

# Lattice-dynamics of the intermediate oxide of tin

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The lattice-dynamical properties of the intermediate oxide of tin (IO) have been investigated over the temperature range 80–295 K. The logarithm of the recoil-free fraction varied linearly with temperature. However, a Debye model does not give a good account of this dependence. By comparison with the other oxides of the Sn–O system, the recoil-free fraction for tin atoms with 2+ and 4+ oxidation states of the IO were estimated. At room temperature, they are 0.46<sub>3</sub> and 0.32<sub>3</sub> for 4+ and 2+ states respectively.

## 1. Introduction

It is well known that at increasing temperatures the SnO becomes thermodynamically unstable and undergoes a disproportionation reaction. Depending on the temperature, SnO<sub>2</sub>, β-Sn and an IO displaying 2+ and 4+ oxidation states are formed irrespectively of the atmosphere: air, Ar or vacuum. The composition and mechanisms of formation of the IO is still an open question [1].

An insight into the composition, structure and mechanisms of formation of the IO is possible using MS. For these purposes it is necessary to determine the recoil-free fractions of each oxidation state, and characterize the hyperfine interactions of tin atoms in the IO. In previous studies [2] this was successfully done for the 2+ oxidation state but the impossibility of separating at room temperature (RT) the interactions of SnO<sub>2</sub> and those of Sn<sup>4+</sup> in the IO was also evident.

In this paper we have determined the *f* factors of tin atoms at sites with the two (hereafter 2+ and 4+) IO oxidation states and give account of some dynamical properties of the crystal lattice.

## 2. Experimental

MS measurements were performed on the products of disproportionation of SnO heated in Ar (10 Torr) at 450°C, namely SnO<sub>2</sub>, IO and β-Sn. A variable temperature cryostat operating in the range 80–295 K (±0.1 K) was used for the Mössbauer spectra acquisition. The spectra were recorded in a conventional con-

stant acceleration apparatus with a transmission geometry. The data were fitted with a non-linear least-squares program with constraints to Lorentzian line shapes.

### 3. Results and discussion

A simple way to study lattice-dynamical properties of solids is to normalize the absorption area  $A(T)$  to a particular temperature  $T_0$ , and plot  $\ln A(T)/A(T_0)$  versus  $T$ . If the absorber is thin the temperature behaviour of  $A(T)$  is the same as that of the absorber recoilless fraction  $f_a(T)$ . Its knowledge permits the evaluation of characteristic temperatures which are functions of the frequency moments of the phonon frequency spectrum.

The relevant parameters extracted from the temperature-dependent Mössbauer experiments are summarized in table 1. The spectra taken at extreme temperatures are displayed in fig. 1. The spectra were fitted with two quadrupole doublets and a single line. The quadrupole doublets correspond to the 4+ oxidation state (unresolved doublet centered at about  $0.0 \text{ mm s}^{-1}$ ) and to the 2+ oxidation state (doublet centered at about  $2.5 \text{ mm s}^{-1}$ ). The single line stems from  $\beta$ -Sn.

The linewidth of the 2+ and 4+ oxidation states subspectra were constant in the temperature range observed. The effective thickness was estimated to  $t_a \approx 1$  which justifies the thin absorber approximation used. The linewidth of the subspectrum corresponding to the 2+ oxidation state of IO is narrower than the values previously reported at RT [3,4]. The evolution of the hyperfine parameters indicates that there is a unique environment for  $\text{Sn}^{2+}$  in the IO. The absence of a distribution of hyperfine fields at the 2+ sites indicates that the IO is a well defined phase, with a narrow composition range. With respect to the line corresponding to the 4+ oxidation state in fig. 1, there are no noticeable differences between

Table 1  
Summary of  $^{119}\text{Sn}$  Mössbauer data for tin oxides.

	$\text{SnO}_2$	$\text{SnO}$	$\text{Sn}^{4+}$	$\text{Sn}^{2+}$
$f$ (77 K)	0.59 <sub>4</sub> <sup>a</sup>	0.55 <sub>3</sub> <sup>b</sup>	0.59 <sup>d</sup>	0.55 <sup>d</sup>
$f$ (300 K)	0.47 <sub>3</sub> <sup>a</sup>		0.46 <sub>3</sub>	0.32 <sub>3</sub>
$d \ln[A(T)/A(80)]/dT$ ( $10^{-3} \text{ K}^{-1}$ )		3.405 <sup>c</sup>	1.139	2.345
$d\delta_{\text{IS}}/dT$ ( $10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}$ )		2.465 <sup>c</sup>	2.053	2.321
mean $\Gamma_{\text{exp}}$ (80–295 K) (mm/s)			0.93 <sub>1</sub>	0.78 <sub>1</sub>
$\Theta_{\text{M}}$ <sup>a</sup> (K)		229 <sub>3</sub>	403 <sub>6</sub>	281 <sub>5</sub>

<sup>a</sup> Taken from ref. [8].

<sup>b</sup> Taken from ref. [9].

<sup>c</sup> Taken from ref. [7].

<sup>d</sup> Values proposed from comparison with those of SnO and SnO<sub>2</sub>.

<sup>e</sup> Mössbauer lattice temperature calculated from  $A(T)$  dependence and using the atomic mass of  $^{119}\text{Sn}$ .

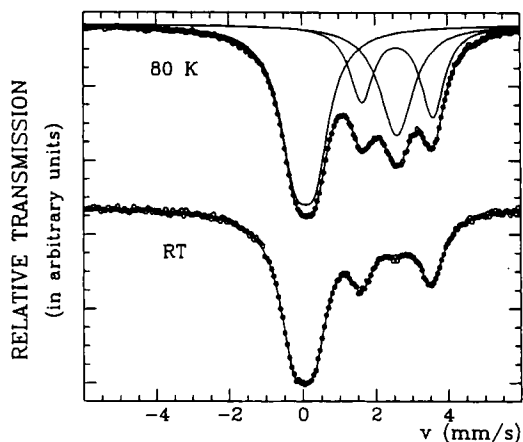


Fig. 1. Mössbauer spectra taken at different temperatures.

the interactions of  $\text{SnO}_2$  and those of IO. This means that the nearest neighborhood oxygen coordination for  $\text{Sn}^{4+}$  in IO must be very similar to that of  $\text{SnO}_2$ , as confirmed by EXAFS [5].

The IS and quadrupole splitting ( $\Delta$ ) varied linearly with temperature. This dependence and the fact that  $\Delta^{2+}$  was weakly dependent, with a slope of  $\sim 1.35 \cdot 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}$ , are evidences that a phase change did not take place in the IO over this range.

Fig. 2 displays the temperature dependence of the  $f$  factors for the 4+ and 2+

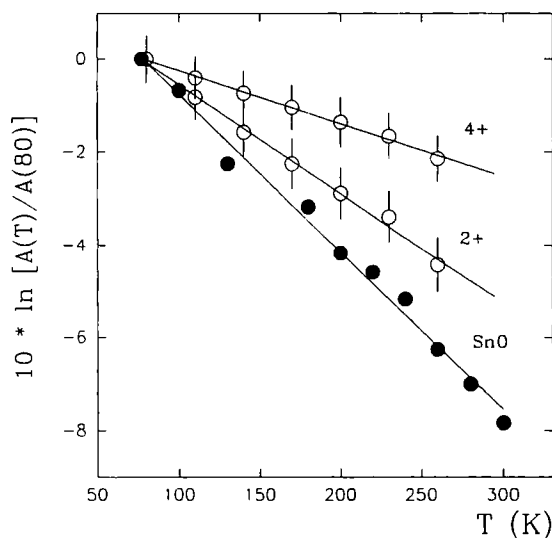


Fig. 2. Temperature dependence of the normalized areas of the oxidation states of the IO. That of SnO was taken from ref. [7].

states. The data are well fitted by linear relationships. This seems to indicate that anharmonic effects are not present in the investigated temperature range. However, the rates of variation of  $f_a$  are lower than predicted by a Debye model, a fact also known for  $\text{SnO}_2$ . In this system the existence of a low-temperature anharmonicity has to be discarded because of the high  $f$  value at low temperatures ( $f(4.2\text{ K}) = 0.89$ ). This behaviour was explained qualitatively by Kagan and Maslov [6], who concluded that the optical branch contributes significantly to the phonon spectrum and that it is difficult to attribute the smaller slope to any mechanism other than to the activation of optical modes in this system formed by very unlike atoms. This seems likely to be also the reason for the temperature dependence observed for the IO.

It is worth mentioning that the  $f_a(T)$  versus  $T$  plot does not supply absolute  $f$  values, a fact not taken into account by Herber [7] in his study of  $\text{SnO}$ , where he gave absolute  $f$  factors  $f_a(80\text{ K}) = 0.78$  and  $f_a(295\text{ K}) = 0.37$ . These were values obtained relative to those at 0 K. Table 1 shows the  $f$  factors for  $\text{SnO}$  and  $\text{SnO}_2$  obtained from a survey in the literature. In spite of their different crystalline structures and characteristic temperatures, the respective  $f$  at 80 K are nearly equal. Assuming the  $f$  factor of  $\text{Sn}^{4+}$  (IO) equal to that of  $\text{SnO}_2$  and of  $\text{Sn}^{2+}$  (IO) equal to that of  $\text{SnO}$  at 80 K we could get at RT the values shown in table 1 for the IO.

#### 4. Conclusions

Some dynamical properties of the IO were investigated by Mössbauer spectroscopy. We have determined the  $f$  factors of the two IO oxidation states and the dependence of  $f(T)$ . This varied more slowly than that predicted by a Debye model. The activation of optical branches is likely to be the only mechanism capable of giving account of the  $f(T)$  behaviour of both  $\text{SnO}_2$  and IO.

For the IO no phase transitions were detected in the range 80 K–RT.

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