

## The Non-existence of $\text{Sb}_2\text{S}_5$ : a Mössbauer Spectroscopic Investigation of Some Antimony Chalcogenides and Oxides

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**Summary**  $^{121}\text{Sb}$  Mössbauer spectroscopy has been used to study some antimony chalcogenides: no evidence could be found to support the existence of  $\text{Sb}_2\text{S}_5$ .

sulphurs at  $2.50\text{\AA}$  and no others closer than  $3.14\text{\AA}$ , while the other antimony has one sulphur at  $2.38\text{\AA}$ , two at  $2.67\text{\AA}$ , and two at  $2.83\text{\AA}$ . Each site will give rise to a separate

THE feasibility of obtaining useful chemical information using the Mössbauer nucleus  $^{121}\text{Sb}$  has been demonstrated by Ruby and his co-workers.<sup>1</sup> We have reported preliminary  $^{121}\text{Sb}$  Mössbauer data for some antimony chalcogenides and oxides and conclude that  $\text{Sb}_2\text{S}_5$  does not exist.

Our data are summarised in the Table: although we have not yet fitted the absorption envelopes to the eight-line quadrupole splitting pattern, the isomer shifts can be obtained reasonably accurately and yield useful chemical information. The shifts fall into two groups, namely those at very negative velocities, which are characteristic of  $\text{Sb}^{\text{III}}$ , and those at more positive velocities,  $-5.7\text{ mm/sec}$  and above, typical of  $\text{Sb}^{\text{V}}$ . In the  $\text{Sb}_2\text{X}_3$  series there is a considerable change to more negative velocities from oxygen to tellurium indicating an increase in "s" electron density at the antimony nucleus, there being a closer approximation to a bare  $\text{Sb}^{3+}$  in  $\text{Sb}_2\text{Te}_3$  than in  $\text{Sb}_2\text{O}_3$ . This is in accord with the structures as far as they are known,<sup>4,5</sup> with the telluride having a more ionic lattice. Antimony(III) sulphide and selenide are isostructural, each consisting of hexagonal rings condensed together to form long chains.<sup>5</sup> Within each structure there are two antimony sites. For example, in  $\text{Sb}_2\text{S}_3$  one antimony has three

$^{121}\text{Sb}$  Mössbauer data at  $80^\circ\text{K}^a$

Compound <sup>b</sup>	Isomer shift mm/sec] [relative to $\text{Ba}^{121}\text{SnO}_3(\text{Sb})$ ]	% Absorption
$\text{Sb}_2\text{O}_3$	$-11.6 \pm 0.1$	9
$\text{Sb}_2\text{S}_3$	$-14.6 \pm 0.2$	7
$\text{Sb}_2\text{Se}_3$	$-14.6 \pm 0.4$	5
$\text{Sb}_2\text{Te}_3$	$-15.3 \pm 0.2$	3.5
$\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$	$-5.7 \pm 0.1$	4
$\text{Sb}_2\text{O}_5$	$+0.1 \pm 0.3$	9
$\text{Sb}_2\text{O}_4$	$+0.3 \pm 0.2$	9
	$-14.5 \pm 0.2$	7

<sup>a</sup> Spectra were recorded as already described (ref. 2) except that a Xe- $\text{CO}_2$  proportion counter was used to count the escape peaks from the  $^{121}\text{Sb}$   $\gamma$ -ray.

<sup>b</sup>  $\text{Sb}_2\text{Se}_3$  and  $\text{Sb}_2\text{Te}_3$  were purchased from Alfa Inorganics and all other samples were prepared according to the procedures in Brauer (ref. 3). A commercial sample of  $\text{Sb}_2\text{S}_3$  contained only  $\text{Sb}^{\text{III}}$ .

eight-line quadrupole split absorption which we are unable to resolve, and which precludes a meaningful analysis in terms of quadrupole splitting and asymmetry parameters for each site. The isomer shifts reported for these two compounds are therefore average shifts for the two kinds of antimony present. Antimony(III) telluride on the other

hand has the face-centred cubic  $\text{Bi}_2\text{Te}_3$  structure with only one kind of Sb site.<sup>5b</sup> Unfortunately, the interatomic distances in  $\text{Sb}_2\text{Te}_3$  are not known but, by analogy to  $\text{Bi}_2\text{Te}_3$ , each antimony should have three tellurium near-neighbours and three more distant in the five-layer sandwich, resulting in six-co-ordination. If the antimony 5s

electron pair is also stereochemically active a quite distorted structure would result giving rise to an asymmetric Mössbauer absorption. An asymmetric line is observed (see Figure) and, although the absorption is relatively weak, the quadrupole splitting appears to be negative in contrast to that so far observed for other  $\text{Sb}^{\text{III}}$  compounds.

The nature of the sulphide  $\text{Sb}_2\text{S}_5$  is unknown.<sup>4b</sup> We have repeated literature preparations<sup>6</sup> of this material and find it to have variable composition. The Mössbauer spectrum in every case consisted of only one absorption at  $-14.6$  mm/sec, clearly in the  $\text{Sb}^{\text{III}}$  region of the spectrum. We were unable to detect any  $\text{Sb}^{\text{V}}$  in these products. Furthermore, an examination of the Sb-S phase diagram<sup>7</sup> shows no evidence for compound formation at the 2Sb:5S composition. There appears to be no evidence for the existence of the compound  $\text{Sb}_2\text{S}_5$ . Thioantimonate salts have however been prepared, the antimony being tetrahedrally co-ordinated by sulphur.<sup>8</sup> The symmetrical Mössbauer absorption obtained for this compound is consistent with this structure. The isomer shift of  $-5.7$  mm/sec is the most negative yet reported for a compound of  $\text{Sb}^{\text{V}}$ , being outside the limits suggested by Long,<sup>9</sup> and indicates considerable covalent character in the Sb-S bonds.

We also include our data on  $\text{Sb}_2\text{O}_5$  and  $\text{Sb}_2\text{O}_4$  which agree well with the literature values.<sup>1,9</sup> The isomer shift of the absorption in the  $\text{Sb}^{\text{V}}$  region of  $\text{Sb}_2\text{O}_4$  is virtually the same as that for antimony(v) oxide. Since the  $\text{Sb}^{\text{V}}$  in  $\beta\text{-Sb}_2\text{O}_4$  is at the centre of a somewhat distorted octahedron of oxygens<sup>10</sup> it seems reasonable to suppose that the antimony in antimony(v) oxide is also six-co-ordinate. In view of the methods of preparation it is possible that antimony(v) oxide contains co-ordinated OH groups and  $\text{Sb}_2\text{O}_5$  does not exist in a pure form.

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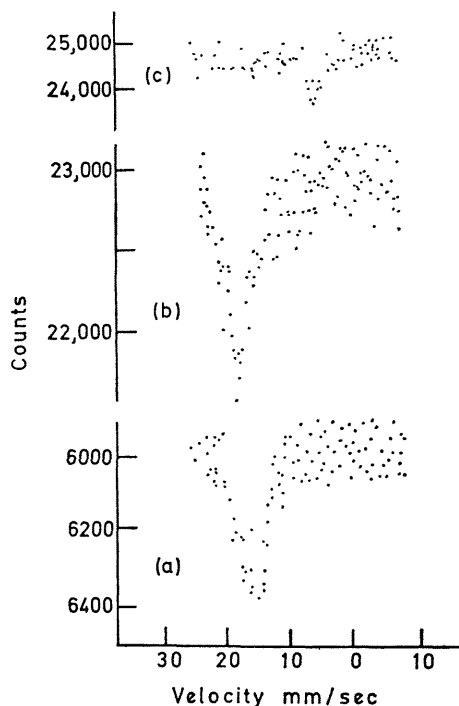


FIGURE.  $^{121}\text{Sb}$  Mössbauer spectra: (a)  $\text{Sb}_2\text{S}_3$ , (b)  $\text{Sb}_2\text{Te}_3$ , (c)  $\text{Na}_3\text{SbS}_{4.9}\text{H}_2\text{O}$ .

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