

MÖSSBAUER STUDY OF THE $\text{La}_{2-x}\text{Sr}_x\text{Ni}_{0.99}\text{Fe}_{0.01}\text{O}_{4\pm\delta}$ SYSTEM.*

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A series of nonsuperconducting $\text{La}_{2-x}\text{Sr}_x\text{Ni}_{0.99}\text{Fe}_{0.01}\text{O}_{4\pm\delta}$ samples, with $x = 0, 0.15, 0.45, 0.65$ and 1.0 , were prepared by solid state reaction. In the undoped system (without Fe), the c lattice parameter goes through a maximum and the a lattice parameter through a minimum at $x \sim 0.5$ and the cell volume decreases steadily from $x = 0$ to $x = 1.2$. The resistivity also shows a maximum for $x \sim 0.32$ and then decreases until a minimum value is achieved around $x \sim 1.1$. Mössbauer spectra consist of three quadrupole doublets whose quadrupole splittings vary in a similar way as the c lattice parameter does with Sr content. The possibility of Jahn-Teller distortions associated with these variations is discussed.

The interest in transition-metal ternary compounds with tetragonal K_2NiF_4 structure, has augmented since the discovery of the high-temperature superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\delta}$ system, and has motivated several studies in related non superconducting systems. Among them, the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4\pm\delta}$ has been recently studied by Cava et al¹ and by Takeda et al². However, the study of local microscopic properties would help to complement their results. In this paper we present electric and structural results in a series of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4\pm\delta}$ samples and Mössbauer results on another similar series of ⁵⁷Fe doped $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4\pm\delta}$ samples.

A series of $\text{La}_{2-x}\text{Sr}_x\text{Ni}_{0.99}\text{Fe}_{0.01}\text{O}_{4\pm\delta}$ samples, with $x = 0, 0.15, 0.45, 0.65$ and 1.0 , were prepared from the component oxides by the usual solid state reaction. The obtained pellets were finally treated in a oxygen flow at 800 C for 12 hs. X-ray diffractograms show pure phases in all cases. In the Fe-undoped samples, the c lattice parameter goes through a maximum and the a lattice parameter through a minimum at $x \sim 0.5$ and the cell volume decreases steadily from $x = 0$ to $x = 1.2$. The resistivity also shows a maximum at $x \sim 0.32$ and then decreases until a minimum value is achieved at $x \sim 1.1$ (Tavizón³). Room temperature Mössbauer spectra (Fig. 1), obtained in transmission geometry with a constant-acceleration spectrometer, consist of three quadrupole doublets whose parameters vary with Sr concentration (Table 1). The velocity scan was $\sim \pm 12$ mm/s.

Notwithstanding the fact that all Ni sites are structurally equivalent in this system, the Mössbauer spec-

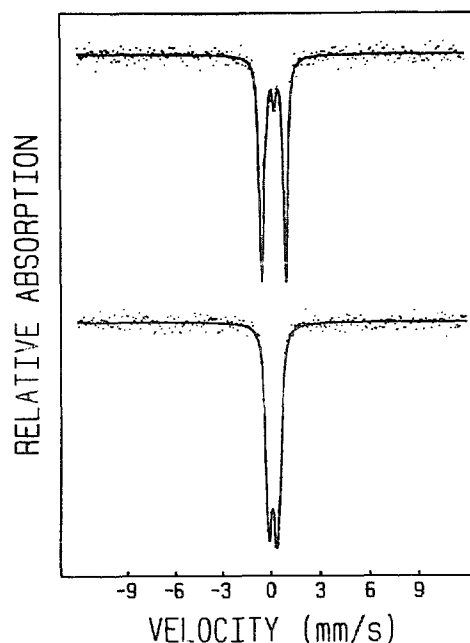


Figure 1. Room temperature Mössbauer spectra for $x = 0$ and $x = 1.0$

tra could only be well fitted, using a constrained least squares program, with three quadrupole doublets. It is interesting to note that the variations of the quadrupole splittings (ΔQ) of doublets A and B (Fig. 2) with Sr concentration, somewhat follow the variation of the c lattice parameter. This seems to be a clear indication

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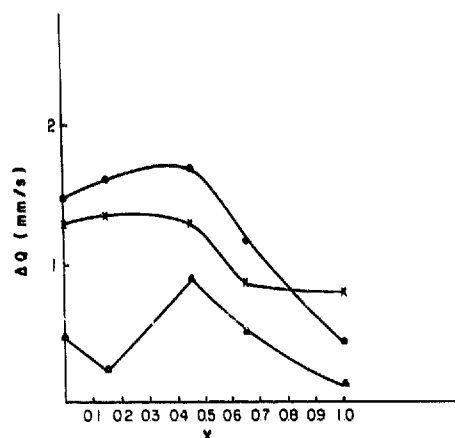


Figure 2. Variations of the ΔQ 's of the three quadrupole doublets.

that Fe atoms substitute the Ni atoms in the structure. As is well known, Sr doping changes the formal valence of the Ni-ions from 2+ to 3+ and a concomitant electronic rearrangement takes place. On the other hand, it has been suggested⁴ that, as x increases, the electronic configuration of trivalent nickel switches from $t_{2g}^6 d_{z^2}$ to $t_{2g}^6 d_{x^2-y^2}$. Depending on Sr concentration, both effects would then produce different electronic environments around the Fe ions, which would produce variations in the quadrupole splittings. One could also expect changes in the isomer shifts (IS), but these changes would depend on the ionic and spin states of the iron atoms. In low-Sr concentrations, our results indicate, via the ΔQ - IS combined values of doublets A and B, a characteristic Fe^{+3} -low spin state, in agreement with the known low-spin state of Ni in oxides. On the other hand, the values of doublet C parameters do not allow

us to make a definitive assignment to the ionic state of the Fe-ions responsible of this doublet. The lowering of the ΔQ 's as Sr concentration is increased, indicates a spin state change from low- to high-spin, which has to be associated with the expected weakening of the crystal field intensity, due to the valence changes of the different ions and to the suggested d-electron rearrangement. The noticeable changes in the ΔQ 's could be associated with a Jahn-Teller (J-T) distortion and the tendency of the structure to tetragonality, as Sr content is increased, is clearly seen from the quadrupole splittings decrement. However, even at $x = 1$ the ΔQ 's are small, but measurable, indicating that the possible J-T distortion is still present.

The temperature evolution of the Mössbauer parameters does not show any evidence of disproportion between distinguishable regular positions for Ni^{+2} ions, expected if a charge density wave had developed. Instead, a relaxed magnetic order is observed at low temperatures for $x > 0.15$. These results will be discussed elsewhere.

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Table 1.

x	IS_A	ΔQ_A	%A	IS_B	ΔQ_B	%B	IS_C	ΔQ_C	%C
0.00	0.32(5)	1.4(8)	63	0.3(4)	1.3(1)	23	0.1(5)	0.4(1)	14
0.15	0.33(2)	1.6(1)	52	0.32(4)	1.3(6)	41	0.3(4)	0.2(4)	7
0.45	0.32(8)	1.70(3)	35	0.31(6)	1.32(6)	43	0.31(4)	0.9(1)	22
0.65	0.28(8)	1.1(5)	27	0.28(1)	0.8(8)	43	0.27(6)	0.5(3)	30
1.00	0.27(2)	0.4(5)	47	0.27(8)	0.8(2)	34	0.29(9)	0.1(4)	19