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Mössbauer Study of Tin Phosphides

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A Mössbauer spectroscopic study of SnP_3, Sn_3P_4 and Sn_4P_3 has provided values for the isomer shifts close to the one for β-Sn. The presence of small electric quadrupole interactions is indicated.

1. Introduction

In the binary system Sn–P the following phases have been reported: SnP_3, Sn_3P_4, SnP, and Sn_4P_3.

Gullman and Olofsson (*1*) have recently solved the crystal structure of SnP_3. Here, all tin atoms are surrounded by six phosphorus atoms in a slightly distorted octahedron.

The compound Sn_3P_4, has been indexed by Olofsson (*2*) on a trigonal cell, but its crystal structure and exact composition have not been determined.

As concerns SnP, the occurrence of high pressure phases is well established (*3*), while the existence of a phase stable at normal pressure is doubtful (*2*).

The crystal structure of Sn_4P_3 was independently determined by Eckerlin and Kischio (*4*) and Olofsson (*2*). In the hexagonal unit cell there are two nonequivalent sixfold tin positions. Sn(1) has a near environment of three phosphorus atoms and three Sn(1) atoms in a distorted octahedron, whereas Sn(2) is surrounded by "three plus three" phosphorus atoms in a slightly distorted octahedron.

Mössbauer spectroscopic data for Sn_4P_3, SnP (low pressure phase), and Sn_3P_4 have been published by Vasilev et al. (*5*), and are discussed further in Section 3.

2. Sample Preparation and Experimental Details

SnP_3 was synthesized at 520°C in a sealed evacuated silica tube, the nominal composition of the sample being SnP_4. The heat treatment was carried out for one week and was followed by slow cooling to room temperature.

For the synthesis of Sn_4P_3, 1.000 g grey tin and 50 mg red phosphorus were heated in a sealed silica tube *in vacuo* to 600°C and slowly cooled. The excess tin was dissolved in mercury at room temperature, and the tin phosphide was subsequently washed in 3 *M* nitric acid and 3 *M* hydrochloric acid. After rinsing, first in water and then in acetone, the sample was dried in air at room temperature.

In the preparation of Sn_3P_4 stoichiometric amounts of tin and phosphorus were pressed to a pellet and heat-treated in a sealed evacuated silica tube for one week at 460°C, and quenched in water to room temperature.

The starting materials for all preparations were tin rods (Johnson, Matthey and Co., Ltd spectrographically standardized) and red phosphorus (purity higher than 99%). Before using the tin, it was converted into α-tin by seeding and cooling.

Phase analysis was carried out by X-ray powder diffraction, using a Guinier–Hägg type focussing camera with $CuK\alpha_1$ radiation. For each sample all lines could be indexed in terms of the lattice parameters of the phase concerned. In Sn_3P_4 small traces of SnP_3 were detected, while for SnP_3 and Sn_4P_3 no line belonging to any other phase was seen.

The samples were crushed to a fine powder and thoroughly mixed with boron nitride powder. The mixtures were pressed to circular discs with an average thickness of ~5 mg/cm² of tin. Room temperature transmission Mössbauer spectra were recorded, using a constant

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acceleration spectrometer and a $Ba^{119m}SnO_3$ source.

Least-squares fits of the Mössbauer spectra were carried out on an IBM 370/155 computer, using Lorentzian line shapes.

3. Results and Discussion

3.1. SnP_3

The near environment of the crystallographically equivalent tin atoms in SnP_3 is shown in Fig. 1. Interatomic distances and angles around the tin atom are presented in Table I. From the figure and the table it can be concluded that the tin atoms are situated in distorted octahedra with phosphorus atoms at the corners. This surrounding implies that an electric quadrupole interaction is likely to be found.

The measured spectrum consists of a symmetric absorption line. Fittings with and without electric quadrupole interaction gave a difference in χ^2 which is too small for establishing the existence of an electric quadrupole interaction. However, if it exists, it would be of the order of ~0.16(5) mm/s. The corresponding two line fit is shown in Fig. 2 and the line positions are given in Table II. The linewidths from that fit were 0.78(2) mm/s, which should be compared with the value from the single line fit of 0.83(1) mm/s. A similar situation is

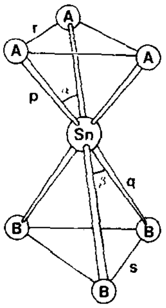

FIG. 1. The near environment of tin atoms for SnP_3 and Sn_4P_3. The values of the distances and angles are given in Table I.

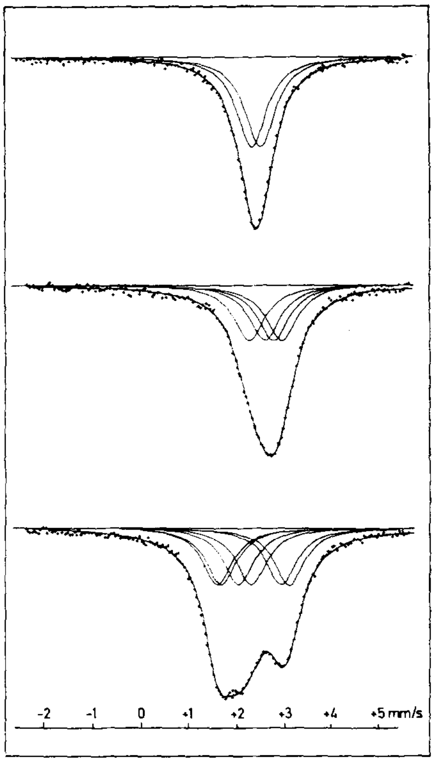

FIG. 2. Mössbauer spectra of SnP_3, Sn_4P_3 and Sn_3P_4 recorded at room temperature (295 K).

TABLE I[a]

Compound and atomic site		Kind of atom A	Kind of atom B	*p*	*q*	*r*	*s*	α	β
SnP_3		P	P	2.662	2.925	3.997	3.382	94.7	70.7
Sn_4P_3	Sn (1)	P (1)	Sn (1)	2.664	3.250	3.968	3.968	96.3	75.3
	Sn (2)	P (2)	P (1)	2.765	2.931	3.968	3.968	91.7	85.2

[a] Distances (Å) and angles (degrees) in the coordination polyhedra for SnP_3 and Sn_4P_3. Labels in accordance with Fig. 1.

TABLE II[a]

Compound	Line positions in mm/s	Γ	χ^2
SnP_3	2.43 (3), 2.59 (3)	0.78 (2)	0.68
Sn_4P_3	2.30 (3), 2.65 (3), 2.83 (3), 2.97 (3)	0.79 (3)	0.80
Sn_3P_4	1.62 (3), 1.70 (3), 2.06 (3) 2.34 (3), 2.96 (3), 3.13 (3)	0.77 (2)	0.99

[a] Line positions in mm/s for the absorption lines in the fitted Mössbauer spectra. Γ is the linewidth (*FWHM*) in mm/s for the individual absorption lines. All values are given with respect to a room temperature $Ba^{119m}SnO_3$ source.

present in β-Sn. In connection with the measurements of the tin phosphides a calibration of the spectrometer was carried out using a β-Sn foil (12 mg/cm^2) with the following results.

Single line fit: $\delta = 2.56(1)$; $\Gamma = 0.81(2)$; $\chi^2 = 0.79$

Two line fit: $\delta = 2.56(1)$; $\Delta = 0.29(4)$; $\Gamma = 0.81(2)$; $\chi^2 = 0.78$

However, a DPAC measurement (*6*), has unambiguously shown, that an electric quadrupole interaction is present, giving the value of $\Delta = 0.234(8)$. This emphasizes the difficulty in measuring electric quadrupole interactions of the present magnitude for tin, using Mössbauer spectroscopy.

The chemical isomer shift was found to be 2.51(1) mm/s, which is close to the value for β-Sn. The atoms in β-Sn are often regarded as incompletely ionized (*7*), and the measured isomer shift in SnP_3 might therefore support the assumption (*1*) of an oxidation number of +3 for the tin atoms in SnP_3.

3.2. Sn_4P_3

The structure of Sn_4P_3 contains two nonequivalent crystallographic tin positions, which are equally populated. The surrounding of one of these positions, Sn(2), is very similar to the tin environment in SnP_3; the other position, Sn(1), has a more asymmetric surrounding with three tin and three phosphorus neighbours (Fig. 1 and Table I).

The first attempt to fit the Mössbauer powder spectrum of this compound was made with two lines of equal intensity. This fitting, representing a vanishing electric quadrupole interaction for both types of tin atoms gave $\chi^2 = 1.00$. A small asymmetry in the absorption line was detected from that fit, and therefore a new fitting was carried out using four lines of equal intensity and halfwidths, representing the case of electric quadrupole interaction for both types of tin atom. The χ^2 of this fit was 0.80, and the linewidth was 0.79(3) mm/s. The line positions are given in Table II.

For a full interpretation of the Sn_4P_3 spectrum, reference can be made to a recent study of tin sulphides (*8*). In the crystal structure of Sn_2S_3 (*9*), the tin atoms are situated in two different crystallographic positions of equal populations. The near environment of Sn(1) closely resembles the one in SnS_2, while a corresponding similarity is found between Sn(2) and the tin atom in SnS(*9*). The Mössbauer spectrum of Sn_2S_3 also conforms to this picture, since it closely corresponds to a superposition of the spectra for SnS_2 and SnS(*8*).

If this way of arguing can be carried over to the tin phosphides we would expect to find, in the Mössbauer spectrum of Sn_4P_3, a component from Sn(2) resembling the spectrum of SnP_3.

Grouping the absorption lines in Sn_4P_3, two by two, gives three possible sets of isomer shifts and electric quadrupole splittings (Table III). It is difficult to make a definite choice between these alternatives. However, alternative C seems most reasonable, since the similarity between δ_2 and Δ_2 and the corresponding values found for SnP_3 is most pronounced in this case. Furthermore, a large electric quadrupole interaction for Sn(1) is not astonishing in view of its asymmetric near surrounding.

TABLE III[a]

	δ_1	δ_2	Δ_5	Δ_2
Alternative A	2.57 (4)	2.81 (4)	0.53 (6)	0.32 (6)
Alternative B	2.48 (4)	2.90 (4)	0.35 (6)	0.14 (6)
Alternative C	2.64 (4)	2.74 (4)	0.67 (6)	0.18 (6)

[a] Isomer shifts (δ) and electric quadrupole splitting ($\Delta = (eQV_{zz}/2)$ in mm/s for the possible binary groupings of the absorption lines.

As is evident from Fig. 2 the absorption pattern for Sn_4P_3 is displaced ~0.2 mm/s towards higher velocities, with respect to SnP_3. A similar observation, i.e., an increasing tin content leading to an increasing isomer shift, can be made from the Mössbauer studies of the octahedrally coordinated tin arsenides (*10*), viz SnAs and Sn_4As_3.

Vasilev et al. (*5*) have also presented Mössbauer spectroscopic studies of Sn_4P_3, where the spectrum is interpreted as a single absorption line with $\delta = 2.82(5)$ and $\Gamma = 1.25(7)$ mm/s. A closer examination of their displayed spectrum reveals, however, the same asymmetry as found in the present study.

3.3. Sn_3P_4

As concerns Sn_3P_4 the crystal structure is not known. The lattice parameters have, however, been determined (*2*), being $a = 4.4330(4)$ and $c = 28.394(5)$ (hexagonal indexing). Preliminary X-ray diffraction results indicate the presence of three nonequivalent tin positions, equally populated. A full account of the crystal structure will be published elsewhere by one of the present authors (J.G.).

The Mössbauer spectrum for Sn_3P_4 is shown in Fig. 2, and is more complicated than the other two. The first attempt to fit the spectrum was based on only three lines, but by allowing for a small electric quadrupole splitting of these lines (Fig. 2) a marked reduction in χ^2 was obtained. The resulting line positions are given in Table II. An interpretation must, however, await till the structure has been solved by X-ray diffraction methods. Finally, it should also be mentioned that Vaselev et al. have reported a single line with an isomer shift of 2.65(5) and a linewidth of 1.20(7) mm/s for Sn_3P_4.

4. Conclusions

The bonding situation for the tin atoms in SnP_3 and Sn_4P_3 resembles the bonding in the tin arsenides. The isomer shifts diminish as the number of nonmetal atoms per tin atom increases. For SnP_3 the value of δ is close to the one for β-Sn. The isomer shift in the tin phosphides studied can be taken as an indication of tin in oxidation state +3.

The near environments of the tin atoms in Sn_3P_4 are probably rather different from the ones in the other tin phosphides in view of the wide distribution of absorption lines.

The magnitude of the electric quadrupole interactions cannot be determined accurately from a powder Mössbauer spectrum. Measurements on magnetized samples might clarify this obscurity.

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