

**$^{121}\text{Sb}$  Mössbauer Studies on  $\text{NbSb}_2$  and  $\text{TaSb}_2$** L. BRATTÅS,<sup>a</sup> J. D. DONALDSON,<sup>b</sup> A. KJEKSHUS,<sup>a</sup> D. G. NICHOLSON<sup>a</sup> and J. T. SOUTHERN<sup>b</sup><sup>a</sup>Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway and <sup>b</sup>Department of Chemistry, Chelsea College, University of London, Manresa Road, London S.W.3, England

$^{121}\text{Sb}$  Mössbauer spectra of  $\text{NbSb}_2$  and  $\text{TaSb}_2$  have been obtained at 4.2 K and are discussed in relation to their  $\text{NbAs}_2$  type structure.

Our previous experience<sup>1–5</sup> in the use of  $^{121}\text{Sb}$  Mössbauer spectroscopy as a tool in the exploration of the bonding properties of transition metal ( $T$ ) antimonides has encouraged us to pursue this line further. Another intention has been to gain some insight into the influence of the stereochemical environment around the Sb atoms on the Mössbauer parameters. In the compounds studied so far the Sb environments take approximately  $C_{3v}$  symmetry with coordination  $\text{Sb}T_3\text{Sb}$  [*e.g.* in the compounds with the  $\text{FeS}_2$ - $p$  ( $p$  = pyrite),  $\text{FeS}_2$ - $m$  ( $m$  = marcasite), and  $\text{CoSb}_2$  (arsenopyrite,  $\text{FeAsS}$ ) type structures<sup>1</sup>] or  $\text{SbS}_3$  [as in the structure of berthierite ( $\text{FeSb}_3\text{S}_4$ )<sup>2</sup>], approximately  $C_{2v}$  symmetry with coordination  $\text{Sb}T_2\text{Sb}_2$  [*e.g.* in the compounds with the  $\text{CoAs}_3$  (skutterudite) type structure<sup>3,4</sup>], and two different tetrahedral Sb sites with coordinations  $\text{Sb}T_4$  and  $\text{Sb}T_3\text{Sb}$  [as in the structure(s) of  $\text{Mo}_3\text{Sb}_7$  (and  $\text{Nb}_3\text{Sb}_7\text{Te}_6$ )<sup>5</sup>]. The analyses of the data for  $\text{Mo}_3\text{Sb}_7$  and  $\text{Nb}_3\text{Sb}_7\text{Te}_6$  were made possible through the use of the Fourier transform sharpening technique prior to the least squares refinements. This has in turn led us to examine  $\text{NbSb}_2$  and  $\text{TaSb}_2$  which are other compounds having two Sb sites.  $\text{NbSb}_2$ <sup>6–8</sup> and  $\text{TaSb}_2$ <sup>9</sup> are the only antimonides among eleven isostructural transition metal group VB compounds which belong to the  $\text{NbAs}_2$  type structure.

**EXPERIMENTAL**

The experimental details concerning the purity of the elements, sample preparation and

characterization (at and below room temperature),  $^{121}\text{Sb}$  Mössbauer measurements, and data reduction have been presented in previous communications.<sup>1,4,7,8,10</sup>

**RESULTS AND DISCUSSION**

The  $^{121}\text{Sb}$  Mössbauer spectra of  $\text{NbSb}_2$  and  $\text{TaSb}_2$  are very similar, that of  $\text{NbSb}_2$  at 4.2 K being shown in Fig. 1. The sharpness of the spectra shows that the envelopes which must arise from the two different Sb sites must overlap almost exactly. In line with this the Fourier transform sharpened spectra (shown in Fig. 1 for  $\text{NbSb}_2$ ) *do not* reveal the presence of more than one Sb site in these compounds. The curve through the experimental points on Fig. 1 represents a least squares fit with the parameters  $\delta = -9.0 \pm 0.1$  mm/s,  $eQV_{zz} = 9.0 \pm 0.5$  mm/s,  $\Gamma = 2.9 \pm 0.2$  mm/s, and  $A = 12\%$  for  $\text{NbSb}_2$ , those for  $\text{TaSb}_2$  being  $\delta = -9.2 \pm 0.1$  mm/s,  $eQV_{zz} = 6.4 \pm 0.5$  mm/s,  $\Gamma = 3.8 \pm 0.2$  mm/s, and  $A = 14\%$ .

In order to appreciate the full impact of this result it is necessary to recapitulate on the essential details of the  $\text{NbAs}_2$  type structure.<sup>6</sup> The structure contains two non-equivalent X atoms and the crystallographic formula is  $TX_{\text{I}}X_{\text{II}}$ . Each  $T$  is surrounded by six close X (four  $X_{\text{I}}$  and two  $X_{\text{II}}$ ) at the corners of a triangular prism and by two other close X ( $X_{\text{I}}$  and  $X_{\text{II}}$ ) outside the rectangular faces of the prism, interatomic distances and angles for  $\text{NbSb}_2$  being given in Table 1. (In addition there is one relatively close  $T$  outside the third rectangular face of the prism.) The coordinations around the X atoms are illustrated in Fig. 2. The  $X_{\text{I}}$  atoms are surrounded by five near  $T$  in a distorted square pyramidal arrangement.

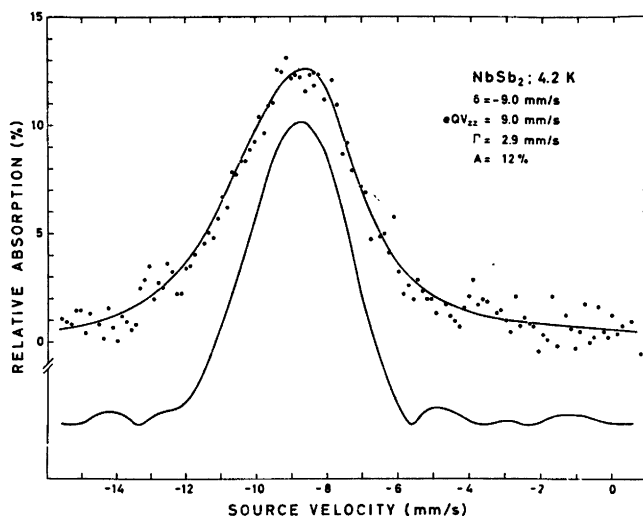


Fig. 1.  $^{121}\text{Sb}$  Mössbauer spectrum of  $\text{NbSb}_2$  with its Fourier transform shown below.

Each  $X_{\text{II}}$  is coordinated to three near  $T$  and one near  $X_{\text{II}}$  at the corners of a distorted tetrahedron, the  $X_{\text{II}}$  atoms forming  $X_{\text{II}}-X_{\text{II}}$  pairs with a short interatomic distance. The distance within the  $\text{Sb}_{\text{II}}-\text{Sb}_{\text{II}}$  pair in  $\text{NbSb}_2$ , which is shorter than those normally found in similar structures, is still in reasonable agreement with the corresponding expectation value for single  $\text{Sb}-\text{Sb}$  bonds.<sup>11</sup> The second shortest  $\text{Sb}_{\text{II}}-\text{Sb}_{\text{II}}$  distance (being the next shortest  $\text{Sb}-\text{Sb}$  distance) is distinctly longer (3.06 Å) and any bonding interaction between these atoms is probably negligible.

Obviously, with such widely differing stereochemical environments at the two Sb sites, the observation of narrow single line  $^{121}\text{Sb}$  Mössbauer spectra for both  $\text{NbSb}_2$  and  $\text{TaSb}_2$  requires an explanation. Since the structural data apply to the situation at room temperature and the Mössbauer spectra are taken at 4.2 K these findings could have been indicative of low temperature phase transitions to structures where all Sb atoms are equivalent. However, this explanation can be excluded since X-ray powder diagrams taken at 78 and 4.2 K show only reflections characteristic of the  $\text{NbAs}_2$  type

Table 1. Bond distances (Å) and angles ( $^\circ$ ) in  $\text{NbSb}_2$ .

$\text{Nb}-\text{Sb}_{\text{I}}$	2.91	$\text{Nb}-\text{Sb}_{\text{II}}$	2.84
$\text{Nb}-\text{Sb}_{\text{I}}$	2.92	$\text{Nb}-\text{Sb}_{\text{II}}$	2.85
$\text{Nb}-\text{Sb}_{\text{I}}$	2.94	$\text{Nb}-\text{Sb}_{\text{II}}$	2.85
$\text{Nb}-\text{Sb}_{\text{I}}$	2.94	$\text{Sb}_{\text{II}}-\text{Sb}_{\text{II}}$	2.71
$\text{Nb}-\text{Sb}_{\text{I}}$	2.97		
$\text{Sb}_{\text{I}}-\text{Nb}-\text{Sb}_{\text{I}}$	67.5	$\text{Nb}-\text{Sb}_{\text{I}}-\text{Nb}$	76.3
$\text{Sb}_{\text{I}}-\text{Nb}-\text{Sb}_{\text{I}}$	68.1	$\text{Nb}-\text{Sb}_{\text{I}}-\text{Nb}$	77.1
$\text{Sb}_{\text{I}}-\text{Nb}-\text{Sb}_{\text{I}}$	76.3	$\text{Nb}-\text{Sb}_{\text{I}}-\text{Nb}$	112.1
$\text{Sb}_{\text{I}}-\text{Nb}-\text{Sb}_{\text{I}}$	77.0	$\text{Nb}-\text{Sb}_{\text{I}}-\text{Nb}$	112.1
$\text{Sb}_{\text{I}}-\text{Nb}-\text{Sb}_{\text{II}}$	89.9	$\text{Nb}-\text{Sb}_{\text{I}}-\text{Nb}$	133.6
$\text{Sb}_{\text{I}}-\text{Nb}-\text{Sb}_{\text{II}}$	89.9	$\text{Nb}-\text{Sb}_{\text{I}}-\text{Nb}$	133.6
$\text{Sb}_{\text{I}}-\text{Nb}-\text{Sb}_{\text{II}}$	93.1	$\text{Nb}-\text{Sb}_{\text{II}}-\text{Nb}$	79.3
$\text{Sb}_{\text{I}}-\text{Nb}-\text{Sb}_{\text{II}}$	93.4	$\text{Nb}-\text{Sb}_{\text{II}}-\text{Nb}$	114.8
$\text{Sb}_{\text{I}}-\text{Nb}-\text{Sb}_{\text{II}}$	135.2	$\text{Nb}-\text{Sb}_{\text{II}}-\text{Nb}$	114.8
$\text{Sb}_{\text{II}}-\text{Nb}-\text{Sb}_{\text{II}}$	79.3	$\text{Sb}_{\text{II}}-\text{Sb}_{\text{II}}-\text{Nb}$	114.5
$\text{Nb}-\text{Sb}_{\text{I}}-\text{Nb}$	67.2	$\text{Sb}_{\text{II}}-\text{Sb}_{\text{II}}-\text{Nb}$	114.5
$\text{Nb}-\text{Sb}_{\text{I}}-\text{Nb}$	67.2	$\text{Sb}_{\text{II}}-\text{Sb}_{\text{II}}-\text{Nb}$	114.5

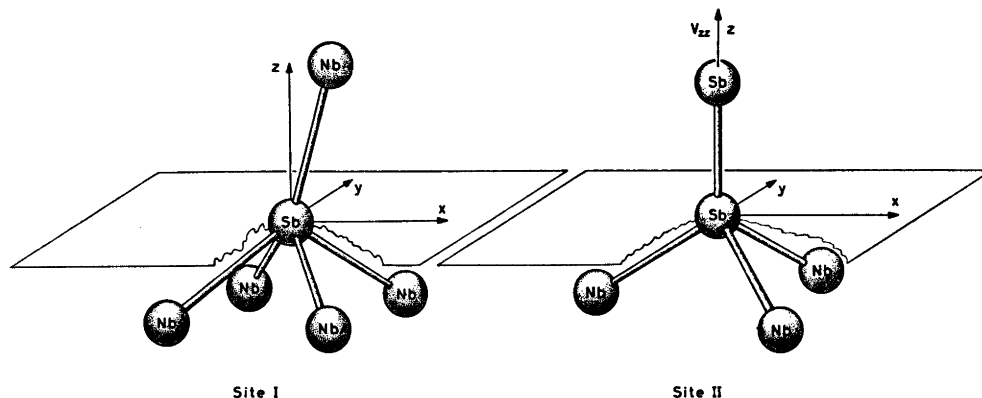


Fig. 2. Models showing the environments of the two Sb sites in NbSb<sub>2</sub> and TaSb<sub>2</sub>.

structure and hence no evidence of low temperature phase transitions. In fact improbably large rearrangements would have been required below room temperature in order to accomplish crystallographic equivalence between the Sb atoms.

A more likely interpretation of the data seems to be that each spectrum consists of two overlapping peaks with similar Mössbauer parameters. To obtain approximately the same chemical shift for the two sites the total *s* electron density withdrawn from both kinds of Sb must be very similar. Since the four-coordinate Sb has a shorter average Sb–*T* bond length than the five-coordinate Sb, this interpretation would not be inconsistent with the structural data. Similarly, the quadrupole splittings ( $eQV_{zz}$ ), and consequently also the electric field gradients, at both sites would have to be relatively small in order to produce narrow Mössbauer spectra. Nevertheless, it is possible to envisage that  $eQV_{zz}$  differs appreciably for the two sites, the overall shape of the envelope being dominated by that with the larger quadrupole coupling constant. The Sb<sub>II</sub> site, which has nearly perfect  $C_{3v}$  symmetry, would thus expectedly be responsible for the smallest  $eQV_{zz}$  value (cf., e.g.,  $eQV_{zz}=2.7$  mm/s in PtSb<sub>2</sub>,<sup>1</sup> where the Sb environment resembles that of Sb<sub>II</sub> in the present compounds) whereas the Sb<sub>I</sub> site with the more irregular environment might give rise to a larger  $eQV_{zz}$  value (e.g.  $eQV_{zz}$  has values of ~9.0 and 6.4 mm/s for Sb<sub>I</sub> in NbSb<sub>2</sub> and TaSb<sub>2</sub>, respectively).

It should be emphasized that the Mössbauer

parameters presented above are derived for a single site fit to each of the absorption envelopes and that no attempt has been made to take account of the presence of the two Sb sites with individual characteristics. Further experiments on similar substances are being carried out in order to substantiate the above interpretation of the Mössbauer data for NbSb<sub>2</sub> and TaSb<sub>2</sub>.

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