

^{121}Sb Mössbauer Studies on Antimony(III) ChalcogenohalidesJ. D. DONALDSON,^a A. KJEKSHUS,^b D. G. NICHOLSON^b and J. T. SOUTHERN^a^aDepartment of Chemistry, Chelsea College, University of London, Manresa Road, London S.W. 3, England and ^bDepartment of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

^{121}Sb Mössbauer spectra of SbSBr , SbSeBr , SbSI , SbSeI , and SbTeI have been obtained at 4.2 K and are discussed in relation to available structural data. A remarkable feature of the iodides is that the quadrupole coupling constant decreases in the order $\text{SbSI} > \text{SbSeI} > \text{SbTeI}$, becoming negative for the latter.

Some one hundred years after Schneider¹ reported the first antimony(III) chalcogenohalide Dönges^{2,3} showed that the compounds SbXY ($X = \text{S, Se, or Te}$; $Y = \text{Br or I}$) constitute an isostructural series. The fact that the compounds are composed of one element from each of three consecutive main groups arouses interest in their bonding characteristics. Moreover, the isostructural nature of the compounds permits systematic studies as to the variations in the properties within the series.

More recent investigations include *inter alia* measurements of their ferroelectric^{4,5} and semi-conducting^{6,7} behaviours, improved structure determinations of SbSBr ⁸ and SbSI ⁹ (above and below the ferroelectric transition temperature), nuclear quadrupole resonance (NQR),^{10,11} Mössbauer,^{12,13} and IR/Raman^{14–16} studies. The available ^{121}Sb Mössbauer data^{12,13} are incomplete in several respects. We report here the results after least squares and Fourier transform data reduction for SbSBr , SbSeBr , SbSI , SbSeI , and SbTeI taken at 4.2 K.

EXPERIMENTAL

The SbXY compounds were prepared by heating stoichiometric quantities of Sb , X , and SbY_3 for one week in sealed, evacuated ampoules at 280 and 400 °C for $Y = \text{Br}$ and I , respectively. SbBr_3 and SbI_3 were prepared by addition of the halogen to a suspension of

freshly powdered Sb in refluxing anhydrous benzene under a nitrogen atmosphere. The resulting crystalline products of SbBr_3 and SbI_3 were purified by sublimation *in vacuo*.

X-Ray (Guinier) powder photographs were taken of the various SbXY samples using monochromatized $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54050$ Å) and KCl as internal standard. The least squares fitted unit cell dimensions confirm that the present samples match those previously documented.^{2,3} The experimental details concerning the ^{121}Sb Mössbauer measurements and data reductions have been presented in previous communications.^{17,18}

RESULTS AND DISCUSSION

Fig. 1 shows the ^{121}Sb Mössbauer spectra of SbSI , SbSeI , and SbTeI at 4.2 K, presented as typical examples of those obtained for all compounds. The corresponding Fourier transformed sharpened spectra confirm the presence of only one Sb site for all of the pure compounds.

The preparations of SbSBr yielded two products which, although clearly differing in appearance (orange and black), gave identical X-ray powder patterns. The preparative procedures for the two samples differed only slightly in that the reaction temperatures for $2\text{Sb} + 3\text{S} + \text{SbBr}_3 \rightarrow 3\text{SbSBr}$ were 250 and 280 °C for the black and orange samples, respectively. Whereas the orange sample gives a Mössbauer spectrum (Fig. 2) characteristic of a single Sb site the black material shows the presence of overlapping peaks. A least squares treatment of the composite spectrum revealed that one of the components is identical to that of the orange sample (*cf.* Table 1) and the other implies an impurity with a chemical shift (δ) of -11.9 ± 0.2 mm/s and line width ($\Gamma =$) 3.5 ± 0.2 mm/s; the quadrupole coupling constant (eQV_{zz}) con-

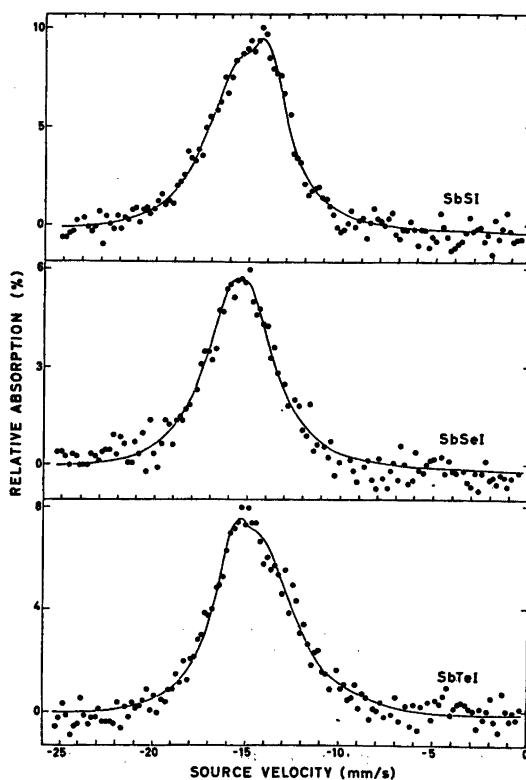


Fig. 1. ^{121}Sb Mössbauer spectra for SbSI, SbSeI, and SbTeI at 4.2 K. Curves show computer fitting to experimental points for parameters given in Table 1.

Table 1. ^{121}Sb Mössbauer (and NQR ^{111}In) parameters for SbSBr, SbSeBr, SbSI, SbSeI, and SbTeI. Chemical shifts with respect to $\text{Ba}^{121}\text{SnO}_3$, $(\text{Ca}^{121}\text{SnO}_3$ and $^{121}\text{SnO}_2$ for data quoted from Refs. 12 and 13, respectively.) Probable experimental errors in present data are ± 0.1 mm/s in δ , ± 0.5 mm/s in eQV_{zz} , and ± 0.2 mm/s in Γ .

Compound	T (K)	δ (mm/s)	eQV_{zz} (mm/s)	Γ (mm/s)	η	A (%)	Ref.
SbSBr	4.2	-14.9	10.4	2.9	0.14	4.9	Present
SbSBr	77	—	11.2	—	0.139	—	11
SbSBr	77	-14.6	—	5.2	—	—	12
SbSBr	77	-15.5	—	4.5	—	—	13
SbSeBr	4.2	-14.5	10.6	4.0	0	5.0	Present
SbSeBr	77	-14.6	—	5.2	—	—	12
SbSI	4.2	-14.8	12.3	3.0	0.31	9.5	Present
SbSI	77	-15.1	10.3	3.0	0.31	4.6	Present
SbSI	77	—	10.41	—	0.31	—	11
SbSI	77	-15.2	—	4.3	—	—	12
SbSI	77	-14.2	—	4.0	—	—	13
SbSeI	4.2	-14.9	6.4	3.1	~ 1	5.7	Present
SbSeI	77	-17.4	—	4.1	—	—	13
SbTeI	4.2	-14.0	-12.0	3.0	0.2	7.5	Present
SbTeI	77	-14.7	—	3.5	—	—	13

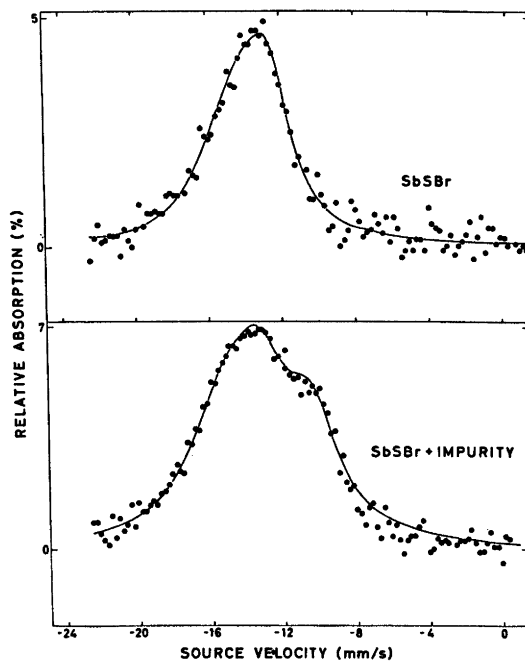


Fig. 2. ^{121}Sb Mössbauer spectra (at 4.2 K) of pure and impure SbSBr.

strained to zero. The latter parameters suggest that the impurity is antimony ($\delta = -11.5$ mm/s, $\Gamma = 2.85$ mm/s, and $eQV_{zz} = 0$ mm/s according to Ref. 19), *viz.* amorphous because its presence was undetected by X-ray diffraction. This illustrates the advantages of the Mössbauer technique in certain situations where impurity detection by other methods proves difficult.

The Mössbauer parameters [δ , eQV_{zz} , Γ , η (asymmetry parameter), and A (maximum absorption effect)] resulting from the least squares fittings are compiled in Table 1. Also included in the table are those values which have been previously reported from NQR and Mössbauer studies.

The crystal structures of the isostructural series SbXY , as typified by those reported ^{8,9} for SbSBr and SbSI, consist of Sb and X atoms arranged in pleated chains with Y atoms positioned outside. Fig. 3 depicts the coordination of Sb in SbXY based on data reported for SbSI above its ferroelectric transition temperature of 295 K. In the case of SbSI, at least, complicating features concern the structural changes below 295 K which destroy the centre of symmetry through displacements of the Sb

and S atoms in the direction of the crystallographic axes. The effect of these displacements are clearly reflected in the temperature dependencies of the NQR determined quadrupole coupling constant and asymmetry parameter.¹⁰ Additional complications in the description of the SbSI structure are caused by two further

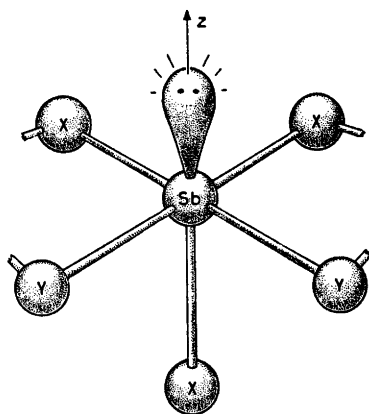


Fig. 3. Model showing the immediate environment of Sb in SbXY , the fully contented lone-pair pointing upwards.

anomalies recorded at 158 and 223 K in the NQR data. However, these presumably only concern finer structural details and because of the polymeric nature of SbSI it appears reasonable to suppose that the gross stereochemistry depicted in Fig. 3 represents a useful approximation at all temperatures. Thus, for the present purpose the immediate coordination symmetry of Sb in all compounds is taken to be C_s .

The chemical shifts for $SbXY$ (Table 1) are of the same order of magnitude as those reported^{20,21} for Sb_2X_3 and SbY_3 , being in every case closest to the value for the corresponding chalcogenide. This indicates that the chalcogen atoms have a greater effect on the antimony valence electrons than the halogen atoms. Moreover, the δ values indicate relatively high total s electron densities at the Sb nuclei and suggest that the Sb(III) non-bonding electrons in these compounds have considerable s character.

The valence orbitals on Sb transform under the operations of point group C_s as the irreducible representations $a'(5s)$, $a'(5p_y)$, $a'(5p_z)$, and $a''(5p_x)$. The direction of the Sb $5p_z$ atomic orbital may not coincide with the direction of the lone pair which probably consists of a mixture of $5p_z$, $5p_y$, and $5s$ (all with a' symmetry). Information concerning the distribution of Sb $5p$ electron density is contained in the quadrupole coupling constants. Since eQ for ^{121}Sb is negative the sign of the principal component of the electric field gradient V_{zz} is known. Apart from SbTeI all the compounds under consideration have positive eQV_{zz} . This would be consistent with the direction (z) of the principal component of the field gradient being aligned along the direction of the lone pair which contains an excess of p electron density. For the SbXI compounds V_{zz} increases in the order $SbSI < SbSeI < SbTeI$ becoming positive for $X=Te$. According to the crystal structures of SbSBr and SbSI the S-Sb-S bond angles should be close to 90° thus implying high p contributions to the Sb-S bonds. The Sb-S bond opposite to the lone pair is, however, considerably shorter than the others (cf. Ref. 9) which indicates a higher s contribution to this bond relative to the other two. The negative sign of V_{zz} for SbSI can be explained in terms of an excess of p electron density in

the lone pair at Sb. As may have been expected, the replacement of S by Se and Te has a pronounced effect on the electron distribution around Sb. Replacement by Se reduced the magnitude of V_{zz} although its negative value shows that there is still an excess of p electron density along the z direction of the principal component of the field gradient. Replacement by Te, however, causes a change in sign of eQV_{zz} ; the positive sign of V_{zz} arising from a p electron deficiency in some direction other than that of the lone pair. The lone pair must consequently have a p electron character similar to those found in some of the bond directions. It seems significant that the trend of decreasing eQV_{zz} follows the increase in size of X , which must have a major effect on the Sb-I bond because of the steric effect of the X atoms within the Sb-X chains. The presence of I together with a large chalcogen atom such as Te must also affect the nature of the Sb-X bonds particularly that opposite to the lone pair. The Sb-I bonds are long (e.g. 3.10 Å in the paraelectric versus 2.99 and 3.25 Å in the ferroelectric phase of SbSI) which may be indicative of considerable charge transfer. This suggestion would be in line with the small ^{127}I NQR determined¹¹ quadrupole coupling constant for SbSI. Such a charge transfer from Sb to I could be the cause of the deficiency of p -electron density of Sb in SbTeI and the decreasing ^{121}Sb coupling constant within the SbXI series. It seems likely, however, that the positive value of V_{zz} arises from a very long Sb-Te bond in the opposite direction to that of the lone pair. Such a bond would involve a relatively high use of Sb p electron density and produce a p electron deficiency in comparison with the other bond and lone pair directions. In the absence of complete structure determinations of SbSeI and SbTeI (now in progress) either of these interpretations must be regarded as tentative.

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