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Fe(IV) Disproportionation in AFeO₃ (A = Ca, Sr) Perovskite Lattices Studied by ¹¹⁹Sn Diamagnetic Probe Mössbauer Spectroscopy

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Abstract. Fe(IV) is an interesting unusual oxidation state of iron stabilized under oxygen pressure. In a perovskite lattice such an oxidation state disproportionates into Fe(III) and Fe(V). The study of this phenomenon is important for a better knowledge of instable valencies. Using ¹¹⁹Sn(IV) as diamagnetic probe in the perovskite lattice of AFeO₃ (A=Ca,Sr) the disproportionation $2\text{Fe(IV)} \rightleftharpoons \text{Fe(III)} + \text{Fe(V)}$ is discussed versus local steric and electrostatic interactions.

1. INTRODUCTION

The formal Fe(IV) oxidation state has been stabilized in different oxygen lattices derived from perovskite or K₂NiF₄ structures using oxygen pressures [1]. In the (AA')₂M_{0.50}Fe(IV)_{0.50}O₄ (A=La, A'=Ca,Sr,Ba, M=Li,Mg,Zn) the high spin state ($t_{2g}^3 d_{z^2}^1$) is mainly observed with a local Jahn-Teller distortion [2]. In the antiferromagnetic perovskite CaFeO₃, the disproportionation $2\text{Fe(IV)} \rightarrow \text{Fe(III)} + \text{Fe(V)}$ was detected at 280 K using ⁵⁷Fe Mössbauer spectroscopy [3]. This phenomenon is not observed in SrFeO₃ characterized by a metallic behaviour [4] confirmed recently by theoretical calculations [5]. The purpose of this study was to evaluate in both oxides the role of the local electronic phenomenon on the Fe(IV) disproportionation. ¹¹⁹Sn was used as diamagnetic Mössbauer probe, the magnetic fields observed by ¹¹⁹Sn being dependent on the electronic configurations of neighbouring ions.

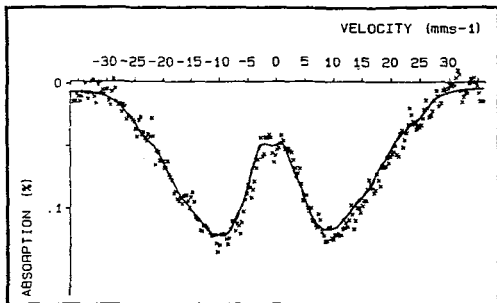
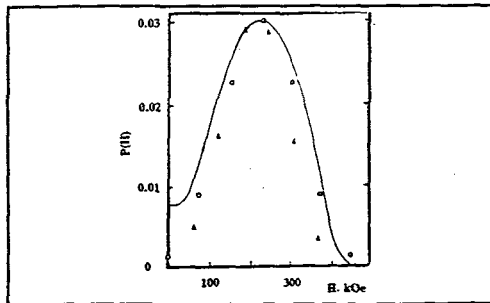
2. PREPARATION OF THE Sn-DOPED AFeO₃ PEROVSKITE (A=Ca,Sr)

These materials were prepared through a thermal treatment of a stoichiometric mixture of calcium or strontium nitrate (or carbonate) and iron hydroxide containing few amounts of Sn. In order to prevent strong modifications of the properties of the perovskite matrix, the doping level is small (0.5% at. Sn for CaFeO₃ and 1% at. Sn for SrFeO₃ enriched at 92% in ¹¹⁹Sn).

3. MÖSSBAUER INVESTIGATIONS

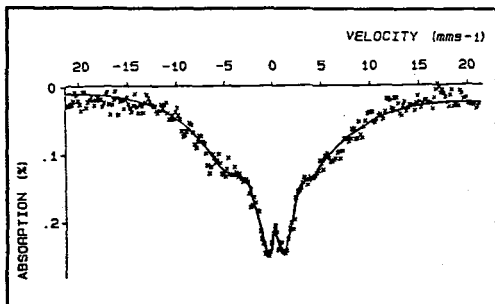
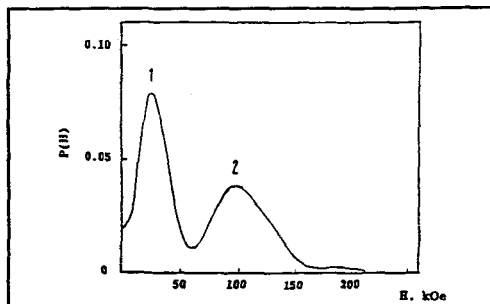
3.1 SrFeO₃ : 1% at. Sn

At 293K, two different absorptions are observed on the ⁵⁷Fe Mössbauer spectrum attributed respectively to Fe(IV) (88%) - $\delta/(\alpha\text{-Fe}) = 0.057 \text{ mm.s}^{-1}$, $\Gamma = 0.47 \text{ mm.s}^{-1}$ - and Fe(III) (12%) - $\delta/(\alpha\text{-Fe}) = 0.27 \text{ mm.s}^{-1}$, $\Gamma = 0.30 \text{ mm.s}^{-1}$. The deduced stoichiometry is SrFeO_{2.94}. At the same temperature, the ¹¹⁹Sn spectrum corresponds to a singlet ($\delta/\text{CaSnO}_3 = 0.11 \text{ mm.s}^{-1}$, $\Gamma = 0.88 \text{ mm.s}^{-1}$) characterizing Sn(IV) in oxides [6]. At 4.2 K, due to the antiferromagnetic ordering of SrFeO₃, the spin polarization of Sn(IV) induces a large diffuse absorption (Fig. 1) attributed to a large distribution of hyperfine fields. Such a distribution was analyzed through the Hesse and Rubartsch's model considering a constant value for δ and Δ equal 0 [7]. The resulting $p(H) = f(H)$ diagram (Fig. 2) is symmetrical versus the average \bar{H} value (220 kOe). This diagram was analyzed [9] in terms of a statistical distribution of Fe(III) ($t_{2g}^3 e_g^2$) [$\text{Sn}(\bar{H}) = 270 \text{ kOe}$] [8] and Fe(V) ($t_{2g}^3 e_g^0$) [$\text{Sn}(\bar{H}) = 30 \text{ kOe}$ for Cr(III)] [10].

Fig. 1: Mössbauer spectrum at 4.2K of SrFeO₃:1%SnFig. 2: ¹¹⁹Sn hyperfine field distribution P(H)=f(H) for SrFeO₃:1%Sn

3.2 CaFeO₃ : 0.5% at.Sn

The ¹¹⁹Sn Mössbauer spectrum is given on figure 3. Using the same analysis than that developed for SrFeO₃ : 1% at.Sn, a different hyperfine fields distribution is observed (Fig. 4) corresponding respectively to 6Fe(V) and 5Fe(V) + 1Fe(III) in the near Sn surrounding [9]. Such a behaviour was attributed to steric effects inducing preferentially small cations in the first Sn(IV) coordination.

Fig. 3: Mössbauer spectrum at 4.2K of CaFeO₃:0.5%SnFig. 4: ¹¹⁹Sn hyperfine field distribution P(H)=f(H) for CaFeO₃:0.5%Sn

4. CONCLUSIONS

The use of Sn diamagnetic probe induces, in the SrFeO₃ lattice, the Fe(IV) disproportionation in the Sn vicinity due to a local slowing of the electronic delocalization. The Fe(III), Fe(V) distribution seems closely dependent on steric effects ($a_{\text{CaFeO}_3} < a_{\text{SrFeO}_3}$).

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