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HIGH OXYGEN PRESSURES AND THE IMPROVEMENT OF THE M^{n+}—O CHEMICAL BOND THROUGH THE STABILIZATION OF THE HIGHEST OXIDATION STATES (n+)

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An evolution of local structure of Ni and chemical bonding, Ni(III)—O in perovskite lattice with strongly distorted structure is investigated with ^{57}Fe Mössbauer spectroscopy. The Mössbauer spectra for ^{57}Fe-doped $TlNiO_3$ were resolved to two quadrupole doublets with different isomer shifts, which underlines a partial charge disproportionation phenomenon: $2Fe^{3+} \rightarrow Fe^{3+\alpha} + Fe^{3-\alpha}$. This result supports the existence of two different crystallographic sites for Ni in the distorted perovskite lattice.

Keywords: Trivalent nickel; Perovskite; Mössbauer spectroscopy; Charge disproportionation

INTRODUCTION

The development of high oxygen pressure has led to the stabilization of the high oxidation states of transition metals in oxide lattices where the strong covalency of M^{n+}—O bond leads to specific physical properties for the corresponding oxides. In the series of $ANiO_3$ perovskite (A = rare earth), which were first prepared in 1970 [1], the insulator → metal (MI) transition occurs as increasing temperature [2] and the transition temperatures (T_{MI}) are strongly related with structural distortion. In particular, for small rare earth nickelates (A = Ho → Lu) the partial charge disproportionation of Ni(III) was proposed as a drive for MI transition [3–4].

Recently we prepared a new Ni(III) perovskite, $TlNiO_3$ [5]. Through a comparative study with rare earth nickelates, it has been revealed that the structural distortion and magnetism for $TlNiO_3$ are significantly modified by strong Tl-O bonds. In this work, an attempt was made to investigate the electronic structure of Ni(III) in $TlNiO_3$. We performed ^{57}Fe Mössbauer spectroscopy measurements for ^{57}Fe-doped $TlNiO_3$ to examine whether the disproportionation of Ni(III) is found as in $ANiO_3$ (A = Ho → Lu) [3–4].

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EXPERIMENTAL

^{57}Fe-doped $TlNiO_3$ was prepared from Tl_2O_3, $Ni(OH)_2$:^{57}Fe (2%) and $KClO_3$ at 700 °C under 7 GPa [5]. The product was identified with powder X-ray diffraction (Philips PW 1050 diffractometer using graphite-monochromated CuK_α radiation). The magnetic susceptibility was measured with SQUID (Quantum Design MPMS-5S) in temperature range from 5 K–300 K. The ^{57}Fe Mössbauer spectra were recorded at 300 K and 100 K using a conventional constant acceleration Mössbauer spectrometer. The radiation source ^{57}Co(Rh) was kept at room temperature. All isomer shifts refer to the α-Fe absorber at 300 K.

RESULTS AND DISCUSSION

The participation of ^{57}Fe to the $ANiO_3$ lattice was evaluated by magnetic measurement, showing that T_N values and magnetic susceptibilities χ_M were slightly modified by iron doping ($T_N = 94$ K for $TlNi_{0.98}Fe_{0.02}O_3$, $T_N = 104$ K for $TlNiO_3$). The Mössbauer spectra of $TlNi_{0.98}{}^{57}Fe_{0.02}O_3$ can be described as a superposition of two quadrupole doublets (Fig. 1)

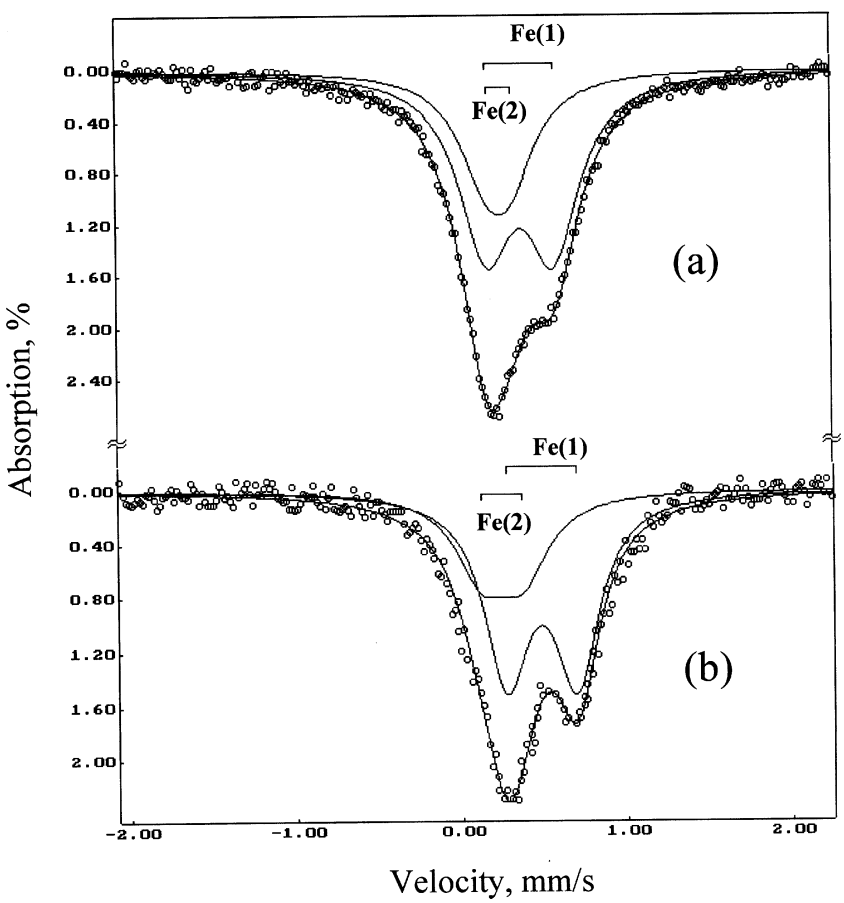

FIGURE 1 Mössbauer spectra for $TlNi_{0.98}Fe_{0.02}O_3$ at (a) 300 K and (b) 100 K.

TABLE I Mössbauer Parameters for $TlNi_{0.98}Fe_{0.02}O_3$.

T(K)	*Fe site*	$\delta\, mm/s$	$\Delta\, mm/s$	$\Gamma\, mm/s$	*A%*
300	Fe(1)	0.36(1)	0.40(1)	0.31(1)	67(2)
	Fe(2)	0.23(1)	0.18(1)	0.30(1)	33(2)
100	Fe(1)	0.49(1)	0.44(2)	0.32(1)	67(3)
	Fe(2)	0.24(1)	0.34(1)	0.31(1)	33(3)

which underlines that Fe is simultaneously stabilized in two non-equivalent crystallographic positions. These Fe sites are characterized by different values for the isomer shift δ and the quadrupole splitting Δ(Tab. I). The isomer shift values for these two kinds of iron ions, Fe(I) and Fe(II), reflect two different degrees of covalency in Fe—O bonds, suggesting a partial disproportionation phenomenon: $2Fe^{3+} \rightarrow Fe^{3+\alpha} + Fe^{3-\alpha}$. This result is consistent with the recent neutron diffraction analysis of small rare-earth nickelates (Ho-Lu and Y) which indicates the reduction in lattice symmetry from orthorhombic (*Pbnm*) to monoclinic ($P2_1/n$) driven by two independent crystallographic positions : Ni(1) and Ni(2)O_6 [3–4].

Considering that an increase of the formal oxidation state of Fe^{n+} cations leads to isomer shift reduction, the δ_2 value would correspond to nickel site characterized by higher oxidation state [$Ni^{(3+\alpha)+}$] and the δ_1 value to nickel site with lower oxidation state [$Ni^{(3-\alpha)+}$]. The quadrupole splittings for the two types of irons, $\Delta_2(Fe^{(3+\alpha)+}) < \Delta_1(Fe^{(3-\alpha)+})$ are also in agreement with the neutron diffraction results which revealed that $Ni^{(3-\alpha)+}O_6$ octahedra might be more distorted than $Ni^{(3+\alpha)+}O_6$ ones [4]. As temperature decreases from 300 K to 100 K, the difference between δ_1 and δ_2 values increases ($\Delta\delta_{300\,K} = 0.13$ mm/s and $\Delta\delta_{100\,K} = 0.25$ mm/s) and the quadrupole splittings (Δ_1 and Δ_2) also increases. Such structural variation of $TlNi_{0.98}\,{}^{57}Fe_{0.02}O_3$ will be compared with those of rare earth nickelates [6]. The occurrence of the disproportionation phenomenon has been recently confirmed through a neutron diffraction study [7].

Conclusively, the presented Mössbauer results support the existence of two different crystallographic sites of Ni in strongly distorted perovskite lattice proposed by recent neutron diffraction studies.

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