

Some Mössbauer and X-Ray Investigations of the α_2 -Sn Formation during the Reduction of SnCl_2 Water Solutions

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Tin structures with very high values of the isomer shifts ($\delta = +4.3 \pm 0.1$ mm/sec and $\delta = +7 \pm 0.4$ mm/sec) of the Mössbauer lines, have been observed not only in thin tin films but also in bulk samples. The samples have been obtained by the reduction of SnCl_2 water solutions with Mg, carried out either in the presence of ferromagnetic impurities (Fe, Co, Ni) or in an external magnetic field. The parallel X-ray studies are in accordance with the RHEED observations of thin tin films. The temperature dependence of the Mössbauer effect on samples rich in α_2 -Sn has been studied and microcalorimetric measurements on samples containing β_1 -Sn and α_2 -Sn have also been performed.

Introduction

Recently, the existence of a Mössbauer line with isomer shift $\delta = +4.4 \pm 0.2$ mm/sec (here and later referred to the line of $\text{Ba}^{119}\text{SnO}_3$) has been reported by several authors (1-5). The value of its isomer shift is at the upper limit of the known isomer shifts of tin and tin compounds. Different tin compounds have been proposed to explain the existence of this peak (2-5), but these explanations are ambiguous since the existence of the proposed compounds has not been confirmed by other methods. Depth Selective Mössbauer Spectroscopy (DSMS) investigations of the thin tin films, which were prepared by thermal evaporation in vacuum 5×10^{-6} Torr, have shown that tin can exhibit an isomer shift $\delta = +4.4 \pm 0.2$ mm/sec (6). Parallel RHEED studies of such films have shown that this isomer

shift is attained if the tin has a diamond cubic lattice exactly identical to that of silicon with lattice parameter $a = 5.42$ Å. The investigations in (6) have also shown the existence of several other peaks with isomer shifts higher than $\delta = +4.4$ mm/sec. These peaks were observed in heated thin tin films containing initially the diamond cubic tin with $a = 5.42$ Å. A possible explanation for the existence of these unusual peaks is proposed by Bonchev and others in Ref. (7), where participation of d electrons in the chemical bonds of tin structures with $\delta \geq +4.4$ mm/sec is proposed. The electron configuration of tin with the lattice of silicon, designated in (7) as α_2 -Sn, is $\text{Kr}4d^95s^15p^4$. The known crystal structures of tin, α -Sn with $\delta = +2.1$ mm/sec, β -Sn with $\delta = +2.6$ mm/sec, are designated as α_1 -Sn and β_1 -Sn, respectively. These designations follow the general idea in (7) that

tin can possess several α_i forms, each having a corresponding β_j form (here i and j are 1, 2, 3, ...).

So far, the unusual tin structures with $\delta \geq +4.4$ mm/sec have been observed in thin films (6, 8, 9). There are some RHEED and X-ray results showing that they can also exist in the initial stages of massive tin crystallization (9). The discovery of the new allotropic tin forms is rather unexpected and requires a detailed study. As has already been pointed out, the new tin structures have been observed in thin surface layers only. It is known that the physicochemical properties of the thin films differ greatly from those of the bulk sample. Hence, our main purpose has been to check, whether the new structures exist in the same form as tin.

Experimental

Preparation of samples. The examined tin samples were prepared by electrochemical reduction of a 20% water solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with Mg. The reaction was carried out in a glass or a Teflon cell. The precipitate was washed in succession with water and alcohol. The product weight varied between 0.5 and 1 g. In some cases, the reduction was performed in the presence of different impurities (ferromagnetic—Fe, Co, Ni and nonferromagnetic—Al, Ag, Zr, Mo, Si), which were introduced into the reaction cell simultaneously with the powder-like reducing agent Mg. The electrochemical reduction was also carried out in an external magnetic field of a permanent magnet ($B \sim 0.5$ T).

Mössbauer spectroscopy. The gamma resonance spectra were obtained in transmission geometry. Standard Mössbauer equipment with a 5-mCi BaSnO_3 source was used. Some of the measurements were performed at low temperatures (the sample temperature could be varied in the range from 77 to 293°K). A computer fitting was

used to resolve the experimentally observed Mössbauer spectra into single Lorentzian lines.

X-Ray diffractometry. The X-ray diffraction pictures were taken by the DRON-20 diffractometer, using the K_α characteristic line of Co ($\lambda = 1.790$ Å). The relative error of the interplanar distance measurements is $\sim 0.1\%$.

Experimental Results and Discussion

Reaction Studies

The method used to obtain tin metal, has one main advantage: it is possible to vary the reaction conditions and is, at the same time, easy and capable of rapid execution. The reduction of differently concentrated water, alcohol, and acetone solutions of the tin halides $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was examined. Several metals namely, Mg, Al, and Zn, were used as reductors. The Mössbauer studies showed that tin with $\delta = 4.3 \pm 0.1$ mm/sec was obtained only in two cases. One of them occurred in the electrochemical reduction of 20% water solution of SnCl_2 with Mg; the present paper summarizes the Mössbauer and X-ray results obtained by this study.

Formally, the reaction can be written as

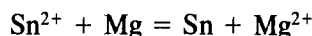


Figure 1 shows several Mössbauer spectra taken under different conditions of the precipitate which was obtained according to the former reaction, after washing with water. Spectrum 1a is of the wet product and was measured immediately after the reaction at room temperature. It is seen that, in addition to the usual line of β_1 -Sn, there is also a line at $+4.3 \pm 0.1$ mm/sec which indicates, according to (7), the presence of the α_2 allotropic form of tin. Spectrum 1b is obtained from the same sample frozen at liquid nitrogen temperature. The lines of SnO and SnO₂ appear in it. After increasing

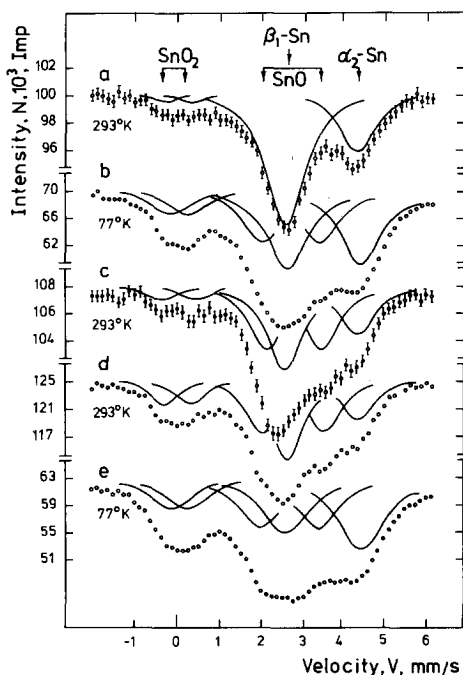


FIG. 1. Mössbauer spectra of wet tin precipitate obtained by reduction of a 20% water solution of SnCl_2 with Mg and rinsed several times with water. Spectra a, b, and c were obtained at 293, 77, and 293°K immediately after the reduction. Spectra d and e were obtained at 293 and 77°K, respectively, after the sample was dried at 300°K.

the sample temperature to 293°K, (spectrum 1c) the SnO line is still present, while it is absent from spectrum 1a. A possible explanation is that the SnO particles enlarge as a result of the freezing. Such an effect has already been reported (10). Spectra 1d and e are taken at 293 and 77°K, respectively, from the dried sample. It is seen that the sample composition is the same, but the quantity of the SnO and SnO_2 has increased due to the additional oxidation of the sample during drying.

The reactivity differences between α_2 -Sn and β_1 -Sn in a tin sample with an initial composition as shown on Fig. 2a, were studied by dissolving equal initial quantities of the tin in 5% KOH, 5% HCl, and the complex forming reagent EDTA, respec-

tively. The Mössbauer spectra obtained after the corresponding treatments, Figs. 2b, c, d, and e showed that the α_2 -Sn was encountered in all three cases, while β_1 -Sn remained practically unchanged.

Investigations of the Electrochemical Reduction of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with Mg in the Presence of Impurities

Spectral studies of the magnesium, which was used as reducing agent in the cases described by Figs. 1 and 2, showed the occurrence of approximately 1% of Fe, Co, Ni, Ti, and Pd. The predominant impurity was iron in the form of microparticles. Figure 3a shows the Mössbauer spectrum of a tin product obtained by the reduction of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with magnesium powder without

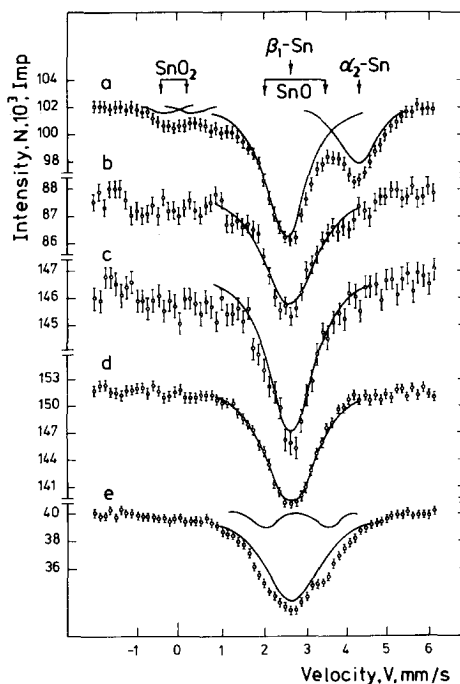


FIG. 2. Mössbauer spectra obtained after different chemical treatments of the tin product: (a) Mössbauer spectrum of the initial tin sample; (b) after treatments with diluted KOH; (c) and (d) after treatments with diluted HCl; (e) after a treatment with the complex-forming reagent EDTA. All spectra were taken at room temperature.

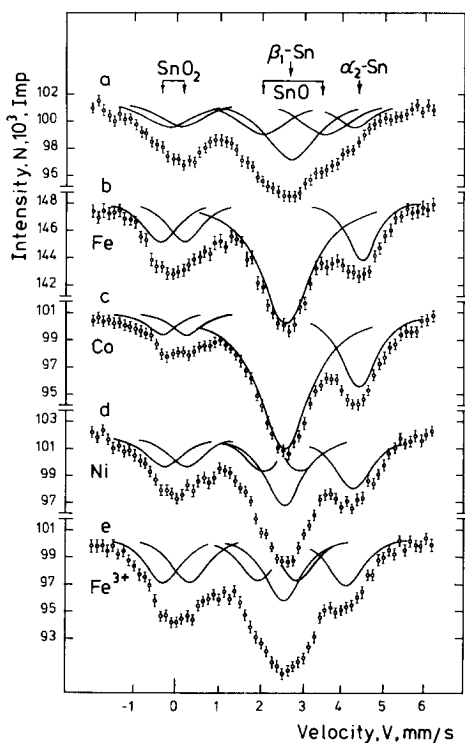


FIG. 3. Mössbauer spectra of tin precipitate obtained by reduction of 20% SnCl_2 solution with purified Mg in the presence of ferromagnetic impurities: (a) reference spectrum obtained from a tin product obtained with purified Mg; (b, c, d, e) the reduction was performed in the presence of impurities which are listed to the left of each spectrum. All spectra were obtained at room temperature.

iron microparticles (they were removed with a permanent magnet). The tin product obtained with Mg without iron particles, designated as purified Mg (Fig. 3a) showed only traces of α_2 -Sn. This is an indication that the α_2 -Sn formation is strongly influenced by the presence of impurities.

Two groups of experiments were performed. The first group includes reactions performed in the presence of known amounts of fine powdered ferromagnetic impurities (about 10% of the total weight of the reducing agent), added to the purified magnesium powder. The resulting Mössbauer spectra are shown in Figs. 3b, c, and

d. It is seen that the quantity of α_2 -Sn increases in the presence of ferromagnetic impurities and that each one of the introduced metals has a specific influence on the β_1 -Sn/ α_2 -Sn ratio on one hand, and on the extent of tin oxidation, on the other. Spectrum 3e was obtained from a precipitate obtained with purified Mg, but in the presence of Fe^{3+} ions in the solution. It is similar to spectra 3b, c, and d, since the Fe^{3+} ions are reduced to Fe, which covers a part of the magnesium particles.

The results, discussed in connection with Figs. 3, show that the impurities Fe, Co, and Ni can be regarded as catalysts in the α_2 -Sn structure formation, while the non-ferromagnetic impurities Al, Ag, Zr, Mo, and Si, which were used in the second group of experiments, are inactive: as shown in Figs. 4, the resulting Mössbauer

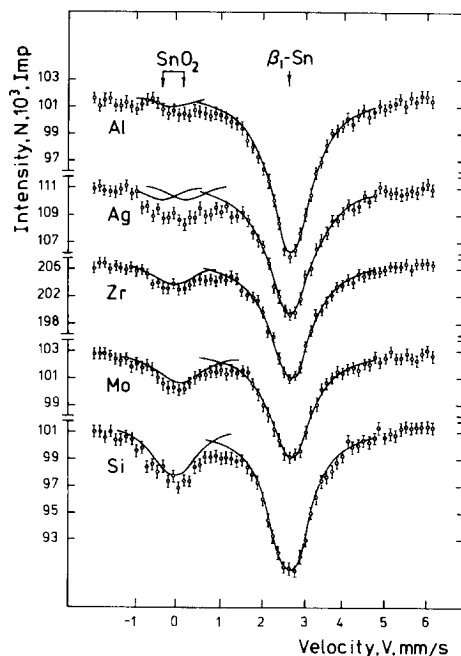


FIG. 4. Mössbauer spectra of tin products obtained by reduction of 20% SnCl_2 water solution with purified Mg in the presence of nonferromagnetic impurities. The impurities are listed to the left of each spectrum. All spectra were obtained at room temperature.

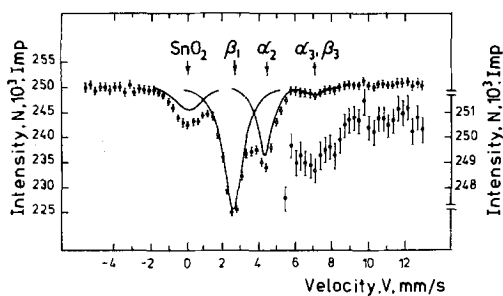


FIG. 5. Mössbauer spectrum of a sample obtained by reduction of a 20% SnCl_2 water solution with purified Mg containing 10% Co. The spectrum was measured at room temperature.

spectra do not differ from each other and the products contain mainly β_1 -Sn, slightly oxidized to SnO_2 .

The origin of the ferromagnetic impurities activity in the α_2 -Sn formation was studied by performing the reduction in an external magnetic field. The Mössbauer spectra of tin products obtained in this manner, (Fig. 6b), are similar to those presented in Figs. 3b–e, which indicates that the magnetic field, no matter what its source is, stimulates the formation of the α_2 -Sn structure.

The existing data of magnetic interactions during chemical reactions (11) show that two effects determine the structure of the final product. The magnetospin effect leads to the $\text{Kr}4d^95s^15p^4$ electron configuration of the tin atoms. The magnetopolarization effect determines the alignment of the magnetic moments of these atoms with the applied magnetic field, resulting in the α_2 -Sn crystal growth. The observed influence of the magnetic field on the growth of different polymorphic forms is a new phenomenon; details of the observed effects will be published later.

A Mössbauer line at +7 mm/sec was observed occasionally, when performing the reduction in the presence of Co (Fig. 5). The considerable error (± 0.4 mm/sec) of δ makes it difficult to determine the type of

the tin structure which corresponds to the observed Mössbauer line: the values of the isomer shifts of both α_3 -Sn and β_3 -Sn are within the limits of the error interval.

X-Ray Structural Studies

X-Ray data of the reaction products, obtained by reduction of water solutions of SnCl_2 : (i) with Mg containing less than 1% Fe; (ii) with purified Mg mixed with 10% Co; and (iii) with purified Mg but in the presence of an external magnetic field, are summarized in Table I, samples 1, 2, and 3. The Mössbauer spectra of samples 2 and 3 are shown in Fig. 6. The Mössbauer spectrum of sample 1 is identical to that of sample 2. It is seen (Fig. 6a) that samples 1 and 2 consist of β_1 -Sn, α_2 -Sn, and of SnO_2 . Sample 3, Fig. 6b, contains β_1 -Sn, α_2 -Sn, SnO_2 , and α_1 -Sn. The amounts of β_1 -Sn, α_1 -Sn, and α_2 -Sn are comparable. The Mössbauer results in Fig. 6 do not provide any evidence for the presence of SnO in the three samples.

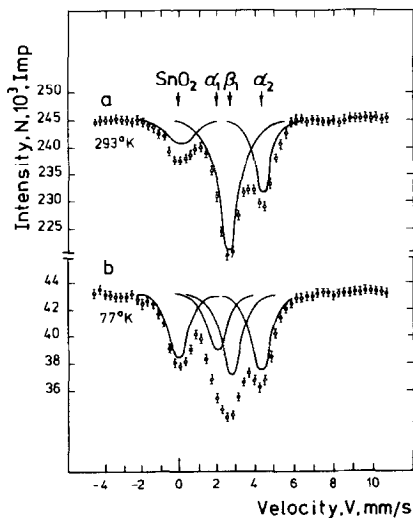


FIG. 6. Comparison between the Mössbauer spectra of the tin products obtained: (a) by reduction with purified Mg containing 10% Co; (b) by reduction with purified Mg in an external magnetic field, $B \sim 0.5T$. The temperatures measurement are shown on the left of the corresponding spectrum.

TABLE I
X-RAY DIFFRACTOMETER DATA OF THREE TIN SAMPLES

No	Samples						Sn ASTM 4-673 a = 5.83 Å c = 3.18 Å (β_1)	Sn ASTM 19-1865 a = 3.70 Å c = 3.37 Å high pressure	Sn ASTM 18-1380 a = 3.81 Å c = 3.48 Å high pressure	α -Sn ASTM 6-390 a = 5.489 Å (α_1)	α_2 -Sn a = 5.35 Å	α_3 -Sn a = 5.42 Å	α_4 -Sn a = 5.61 Å	α_5 -Sn a = 5.66 Å	α_6 -Sn a = 5.73 Å
	1 d (Å)	1 hrel	2 d (Å)	2 hrel	3 d (Å)	3 hrel									
1	5.11	VW													
2			5.05	W											
3	4.91	VW	4.90	W											
4	4.78	VW	4.75	W											
5															
6	4.14	M	4.13	M	4.56	W									
7					3.90	M									
8	3.63	VW	3.64	W	3.55	S			3.75/100/111						
9															
10	3.50	W	3.50	W											
11					3.46	VW									
12	3.41	W	3.41	W											
13					3.34	VW									
14					3.31	M									
15	3.27	M	3.27	M											
16	3.23	M	3.24	M	3.22	VW			3.22/200 ^a						
17	3.14	W	3.14	W											
18	3.09	W	3.09	W	3.10	VW				3.09/111		3.13/111	3.24/111		
19	2.98	VW	2.99	W	2.99	M									
20	2.92	V	2.91	V	2.91	V	2.915/100/200								
21					2.86	VW									
22	2.83	M	2.84	M	2.82	VW									
23	2.80	V	2.79	V	2.80	V	2.793/90/101								
24	2.71	VW	2.71	VW											
25	2.69	W	2.68	W	2.68	VW			2.70/50/110		2.68/200		2.71/200	2.80/200	2.83/200
26	2.63	VW	2.62	VW			2.62/55/110		2.57/100/101						
27	2.53	M	2.53	M			2.49/100/101								
28	2.49	W	2.49	W											
29					2.51	M									
30	2.39	VW	2.39	W	2.39	W									
31					2.36	VW									
32	2.27	W	2.27	W	2.28	W									
33	2.23	W	2.23	W					2.29/83/220						
34					2.20	VW									
35					2.12	VW									
36	2.06	V	2.06	S	2.06	S	2.062/34/220								2.02/220
37	2.01	V	2.01	V	2.01	V	2.017/74/211								
38					1.99	VW									
39	1.94	W	1.94	W	1.95	M			1.91/40/200		1.96/53/311		1.98/220		
40					1.92	M									
41	1.89	W	1.89	W	1.88	VW			1.85/20/200		1.86/222 ^a	1.89/220	1.92/220		
42	1.82	VW	1.82	VW	1.82	W									
43					1.78	M									
44					1.74	M			1.74/10/002						
45					1.73	W									
46	1.71	VW	1.71	W											
47					1.69	W			1.68/5/002						
48	1.67	VW													
49	1.66	M	1.66	S	1.659/17/301										
50	1.61	W			1.62	W									
51					1.59	VW									
52					1.57	W									
53	1.55	VW													
54					1.53	VW									
55	1.49	S	1.48	M	1.48	M	1.484/23/112	1.48/35/121		1.53/30/211		1.49/20/331			
56					1.47	W									
57	1.46	M	1.46	M	1.46	M	1.458/13/400		1.46/5/112						
58	1.44	S	1.44	M	1.44	M	1.442/20/321	1.42/15/112			1.44/420 ^a				

Note. Sample 1, reduction of 20% SnCl₂ water solution with Mg containing less than 1% Fe; sample 2, the same, but with purified Mg containing 10% Co; sample 3, the reduction was carried out with purified Mg in an external magnetic field. The data of the various tin structures, described in the ASTM-tables are included for reference. The unindexed powder diffraction lines are attributed to various tetravalent tin oxides.

^a Forbidden reflection.

The interpretation of the X-ray diffractometer data was carried out taking into account the Mössbauer results, the data from the ASTM-tables, and the single crystal RHEED results of Djuneva (8). The data in Table I show that sample 3, obtained in an external magnetic field, consists of theoretical β_1 -Sn and of α_2 -Sn constituents with $a = 5.73$ and 5.35 Å. The intensities of the diffraction lines indicate that the amount of the first α_2 -Sn substructure is considerable. A comparison between the X-ray and the Mössbauer results shows that the α_1 -Sn

structure, observed in sample 3, does not exhibit the theoretical lattice structure of α_1 -Sn, described by the ASTM-tables, but has, according to the Mössbauer results, the first coordination sphere of α_1 -Sn. This observation is similar to the RHEED results in (8), where thin tin films with widely differing structures, but with the isomer shift of α_1 -Sn, have been observed. These structures have lattice parameters irrationally related to the lattice parameter of α_1 -Sn, and are treated as its 3DIS (three-dimensional incommensurate states) (12-

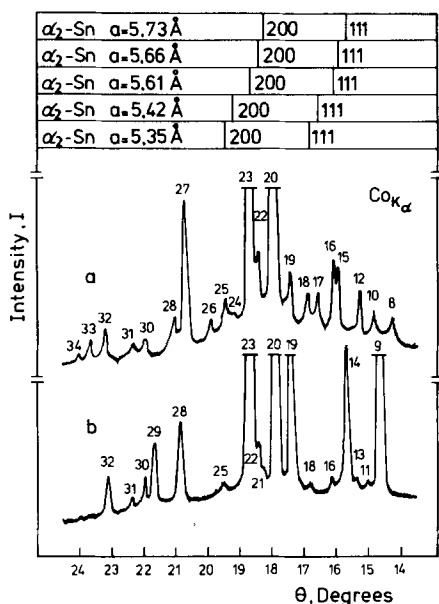


FIG. 7. Part of the X-ray diffractometer records of samples 2 and 3: (a) X-ray results of sample 2; (b) X-ray results of sample 3.

14). Powder data indexing of such structures is unreliable.

The X-ray powder data of samples 1 and 2 indicate the presence of more than two α_2 -Sn substructures. Part of the diffractometer record of sample 2 is included for illustration in Fig. 7a. The diffractometer record of sample 3, where the variety of the α_2 -Sn substructures is not so large, is included for reference in Fig. 7b. The result that the lattice parameter of α_2 -Sn can have several particular values, $a = 5.66, 5.61, 5.42,$ and 5.35 \AA , is in accordance with the RHEED observations in (8) and (9), where single crystal islands of α_2 -Sn with a lattice parameter either close to the lattice parameter of Si ($a = 5.42 \text{ \AA}$), or to that of Ge ($a = 5.66 \text{ \AA}$) have been observed. Some single-crystal RHEED data also yielded the value $a = 5.80 \text{ \AA}$ (8). The poor resolution of the RHEED studies does not permit an unambiguous determination of all possible values of the α_2 -Sn lattice parameter to be made;

therefore, the existence of other possible lattices does not appear unlikely.

Formally, part of the powder data in Table I could be interpreted in terms of the high-pressure tin structures, described in the ASTM-tables, and included for references in Table I. Such a comparison was not made, since there are no data on the chemical bonding among the tin atoms in these high-pressure tin forms.

All samples described in Table I, contain tetravalent tin oxides. The RHEED, X-ray, and Mössbauer studies show that the structures of these tin oxides in thin films and in the initial stages of massive tin oxidation are complicated (15); several tetravalent tin oxides may coexist in the respective samples. Such oxides are often in 3DIS and their identification from powder data alone, is unreliable.

A Study of the Temperature Dependence- $\epsilon(T)$

The tin product for this investigation was obtained by electrochemical reduction of a 20% water solution of SnCl_2 with purified Mg containing 10% Co. The reaction product consisted of β_1 -Sn, SnO_2 , and α_2 -Sn, where $\sim 5 \text{ mg/cm}^2$ corresponded to α_2 -Sn (in a total weight of 20 mg/cm^2). The Mössbauer spectra of the reaction product were obtained for seven temperatures in the range $77\text{--}293^\circ\text{K}$. Similar experiments were performed with a standard β_1 -Sn foil, 10 mg/cm^2 . The values of the Mössbauer effect and the corresponding errors were estimated after a computer fitting of the resulting spectra. The temperature dependences of the relative values of the effect $\epsilon(T)/\epsilon(77^\circ\text{K})$ of both samples are shown in Fig. 8. Though a tendency of differentiation of the temperature dependences is observed, a single curve approximates the results of both studies. Evidently, in this case, the α_2 -Sn structure has a phonon spectrum similar to that of the metal β_1 -Sn foil.

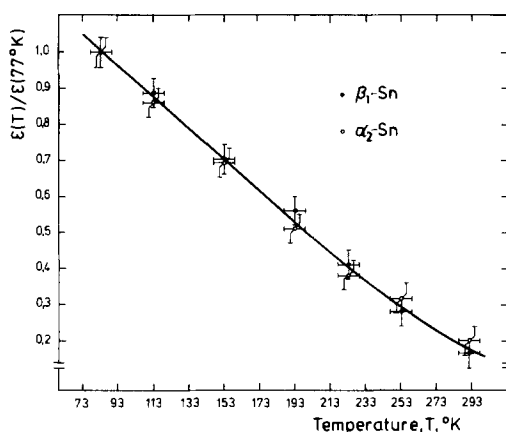


FIG. 8. The temperature dependence of $\epsilon(T)/\epsilon(77^\circ\text{K})$ for β_1 -Sn and α_2 -Sn.

Microcalorimetric Measurements

Differential Scanning Calorimetry was applied to a tin sample obtained in a manner similar to that described in the last section. The results from two scannings of one and the same sample are shown in Fig. 9. The Mössbauer measurement of the initial tin product showed that it contained β_1 -Sn, SnO_2 , and a considerable amount of α_2 -Sn. The first scanning of the sample in the range 353–520°K yielded three maxima for the endothermic processes (Fig. 9a). The third maximum corresponds to the melting of β_1 -Sn. The maximum at 460°K is associated with the evaporation of the crystal water from the α and β tin acids, which are obtained during the reaction. The less intensive maximum at 475°K could not be interpreted unambiguously. It is thought that, most probably, it corresponds to an endothermic transition in the multistructural α_2 -Sn system.

The second scan (Fig. 9b), was undertaken after cooling the molten sample down to room temperature. In this case only the peak corresponding to the melting of β_1 -Sn appeared, which shows that the tin precipitate has totally crystallized as β_1 -Sn, and that the α_2 -Sn structures have disappeared.

Conclusions

The experimental investigations, described in the present paper, point to the following principal results:

In different experiments on electrochemical reduction and electrolysis of soluble tin compounds, the conditions for the formation of bulk α_2 -Sn have been found. The identification of the Mössbauer line at +4.3 mm/sec with the α_2 -Sn structure is certain, taking into account the following:

The reaction itself and the preparative conditions leave no possibility other than the formation of tin and tin oxides. To avoid uncertainties, the amount of the reducing agent, i.e., Mg, introduced into the solution, has always been less than the stoichiometric amount which is needed for a

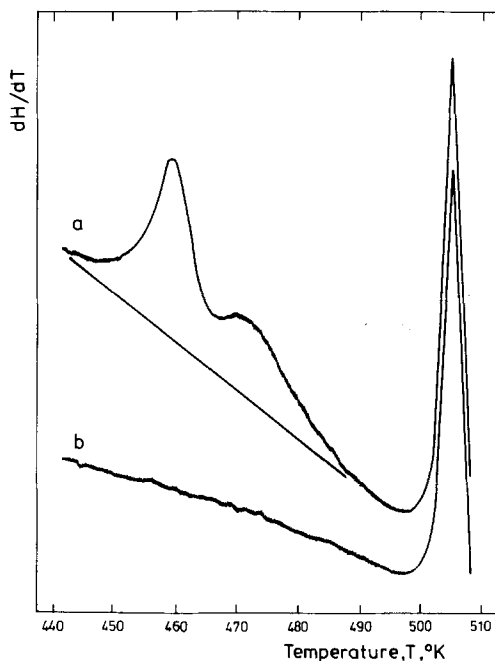


FIG. 9. Comparison between the microcalorimetric results obtained by scanning a tin product consisting of β_1 -Sn, α_2 -Sn, and SnO_2 , obtained by reduction of 20% SnCl_2 water solution, with purified Mg containing Co. Scan b was obtained after melting and cooling down to room temperature of the initial tin sample.

complete reduction of the tin halide. Spectral measurement of the precipitate has also been performed. It indicates the presence of other elements in only microquantities. The X-ray diffractometer data also furnish proof of the α_2 -Sn existence in bulk form. The lattice parameter of the resulting tin has the same value as that of the α_2 -Sn observed in thin films (6).

The presence of a magnetic field is found to be decisive for obtaining the new tin allotropic form. The mechanism of this curious phenomenon has not yet been discovered. Only some speculations on it are included here. If the proposed electron configuration $Kr4d^95s^15p^4$ for the α_2 -Sn (7) is correct, a magnetic polarization effect must be expected. In the α_2 -Sn atoms one of the 4d electrons is promoted to a 5p electron of the valency zone. So α_2 -Sn must be a much stronger paramagnet as compared to β_1 -Sn. The moments of magnet of the α_2 -Sn atoms align with the external magnetic field during the reaction. Such orientation favors the α_2 -Sn crystal growth. Therefore, the observed magnetic field influence may be considered as indirectly supporting the proposed electron configuration.

The study of the temperature dependence of β_1 -Sn and α_2 -Sn shows no difference between their phonon spectra, though their crystal structures presuppose such a difference. In our case the influence of the matrix and the influence of the pressure exerted on the product when preparing the tablet of α_2 -Sn, must be taken into consideration. That is why this present result is not firm.

The X-ray diffractometer measurements have confirmed the RHEED observations concerning the existence of the diamond cubic α_2 -Sn structure in (6, 8) and have in-

creased the number of possible α_2 -Sn substructures.

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