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ANOMALOUS $^{57}\text{Fe}^{\text{m}}$ CHARGE STATES IN COMPLEXES OXIDESJ. Tejada, X. Obradors, J. Fontcuberta, J. Rodriguez⁺, R. Rodriguez⁺ and M. Oliva

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Abstract

Mössbauer measurements on non-stoichiometric spinels ($\text{CoRh}_2\text{O}_{4+x}$, $\text{CoMn}_2\text{O}_{4+x}$) and oxygen deficient oxides with perovskites and perovskite related structures (LnCoO_{3-x} with $\text{Ln}=\text{Eu, La, Dy, Y}$ and $\text{LaCoO}_3 : \text{Sr}^{2+}(\text{Ca}^{2+})$) doped with ^{57}Co have been done. It is argued that the charge states of the $^{57}\text{Fe}^{\text{m}}$ daughter depend on the nature and concentration of vacancies present in the lattice. In perovskites the existence of vacancies both random and of ordered distribution has been observed.

Introduction

The investigation by means of Mössbauer spectroscopy of non stoichiometry in single phases perovskites and spinels is of interest, because the existence of mixed valence states for the Mössbauer cations can be determined (1). The existence of cationic (spinel) or anionic (perovskites) vacancies, with variable concentration, is related to more distorted local structures (2). The present study is concerned with further investigation (3) about the consequences of electronic capture in oxides.

Experimental

Specimens were prepared from appropriate mixtures of highly pure nitrates (for spinels) or oxides (for perovskites) doped with $^{57}\text{CoCl}_2$. The mixture was fired for a long period of time at different oxygen pressures (to be denoted $P\text{O}_2$) at 1000°C (for spinels) or 1200°C (for perovskites). X-ray powder diagrams and Mössbauer spectra were obtained from each specimen.

Results

a) Spinel: In the spinels studied, Co is situated in the T-sites (Tetrahedral anion coordination) with divalent oxidation state. The decay of $^{57}\text{Co}^{2+}$ (T) produces $^{57}\text{Fe}^{2+}$ and $^{57}\text{Fe}^{3+}$ in a ratio depending on the $P\text{O}_2$ during the synthesis (Table I).

b) Perovskites: The octahedral positions are occupied by Co cations. It is assumed that the charge compensation of anion vacancies takes place according to $\text{Ln}^{3+} \text{Co}_{1-2x}^{3+} \text{Co}_{2x}^{2+} \text{O}_{3-x}$ ($\text{Ln} : \text{Eu, La, Dy, Y}$). The non-appearance of Fe^{4+} in the Mössbauer spectra in $\text{La}^{3+} \text{Co}^{3+} \text{O}_3$ doped with Sr^{2+} (Ca^{2+}) led us to suppose that the charge compensation of $\text{Sr}^{2+}(\text{Ca}^{2+})$ doping agrees with $\text{La}_{0.75}^{3+} \text{Sr}_{0.25}^{2+} \text{Co}_{2.875}^{3+}$. Mössbauer spectra have been fitted with single line characteristics of $^{57}\text{Fe}^{2+}$ and $^{57}\text{Fe}^{3+}$. Their ratio depending on the $P\text{O}_2$. The abnormal line's width agrees with the existence of intrinsic or non-intrinsic oxygen vacancies (Table I). For all perovskites synthesized at air pressure the X-ray diagrams have the desired single phase. Additional lines appear in the perovskites synthesized under low $P\text{O}_2$ or with doping of Sr^{2+} (2,4).

Source	$P\text{O}_2$ (atm)	Fe^{3+} (%)	$\Gamma(\text{Fe}^{3+})$ (mm/s)	Fe^{2+} (%)	$\Gamma(\text{Fe}^{2+})$ (mm/s)
La Co O ₃	air	100	0.47 ± 0.01		
La Co O ₃ : Ca	air	100	0.64 ± 0.02		
La Co O ₃ : Sr	air	100	0.71 ± 0.03		
Dy Co O ₃	air	100	0.64 ± 0.03		
	10^{-6}	10	0.62 ± 0.03	90	0.51 ± 0.03
Eu Co O ₃	air	87	0.82 ± 0.09	13	0.38 ± 0.1
	10^{-8}	24	0.47 ± 0.03	76	0.38 ± 0.06
Y Co O ₃	air	45	0.51 ± 0.05	55	0.64 ± 0.05
	10^{-4}	13	0.48 ± 0.06	87	0.67 ± 0.06
Co Rh ₂ O ₄	air	100	0.47 ± 0.01		
	10^{-5}	58	0.46 ± 0.02	42	0.48 ± 0.01
	10^{-8}	47	0.42 ± 0.02	53	0.46 ± 0.01
Co Mn ₂ O ₄	air	53	0.47 ± 0.01	47	0.45 ± 0.02
	10^{-4}	20	0.47 ± 0.02	80	0.43 ± 0.03
	$5 \cdot 10^{-9}$			100	0.40 ± 0.05

Table I. Mössbauer parameters of the sources. The absorbent employed was $\text{K}_4\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$

Discussion

In these oxides the non-appearance of $^{57}\text{Fe}^{m4+}$ in the Mössbauer spectra means that $^{57}\text{Co}^{2+}$ originates at the most $^{57}\text{Fe}^{m3+}$ or $^{57}\text{Fe}^{m2+}$ and $^{57}\text{Co}^{3+}$ always gives $^{57}\text{Fe}^{m3+}$.

In spinels, samples prepared at different PO_2 , differ only in the cationic vacancy concentration, hence we conclude that the presence of such vacancies makes possible the $^{57}\text{Co}^{2+} \rightarrow ^{57}\text{Fe}^{m3+}$ step with a probability depending on the vacancy concentration. The appearance of $^{57}\text{Fe}^{m2+}$ in several perovskites prepared in air shows in these substances a lack of stoichiometry which increases with decreasing PO_2 . The existence of anionic (cationic) vacancies in the crystal is accompanied by the appearance of donor (acceptor) levels in the gap (5). The electric character of these levels is shown in Table II.

	Full	Empty
Donor	Neutral	Positive
Acceptor	Negative	Neutral

Table II. Charge state of the levels in term of their electron occupation.

The Auger electron cascade, produced after the electronic capture has taken place in the ^{57}Co nucleus, gives rise to high charge states for the $^{57}\text{Fe}^m$ daughter. This creates a strong coulombic field which allows one electron, at the most, to remain in the conduction band (C.B.). This electron can go into the levels created by vacancies; being the probability of this capture proportional to the concentration of those levels (N_T) unoccupied by electrons (N_T^1). $N_T^1 = N_T(1-f_T)$ where f_T is the Fermi-Dirac distribution function. This capture process can be described by $N_T^1 + e^- \rightarrow N_T^0$ with a capture cross section σ_n (6) depending both on the electric character of the level and on its energy.

Two different processes could explain our results.

1) The donor (perovskites) and acceptor (spinel) levels are empty and they are acting as traps and recombination centers respectively. For donor levels the capture and posterior reemission to the C.B. takes a time less than 10^{-10} s turning the electron to the emitter atom in the Mössbauer time

scale. For acceptor levels, the time spent by the electron before returning to the C.B. is orders of magnitude greater than 10^{-8} s making possible the appearance of $^{57}\text{Fe}^{m3+}$ in the Mössbauer spectra.

2) The acceptor levels are empty and the donor are full. In this case only the cationic vacancies are able to capture the electron as in the precedent case.

We conclude that in spinels the amount of anomalous $^{57}\text{Fe}^{m3+}$ tells us about the deviations from stoichiometry. In perovskites the amount of $^{57}\text{Fe}^{m3+}$ will be the same as that of $^{57}\text{Co}^{3+}$ hence indicating the oxide composition. From the Mössbauer results concerning to the perovskites prepared under low PO_2 (see Table 1) and doped can be conclude the non existence of a big variation in the surrounding of the Co atoms increasing the vacancy concentration. For this reason the X-ray powder diagrams of those perovskites could be interpreted in terms of intermediate structures between perovskite and brownmillerite.

Fig.1. Mössbauer spectra of some perovskites.

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