the unit cells are stacked along the b -axis in such way that columns with octahedrally coordinated vacant sites become available for alien magnetic ions and their spins. In our previous publications on this material we focussed on the low-temperature magnetic characterization of doped niobate, containing additions of either Fe or other TM and rare earth ions. AC magnetic susceptibility measurements under superimposed static fields up to 9T are fully consistent with magnetically-induced flipping of correlated spins aligned in one dimension (see **Figure 1**, from our previous work [7]). However, such technique is not sufficiently sensitive to disclose the details of the environment around the alien ions.

The present work has been devised to fill this gap. Mossbauer spectroscopy of ^{57}Fe is an adequate tool to answer the main questions left from the previous investigation, as discussed below.

2. Sample Details and Experimental Procedure

The left side of **Figure 2** shows the ac -plane view [6] [7] [8] of the structure of $\text{Nb}_{28}\text{O}_{70}$, displaying unit cells containing stacks of 4×3 and 5×3 NbO_6 octahedra (hatched and dotted squares, respectively). The right side of the Figure shows the view parallel to the crystallographic b -axis, normal to the ac -plane.

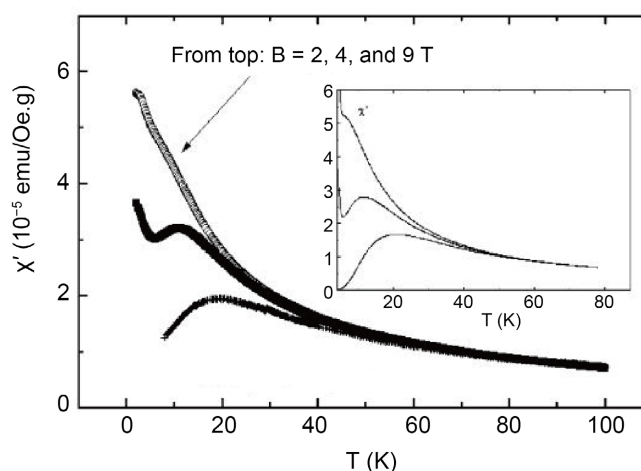


Figure 1. AC susceptibility measurements of Fe-doped $\text{Nb}_{28}\text{O}_{70}$ under static magnetic fields $B = 2, 4$ and 9 T. The picture on the right shows a theoretical simulation of the susceptibility assuming nearest neighbor Ising-like interactions between Fe spins in one dimension [7].

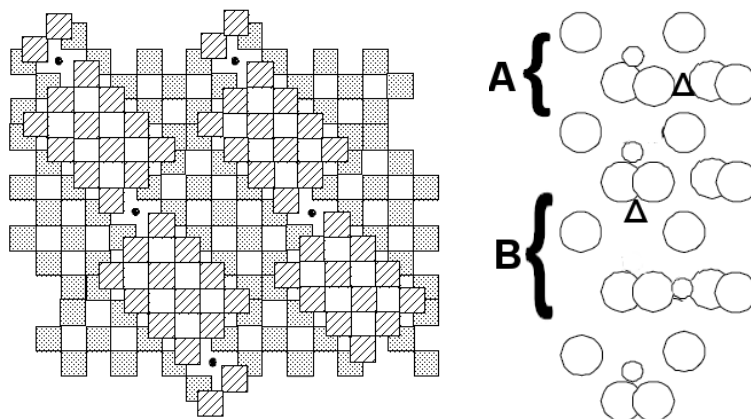


Figure 2. (Left side) Structure of $\text{Nb}_{28}\text{O}_{70}$ in a section normal to the b -axis, displaying unit cells of corner-sharing stacked 12 and 15 NbO_6 blocks (hatched and dotted squares, respectively). Columns contain also alternating Nb-occupied (bold dots), and empty tetrahedrally-coordinated sites. (Right side) The right side figure shows a column along the b axis. Big open circles represent oxygen, and small circles Nb in one of the tetrahedral sites per unit cell. Ideally all octahedral sites around the columns are empty, but when the material is doped with alien atoms (triangles) of size similar to Nb two kinds of altered structures are likely. Structure (A) is simply an alien interstitial atom occupying an octahedral site beside the column. In structure (B), alien and Nb atoms exchange positions, with the alien filling a tetrahedral site in the column and Nb a neighboring octahedral site. A and B should be experimentally different and detectable.

Each unit cell ideally contains a separate Nb atom in a NbO_4 tetrahedral environment, situated along a column with additional empty octahedral sites available around. Alien metals added to the structure might occupy such empty octahedral sites forming columns of localized spins (Structure A). The right side of **Figure 2** shows also the case in which the alien atom exchanges position with a Nb atom in a tetrahedral site (Structure B), a move that depends on the radii difference between Nb and Fe. Therefore, (at least) two different environments (A and B) for alien atoms are expected. The susceptibility measurements in our previous work were not sensitive to such changes of environment though, so that a different technique would be required. Such technique is Mossbauer spectroscopy, which is sensitive to the anions arrangement (and d-orbital electrons occupation) around Fe, added as alien atoms in the sample.

The sample preparation was as follows. Fe_2O_3 and $\text{Nb}_{28}\text{O}_{70}$ powders were mixed in a proportion nominally sufficient to introduce one atom of iron per unit cell of the niobate matrix. The mixture was treated at 1000°C for 24 hours in a box furnace. After the heat treatment a light-greenish powder was obtained. Since the originally white niobate powder is an insulator with a 3 eV gap, and the d-levels of Fe should fit just above the bottom of the gap, by absorption of violet and blue (of about 2.8 eV photons energy) from the incident visible light the reflected light would leave the powder with the observed greenish color.

X-ray diffraction of the powder using Cu- $K\alpha$ radiation displayed the spectrum of the niobate only, without any evidence of phases associated with Fe.

3. Experimental Results and Analysis

The Mossbauer spectra were collected at “room temperature” of about 298 K in the transmission geometry with a 50 mCi ^{57}Co source. The spectrometer was operated with a triangular velocity waveform in a constant acceleration mode. Isomer shifts (δ) are referred to natural alpha iron at ambient temperature.

The spectroscopic data for this sample are similar to the ones obtained by Paduani *et al.* [9] for Fe in soil samples containing the minerals kaolinite, montmorillonite, goethite, and hematite, and we follow their analysis and references. The minerals structures contain tetrahedrally and octahedrally coordinated sites similar to what is found in the niobate. **Figure 3** shows the Mossbauer spectrum of the sample at room temperature. The main features are a large doublet, and a weak superimposed sextet. The analysis was carried out with the MossWinn 4.0 software, which fits theoretical lorentzian curves to obtain the relevant parameters. The doublet can be fitted by two doublets attributable to Fe^{+3} . With reference to the curves in **Figure 3**, one gets the following parameters from the fits: First doublet from top (in green): Isomer Shift (δ) = 0.338 mm/s; Electric Quadrupolar Splitting (QS) = 0.645 mm/s, and Subspectral Area Fraction (A) = 26%. Second doublet (in light blue): δ = 0.328, QS = 1.056, and A = 58%. For the Sextet: δ = 0.364, QS = -0.179, A = 16%, and Hyperfine Magnetic Field B = 51.5 T, which are close to the parameters for Fe_2O_3 . This latter feature characterizes the presence of hyperfine magnetic interactions between Fe atoms.

The isomer shifts for the doublets are consistent with either Fe^{+2} or Fe^{+3} states; however, the values of QS are indeed characteristic of Fe^{+3} rather than Fe^{+2} [9] [10] [11]. The first doublet parameters correspond to Fe in octahedral sites (Structure A), and the Second doublet to Fe in tetrahedral sites (Structure B) [10] [11], which gives support to the configurations proposed in **Figure 2** of this paper. There is a larger proportion of Fe in tetrahedral columnar sites.

Hyperfine magnetic interactions (revealed by the presence of the weak sextet) indicate the formation of clusters of Fe ions, probably close to one nanometer size. This might indicate localized inhomogeneities in Fe distribution during sample preparation and the minor presence of unreacted Fe_2O_3 .

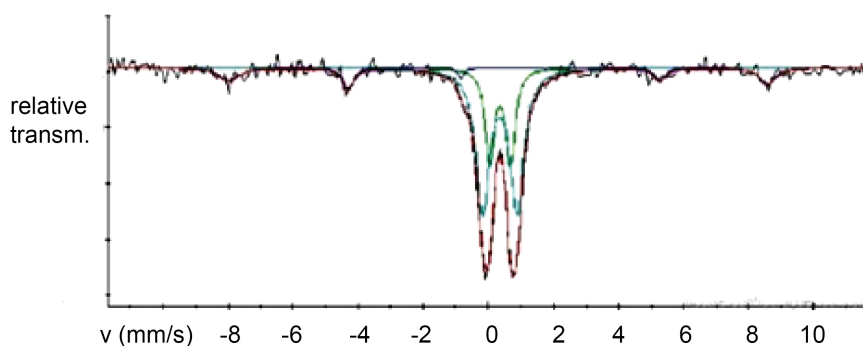


Figure 3. Room temperature Mossbauer spectra of Fe-doped $\text{Nb}_{28}\text{O}_{70}$, and model fits with two doublets (from top, green and light blue lines) and a sextet (dark blue).

4. Conclusion

This paper has presented a Mossbauer spectroscopic study of Fe-doped $\text{Nb}_{28}\text{O}_{70}$. This material was devised to provide an experimental “platform” for the magnetic investigation of linear (or columnar) arrays of spins. Previous measurements of magnetic AC susceptibility under static magnetic fields down to low temperatures gave results consistent with the formation of linear arrays of spins, but other details are not revealed by that technique. Mossbauer spectroscopy, however, is a sensitive tool to probe the actual coordination around the alien atoms. The Fe ions were identified as trivalent, and the study was capable of identifying two kinds of environment around Fe, namely those of octahedral (A) and those of tetrahedral (B) coordination, with a greater proportion of the tetrahedrally-coordinated type.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

References

- [1] Dagotto, E., Hotta, T. and Moreo, A. (2001) Colossal Magnetoresistant Materials: The Key Role of Phase Separation. *Physics Reports*, **344**, 1-153. [https://doi.org/10.1016/S0370-1573\(00\)00121-6](https://doi.org/10.1016/S0370-1573(00)00121-6)
- [2] Burns, G. (1992) High-Temperature Superconductivity: An Introduction. Academic Press, Boston.
- [3] Schilling, O.F. (2016) Green Function Calculations of Properties for the Magnetocaloric Layered Structures Based Upon FeMnAsP. *SPIN*, **6**, 1650010. <https://doi.org/10.1142/S2010324716500107>
- [4] Zhang, Y., Liu, L., Alvarez, G., Moreo, A. and Dagotto, E. (2021) Magnetic States of Quasi One-Dimensional Iron Chalcogenide Ba_2FeS_3 . *Physical Review B*, **104**, 125122. <https://doi.org/10.1103/PhysRevB.104.125122>
- [5] Gao, S., Lin, L.-F., Laurell, P., Chen, Q., Huang, Q., *et al.* (2023) Spinon Continuum in the Heisenberg Quantum Chain Compound $\text{Sr}_2\text{V}_3\text{O}_9$. arxiv: 2307.12093.
- [6] Schilling, O.F. and Ghivelder, L. (2000) Magnetic Properties of Iron-Doped Channels in $\text{H-Nb}_2\text{O}_5$. *Journal of Physics: Condensed Matter*, **12**, 2825-2832. <https://doi.org/10.1088/0953-8984/12/12/321>
- [7] Schilling, O.F. and Ghivelder, L. (2001) Magnetic Impurities in $\text{H-Nb}_2\text{O}_5$. *Journal of Physics: Condensed Matter*, **13**, 11017-11026. <https://doi.org/10.1088/0953-8984/13/48/326>
- [8] Bevan, D.J.M. and Hagemuller, P. (1973) Non-Stoichiometric Compounds. Tungsten Bronzes, Vanadium Bronzes and Related Compounds. Pergamon Press, Oxford.
- [9] Paduani, C., Samudio Pérez, C.A., Gobbi, D. and Ardisson, J.D. (2009) Mineralogical

Characterization of Iron-Rich Clayey Soils from the Middle Plateau in the Southern Region of Brazil. *Applied Clay Science*, **42**, 559-562.

<https://doi.org/10.1016/j.clay.2008.03.008>

- [10] Malden, P.J. and Meads, R.E. (1967) Substitution by Iron in Kaolinite. *Nature*, **215**, 844-846. <https://doi.org/10.1038/215844b0>

- [11] Petit, S. and Decarreau, A. (1990) Hydrothermal (200°C) Synthesis and Crystal Chemistry of Iron-Rich Kaolinites. *Clay Minerals*, **25**, 181-196.

<https://doi.org/10.1180/claymin.1990.025.2.04>