The Non-existence of Sb_2S_5: a Mössbauer Spectroscopic Investigation of Some Antimony Chalcogenides and Oxides

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Summary ^{121}Sb Mössbauer spectroscopy has been used to study some antimony chalcogenides: no evidence could be found to support the existence of Sb_2S_5.

THE feasibility of obtaining useful chemical information using the Mössbauer nucleus ^{121}Sb has been demonstrated by Ruby and his co-workers.[1] We have reported preliminary ^{121}Sb Mössbauer data for some antimony chalcogenides and oxides and conclude that Sb_2S_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 Sb^{III}, and those at more positive velocities, $-5{\cdot}7$ mm/sec and above, typical of Sb^{V}. In the Sb_2X_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 Sb^{3+} in Sb_2Te_3 than in Sb_2O_3. This is in accord with the structures as far as they are known,[4,5] 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.[5] Within each structure there are two antimony sites. For example, in Sb_2S_3 one antimony has three sulphurs at 2·50Å and no others closer than 3·14Å, while the other antimony has one sulphur at 2·38Å, two at 2·67Å, and two at 2·83Å. Each site will give rise to a separate 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

^{121}Sb *Mössbauer data at* 80°K[a]

Compound[b]	Isomer shift mm/sec)] [relative to Ba^{121}SnO$_3$(Sb)]	% Absorption
Sb_2O_3	$-11{\cdot}6 \pm 0{\cdot}1$	9
Sb_2S_3	$-14{\cdot}6 \pm 0{\cdot}2$	7
Sb_2Se_3	$-14{\cdot}6 \pm 0{\cdot}4$	5
Sb_2Te_3	$-15{\cdot}3 \pm 0{\cdot}2$	3·5
$Na_3SbS_4,9H_2O$	$-5{\cdot}7 \pm 0{\cdot}1$	4
Sb_2O_5	$+0{\cdot}1 \pm 0{\cdot}3$	9
Sb_2O_4	$+0{\cdot}3 \pm 0{\cdot}2$	9
	$-14{\cdot}5 \pm 0{\cdot}2$	7

[a] Spectra were recorded as already described (ref. 2) except that a Xe-CO_2 proportion counter was used to count the escape peaks from the ^{121}Sb γ-ray.

[b] Sb_2Se_3 and Sb_2Te_3 were purchased from Alfa Inorganics and all other samples were prepared according to the procedures in Brauer (ref. 3). A commercial sample of Sb_2S_5 contained only Sb^{III}.

hand has the face-centred cubic Bi_2Te_3 structure with only one kind of Sb site.[5b] Unfortunately, the interatomic distances in Sb_2Te_3 are not known but, by analogy to Bi_2Te_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 Sb^{III} compounds.

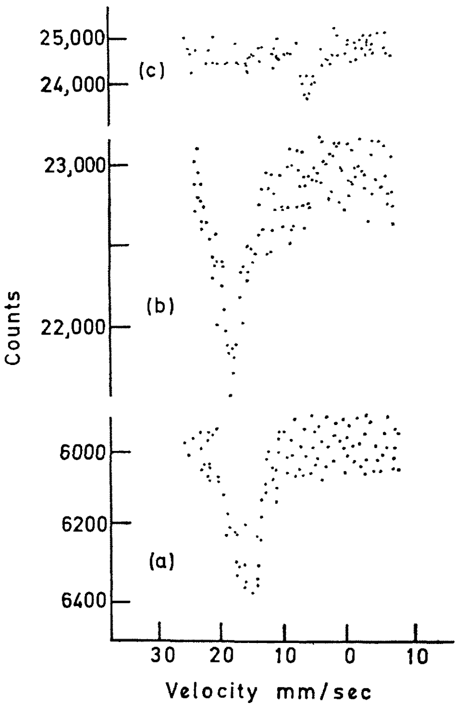

FIGURE. ^{121}Sb *Mössbauer spectra*: (a) Sb_2S_3, (b) Sb_2Te_3, (c) $Na_3SbS_4,9H_2O$.

The nature of the sulphide Sb_2S_5 is unknown.[4b] We have repeated literature preparations[6] of this material and find it to have variable composition. The Mössbauer spectrum in every case consisted of only one absorption at $-14{\cdot}6$ mm/sec, clearly in the Sb^{III} region of the spectrum. We were unable to detect any Sb^V in these products. Furthermore, an examination of the Sb–S phase diagram[7] shows no evidence for compound formation at the 2Sb : 5S composition. There appears to be no evidence for the existence of the compound Sb_2S_5. Thioantimonate salts have however been prepared, the antimony being tetrahedrally co-ordinated by sulphur.[8] The symmetrical Mössbauer absorption obtained for this compound is consistent with this structure. The isomer shift of $-5{\cdot}7$ mm/sec is the most negative yet reported for a compound of Sb^V, being outside the limits suggested by Long,[9] and indicates considerable covalent character in the Sb–S bonds.

We also include our data on Sb_2O_5 and Sb_2O_4 which agree well with the literature values.[1,9] The isomer shift of the absorption in the Sb^V region of Sb_2O_4 is virtually the same as that for antimony(V) oxide. Since the Sb^V in β-Sb_2O_4 is at the centre of a somewhat distorted octahedron of oxygens[10] 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 Sb_2O_5 does not exist in a pure form.

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[1] S. L. Ruby, G. M. Kalvius, G. B. Beard, and R. E. Snyder, *Phys. Rev.*, 1967, **159**, 239.
[2] T. Birchall, *Canad. J. Chem.*, 1969, **47**, 1351.
[3] G. Brauer, "Handbook of Preparative Inorganic Chemistry," vol. 1, Academic Press, New York, 1963.
[4] A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, 1962, (a) p. 668; (b) p. 682.
[5] H. Krebs, "Inorganic Crystal Chemistry," McGraw-Hill, London, 1968, (a) p. 246; (b) p. 244.
[6] P. Pascal, "Nouveau Traité de Chimie Minérale," Masson et Cie, Paris, 1958, vol. XI, p. 629.
[7] F M. Jaeger and H. S. van Klooster, *Z. anorg. Chem.*, 1912, **78**, 245.
[8] A. Grund and A. Preisinger, *Acta Cryst.*, 1950, **3**, 363.
[9] G. G. Long, J. G. Stevens, and L. H. Bowen, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 799.
[10] A. C. Skapski and D. Rogers, *Proc. Chem. Soc.*, 1964, 400.