

Mössbauer and susceptibility studies of FeMoVO_7

G.F. Goya, R.C. Mercader

*Departamento de Física, Universidad Nacional de La Plata, CC 67,
1900 La Plata, Argentina*

M.B. Vassallo, I.L. Botto

*Química Inorgánica (QUINOR), Universidad Nacional de La Plata,
1900 La Plata, Argentina*

and

R. Sáez Puche

Química Inorgánica, Universidad Complutense de Madrid, 28040 Madrid, Spain

The oxidic phase FeMoVO_7 of the Fe_2O_3 – V_2O_5 – MoO_3 system has been synthesized. Susceptibility measurements from 4.2 K to room temperature display an antiferromagnetic behaviour with an effective magnetic moment of $5.80 \mu_B$. This value, and the measured Mössbauer isomer shift of 0.40 ± 0.02 mm/s, are characteristic of high-spin Fe(III). The low T_N value of 15 K suggests a weak interaction among the Fe–O polyhedra. The relative small $QS = 0.28 \pm 0.02$ mm/s found in this compound shows that the Fe–O polyhedra symmetry is close to octahedral and almost undistorted.

1. Introduction

It is known that the phases belonging to the three-component system Fe_2O_3 – V_2O_5 – MoO_3 exhibit interesting catalytic properties. In order to understand the microscopic mechanisms occurring during a catalytic process, it is important to know the structure and properties of the catalyst involved. No studies on the structural, hyperfine and magnetic properties on several of the phases that appear in this system are found in the literature. In the present paper we present an investigation of FeMoVO_7 by means of X-ray, Mössbauer and susceptibility measurements.

2. Experimental

The FeMoVO_7 phase was prepared from FeVO_4 and MoO_3 as precursors. The former was obtained by mixing stoichiometric amounts of α - Fe_2O_3 and V_2O_5 and

sintering at 650°C for 72 h. The latter was obtained from thermal decomposition of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in air at $\sim 300^\circ\text{C}$. Both products were then grounded and sintered at 550°C for 72 h. AC susceptibility measurements were performed between 4.2 and 320 K with an excitation frequency of 33.3 Hz at two different field strengths of 1 and 10 Oe. Mössbauer measurements were taken in transmission geometry with a ^{57}Co of 50 mCi in Rh matrix with a multiscaler of 512 channels with constant acceleration. A non-linear least-squares program with constraints was used to fit the spectra to Lorentzian line shapes. Isomer shifts are referred to $\alpha\text{-Fe}$ at 300 K.

3. Results

The X-ray characterization of the polycrystalline samples was in agreement with those previously reported for this compound [1,2], showing absence of other phases.

The inverse of the susceptibility data could be fitted with a Curie–Weiss law, displaying an antiferromagnetic behaviour with $T_N = 15$ K. The calculated $\mu_{\text{eff}} = 5.8 \mu_B$ is in agreement with a Fe(III) high-spin state for Fe.

The room temperature Mössbauer (fig. 1) spectrum could be fitted with one quadrupolar interaction, with hyperfine parameters $\Delta Q = 0.27 \pm 0.01$ mm/s; $\text{IS} = 0.40 \pm 0.01$ mm/s; $\Gamma = 0.29 \pm 0.01$ mm/s.

4. Discussion

The agreement of our X-ray diffraction peaks with those reported by Kurzawa [1] shows that our samples consisted of FeMoVO_7 .

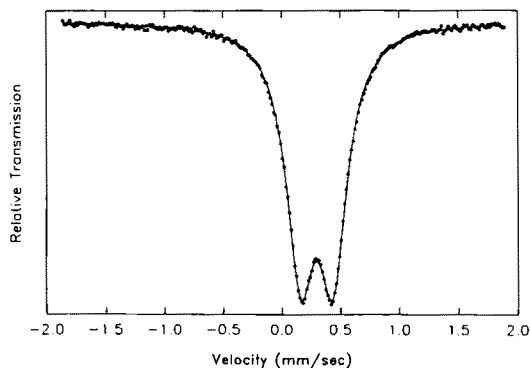


Fig. 1. Mössbauer spectrum of FeMoVO_7 at room temperature.

The susceptibility data indicate that Fe atoms order antiferromagnetically at $T_N = 15$ K. The sharp transition implies that the difference between T_N and the maximum of the susceptibility is small, denoting no evidence of a low-dimensional ordering [3]. The low value of T_N is presumably a manifestation of the weak magnetic interactions existing between the quasi isolated Fe ions bearing the permanent magnetic moments or of long superexchange paths. The present state of knowledge of the system frustrates the possibility of exploring in more detail the way in which the magnetic order is established in the system.

The Mössbauer quadrupole splitting parameter indicates an almost cubic or octahedral environment of the Fe ions. The $3+$ state of Fe is consistent with the overall valence of the ions in the compound. More experiments are in progress to determine whether phase transitions take place that can be observed by means of Mössbauer spectroscopy.

References

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