EFFECT OF STOICHIOMETRY ON THE MOSSBAUER EFFECT IN SnO_2

V. S. ZYKOV, E. V. PETROVICH, and Yu. P. SMIRNOV

A. F. Ioffe Physico-technical Institute, Academy of Sciences, U.S.S.R.

It is suggested that one of the reasons of the broadening of Mossbauer absorption lines observed in SnO_2 is the violation of the exact stoichiometric composition in samples prepared in the usual manner. The resonance absorption spectra of two SnO_2 samples of different stoichiometric composition are compared. It is demonstrated that violation of stoichiometry results in broadening of the absorption lines.

IT is known that the Mossbauer line broadens when a source and an absorber of SnO_2 are used [1-5]. It must be borne in mind that SnO_2 is an n-type semiconductor, with a tin atom content in excess of stoichiometric composition [6,7], and this violation of the stoichiometric ratio can influence the Mossbauer effect [8,9]. We can therefore assume that violation of the stoichiometric ratio in SnO_2 is at least one of the causes of the broadening of the Mossbauer line.

The stoichiometric ratio of tin dioxide can be varied by using the method given in [10,11]. If the SnO_2 sample is annealed for a sufficiently long time in vacuum, thermodynamic equilibrium is established between the oxygen content in the lattice and the partial pressure of the oxygen in the surrounding space. During the establishment of such an equilibrium, some of the oxygen atoms are removed from the lattice. Upon subsequent cooling of the sample, the excess concentration of the tin atoms is 'quenched'. The sample obtained is less stoichiometric. To the contrary, by heat treating a SnO_2 sample at high pressures of oxygen, the sample can be made more stoichiometric.

We have compared the resonance-absorption spectra of two samples of SnO_2 with different stoichiometric compositions.

One of the absorbers was made of tin dioxide, obtained by dissolving metallic tin in HNO_3 with subsequent evaporation of the solution and roasting the residue at $T \approx 1200°C$ in air for thirty hours. Part of the tin dioxide obtained in this manner was roasted in vacuum ($P \approx 10^{-2}$ mm Hg) at $T \approx 600°C$ for twenty four hours with subsequent cooling for one hour. A second absorber was made from this tin dioxide. The absorber thicknesses were the same (7 mg/cm^2).
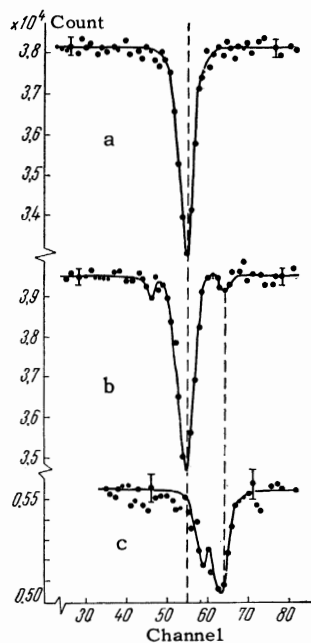
Series No.	Γ	Γ^*
1	4.0	4.8
2	3.8	5.0
3	3.9	4.6
4	3.5	5.1
5	4.1	4.5
	$\Gamma_{av} = 3.9 \pm 0.3$	$\Gamma^*_{av} = 4.8 \pm 0.3$

The measurements were made at room temperature using a set up with an electromagnetic vibrator moving in simple harmonic motion. The resonant-absorption spectrum was registered with a multichannel analyzer. The experimental values of the line widths for absorbers made of standard tin dioxide and tin dioxide roasted in vacuum (Γ and Γ^*) are listed in the table. The measurement unit was one analyzer channel.

The form of the resonance absorption spectra for different absorbers is shown in the figure; the source was SnO_2. It is seen from these data that the Mossbauer line is broader for the sample roasted in vacuum than for the standard sample. Apparently, if the tin dioxide is roasted at high oxygen pressures, the Mossbauer line will be narrower.

The resonance-absorption spectrum for the vacuum roasted sample displays a structure. From a comparison of Figs. b and c we see that one of the absorption peaks on the curve b can be ascribed to SnO. It is possible that when the stoichiometric ratio is violated in tin dioxide, SnO grains are produced and cause the same chemical shift as ordinary tin monoxide. The nature of the second absorption peak is unknown to us.

The results indicate that one must take into consideration the possible influence of the stoichiometric composition of the substance on the Moss-

Form of resonance-absorption spectra for different absorbers: a — standard tin dioxide; b — tin dioxide roasted in vacuum; c — SnO.

bauer effect. From this point of view, the compounds Fe_2O_3, ZnO, WO_3, and SnO are of interest[10-12].

In conclusion, the authors consider it their pleasant duty to express sincere gratitude to D. M. Kaminker for interest in the work, to O. I. Sumbaev for help and valuable remarks, and to A. I. Egorov for help in preparing the samples.

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