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Studies on Bond and Atomic Valences. I. Correlation Between Bond Valence and Bond Angles in Sb^{III} Chalcogen Compounds: The Influence of Lone-Electron Pairs

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Dedicated to Professor Heinz Schulz on the occasion of his 60th birthday

Abstract

In the present bond-valence concept the bond-valence parameter r_o is treated as constant for a given pair of atoms, and it is assumed that the bond valence s_{ij} is a function of the corresponding bond length D_{ij}, and that the atomic valence is an integer equal to the formal oxidation number ${}^{for}V_i$ derived from stoichiometry. However, from a statistical analysis of 76 $[Sb^{III}S_n]$ and 14 $[Sb^{III}Se_n]$ polyhedra in experimentally determined structures, it is shown that for $Sb^{III}—X$ bonds (X = S, Se), r_o is correlated with $\bar{\alpha}_i$, the average of the $X—Sb—X$ angles between the three shortest $Sb—X$ bonds. This is interpreted as a consequence of a progressive retraction of the 5*s* lone-electron pair from the Sb^{III} nucleus, which can be considered as continuous change of the actual atomic valence ${}^{act}V_i$ of Sb from +3 towards +5. A procedure is derived to calculate an effective atomic valence ${}^{eff}V_i$ of Sb^{III} from the geometry, $\bar{\alpha}_i$ and D_{ij}, of the $[Sb^{III}X_n]$ polyhedra, which approximates ${}^{act}V_i$ and is a better description of the actual valence state of Sb^{III} than the formal valence ${}^{for}V_i$. Calculated ${}^{eff}V_{Sb^{III}}$ are found to vary between +2.88 and +3.80 v.u. for $[Sb^{III}S_n]$ and between +2.98 and +3.88 v.u. for $[Sb^{III}Se_n]$ polyhedra. It is suggested that a corresponding modification of the present bond-valence concept is also required for other cations with lone-electron pairs.

1. Introduction

The bond-valence concept (BVC), first developed by Pauling (1929, 1947) and later improved in particular by Donnay & Allmann (1970), Brown & Shannon (1973), Brown & Altermatt (1985), Brese & O'Keeffe (1991) and O'Keeffe & Brese (1992), is widely and very successfully used to describe and interpret crystal structures.* In the BVC an inorganic structure is considered to be an arrangement of atoms of valence V which are linked by bonds between atoms whose valences have opposite signs. The valence V_i of an atom i is distributed over all the bonds between atom i and the atoms j of its environment according to the *valence-sum rule*

$$\sum_j s_{ij} = V_i, \tag{1}$$

where s_{ij} is called the *bond valence* of a particular bond. For each structure the sum of all positive valences is fully compensated by the sum of all negative valences (electroneutrality principle). The validity of (1) is independent of the specific definition of the term valence. It is common practice to set V equal to the oxidation number or *formal valence*, ${}^{for}V$,* of an atom so that it is an integer. If all bonds in a coordination polyhedron are symmetrically equivalent, the bond valence can be directly calculated from (1) provided V_i is known. For instance, in an undistorted $[AX_4]$ tetrahedron (A = 'cations', X = 'anions'†) each $A—X$ bond has a bond valence of $V_A/4$.

In particular, for geometrically distorted coordination polyhedra it has been shown that the bond valences s_{ij} are correlated with the lengths of the corresponding bonds D_{ij}. The most widely adopted formulation, among several empirical equations, used to describe the correlation between bond valence and bond length is

$$s_{ij} = \exp[(r_o - D_{ij})/b]. \tag{2}$$

Here r_o and b are two empirically determined parameters for a given $A—X$ pair, which have been termed bond-valence parameters. Combining (2) with (1) leads to

$$V_i = \sum_j \exp[(r_o - D_{ij})/b]. \tag{3}$$

* Excellent reviews of the present state of the BVC have recently been published by Brown (1992) and O'Keeffe (1992), which may be consulted for a more comprehensive presentation.

* Key for super- and subscripts: left-hand superscripts: for = formal, eff = effective, act = actual; left-hand subscripts: cal = calculated, i = index of an individual $[AX_n]$ polyhedron; right-hand subscripts: i, j = indices of atoms.

† Throughout this manuscript the terms 'cation' and 'anion' are used with quotation marks to indicate that corresponding atoms need not be fully ionized and nothing shall be said about the effective ionic charges of these 'ions' or the ionicity (covalency) of the bonds between them.

From a statistical analysis, based on $V = {}^{\text{for}}V$, of all at that time available accurately determined individual $[AX_n]$ groups, Brown & Altermatt (1985) found that b is approximately 0.37 Å and varies very little for all $[AX_n]$ groups, both for those of the same A—X pair and those of different A—X pairs. By assuming $b = 0.37$ Å they found that for each individual polyhedron $[AX_n]$ of a given A—X pair the values of

$$ {}^{\text{for}}_{i}r_o = b \ln[{}^{\text{for}}V_i / \sum_j \exp(-D_{ij}/b)], \qquad (4) $$

which are of the order of the average A—X bond lengths, vary generally by no more than 0.05 Å. Their tabulated values of r_o, averaged over all ${}^{\text{for}}_{i}r_o$ values of a given A—X pair, are widely used and considered as constants. Brese & O'Keeffe (1991) and O'Keeffe & Brese (1992) have performed similar statistical analyses and added lists of bond-valence parameters r_o for a large number of other A—X as well as X—X pairs. For the majority of inorganic compounds these bond-valence parameters lead to interpretations of experimentally determined bonding geometry, which are in agreement with present crystal chemical knowledge. Atomic valences ${}^{\text{for}}_{\text{cal}}V$, calculated with (3) using the tabulated r_o values and $b = 0.37$ Å, generally deviate by no more than 0.2 v.u. from their (integer) ${}^{\text{for}}V$ value, while deviations, $\Delta V_i = |{}^{\text{for}}_{\text{cal}}V_i - {}^{\text{for}}V_i|$, of up to *ca* 0.1 v.u. are usually assigned to uncertainties in the experimentally determined bond lengths of a correct structure. Larger deviations, if not due to an incorrect structure, have been ascribed to bond strain caused by steric or electronic effects (Brown, 1991; Withers, Thompson & Rae, 1991).

However, during crystal structure analysis of synthetic $K_6[Sb_{12}O_{18}][SbSe_3]_2 \cdot 6H_2O$ (Wang & Liebau, 1991, 1995) and subsequent inspection of other Sb^{III} chalcogen compounds (Wang & Liebau, 1993, 1994*a*; Liebau & Wang, 1993) we found that

(1) deviations $\Delta V_{Sb^{III}}$ up to 0.7 v.u. occur which could not be accounted for by experimental errors only;

(2) bond-valence parameters of individual $[SbX_n]$ polyhedra, ${}^{\text{for}}_{i}r_o$, calculated from literature data for Sb^{III}—X bonds (X = S, Se) are strongly correlated with the X—Sb—X angles rather than being constant.

The present paper reports on the statistical analysis used to derive the bond valences as functions of both bond lengths and bond angles for compounds with $[Sb^{III}X_n]$ polyhedra, X = S, Se, and the attribution of these correlations to the stereochemical influence of the lone-electron pair of Sb^{III}. These correlations are used to derive non-integer effective valences of Sb^{III} which approximate the actual valence state of these atoms in thio and seleno compounds.

2. Procedure

76 $[Sb^{III}S_n]$ and 14 $[Sb^{III}Se_n]$ groups, which can be considered as ψ-$[SbX_3]$ tetrahedra (ψ representing a missing ligand of the tetrahedron) complemented by between 0 and 5 additional X 'ions' with longer Sb—X distances, have been used for the statistical analysis. For each of these groups, most of which have been taken from the literature, we have calculated a ${}^{\text{for}}_{i}r_o$ value from (4) by setting $b = 0.37$ Å and ${}^{\text{for}}V_{Sb^{III}} = +3$ v.u., as commonly accepted, and by including all Sb—X distances up to 4.2 Å for each individual coordination environment. Distances longer than 3.4 Å were found to contribute a total of less than 0.021 Å to ${}^{\text{for}}_{i}r_o$ of any polyhedron. To keep the number of variables that might have an influence on ${}^{\text{for}}_{i}r_o$ as small as possible, we restricted the choice to the compounds in which the only cations other than Sb are alkali or alkali earth elements, NH_4^+, $(CH_3NH_3)^+$ or Tl^+ (Table 1*a*). In Fig. 1 the ${}^{\text{for}}_{i}r_o$ values calculated for the $[Sb^{III}X_n]$ polyhedra are plotted *vs* $\cos\bar{\alpha}_i$, where $\bar{\alpha}_i$ is the average of the three X—Sb—X angles of an individual ψ-$[SbX_3]$ tetrahedron.

3. Results

Although within the current BVC r_o is treated as constant for a given 'anion'–'cation' pair, Fig. 1 clearly demonstrates that for $[Sb^{III}X_n]$ polyhedra with X = S and Se, r_o is correlated with the bond angle $\bar{\alpha}_i$. As a first approximation the data points can be fitted to functions of the type

$$ {}^{\text{for}}_{i}r_o = P\cos\bar{\alpha}_i + Q. \qquad (5) $$

Substitution of (5) in (3) leads to

$$ {}^{\text{for}}_{\text{cal}}V_i = \sum_j \exp[(P\cos\bar{\alpha}_i + Q - D_{ij})/b]. \qquad (6) $$

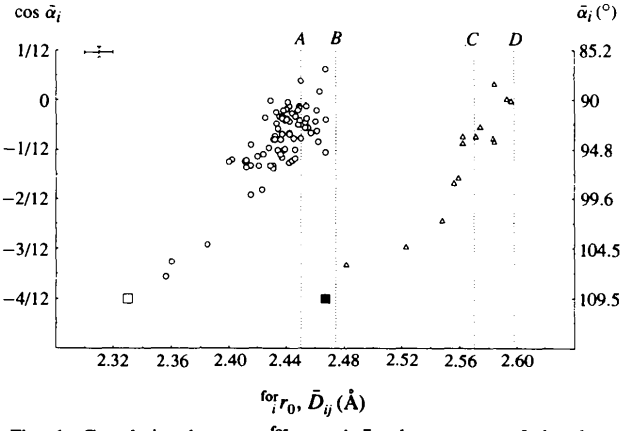

Fig. 1. Correlation between ${}^{\text{for}}_{i}r_o$ and $\bar{\alpha}_i$, the average of the three X—Sb—X angles of an individual ψ-$[SbX_3]$ tetrahedron: ○ – $[Sb^{III}S_n]$ groups and △ – $[Sb^{III}Se_n]$ groups. The broken lines indicate the r_o values tabulated by Brese & O'Keeffe (1991): *A*, *C*; Brown & Altermatt (1985): *B*; Skowron & Brown (1990): *D*. □, ■ – averaged bond lengths and bond angles from Table 1(*b*) for $[Sb^VS_4]$ and $[Sb^VSe_4]$ tetrahedra, respectively. The error bars inserted in the upper left corner of the plot are the estimated upper limits for each of the data points because experimental errors of D_{ij} and α_i are smaller than 0.01 Å and 0.5°, respectively.

Table 1. *Data for $[Sb^{III}X_n]$ and $[Sb^{V}X_4]$ groups*

(*a*) $[Sb^{III}S_n]$ and $[Sb^{III}Se_n]$ groups plotted in Figs. 1 and 3

Central atoms	Bond lengths D_{ij} (Å)								$^{for}r_o$ (Å)	$\tilde{\alpha}_i$ (°)	$^{for}_{cal}V_i$ [equation (6)]	$^{eff}V(\tilde{\alpha}_i)$ [equation (8)]	$^{eff}V(\tilde{\alpha}_i, D_{ij})$ [equation (9)]
Sb_2S_3 (Bayliss & Nowacki, 1972)													
Sb1	2.522	2.540	2.540	3.110	3.110	3.167	3.641		2.461	91.0	2.90	3.04	2.95
Sb2	2.456	2.678	2.678	2.854	2.854	3.373	3.373	4.189	2.463	89.2	2.97	2.97	2.95
$NaSbS_2$ (Olivier-Fourcade, Philippot & Maurin, 1978)													
Sb1	2.431	2.431	2.774	2.774	3.412	3.412			2.439	92.0	3.04	3.08	3.12
$Na_{3.6}(Sb_2O_3)_3[SbS_3](OH)_{0.6}.2.4H_2O$ (Sabelli, Nakai & Katsura, 1988)													
Sb1	2.385	2.385	2.385						2.385	104.1	3.01	3.54	3.53
$(Na,K)_{3+x}(Sb_2O_3)_3[SbS_3](OH)_x.(2.8-x)H_2O$ (Sabelli, Nakai & Katsura, 1988)													
Sb1	2.356	2.356	2.356						2.356	107.3	3.12	3.67	3.80
$KSbS_2$ (Graf & Schäfer, 1975*a*)													
Sb1	2.412	2.412	2.756	2.756	3.894	3.894			2.434	92.8	3.05	3.11	3.16
$K_2Sb_4S_7.H_2O$ (Eisenmann & Schäfer, 1979)													
Sb1	2.409	2.531	2.681	2.877	3.105	3.707			2.453	92.7	2.90	3.10	3.00
Sb2	2.437	2.461	2.461	3.091	3.280	3.708			2.415	94.3	3.15	3.17	3.32
Sb3	2.426	2.489	2.552	2.993	3.249	3.478	4.106		2.432	93.5	3.04	3.13	3.17
Sb4	2.406	2.473	2.665	2.765	3.799				2.440	90.9	3.08	3.03	3.12
$K_3(Sb_2O_3)_3[SbS_3]$ (Graf & Schäfer, 1975*b*)													
Sb1	2.360	2.360	2.360						2.360	105.8	3.15	3.61	3.77
$Rb_2Sb_4S_7$ (Sheldrick & Häusler, 1988*b*)													
Sb1	2.404	2.441	2.716	2.797	3.795	3.865			2.440	91.8	3.04	3.07	3.12
Sb2	2.407	2.475	2.611	2.852	3.706	3.728			2.437	91.8	3.07	3.07	3.14
$Cs_2Sb_4S_7$ (Dittmar & Schäfer, 1978)													
Sb1	2.392	2.477	2.501	3.162	3.802	3.936			2.431	96.6	2.93	3.25	3.16
Sb2	2.417	2.488	2.536	2.997	3.661	4.175			2.442	93.2	2.97	3.12	3.09
Sb3	2.453	2.500	2.637	2.739	3.624	3.826	3.996		2.449	92.0	2.96	3.08	3.04
Sb4	2.408	2.431	2.494	3.166	3.695	4.078			2.420	95.4	3.06	3.21	3.26
$Cs_4Sb_{14}S_{23}$ (Kanishcheva, Kuznetsov, Mikhailov, Batog & Skorikov, 1980)													
Sb1	2.439	2.525	2.541	3.053	3.128	3.583	4.041		2.444	91.3	3.03	3.05	3.08
Sb2	2.434	2.510	2.537	3.116	3.123	3.506	4.013		2.440	91.9	3.04	3.07	3.12
Sb3	2.439	2.485	2.496	3.085	3.291	3.419			2.429	96.3	2.96	3.24	3.18
Sb4	2.419	2.432	2.638	2.971	3.695	4.025			2.446	91.6	3.00	3.06	3.06
Sb5	2.425	2.499	2.514	3.072	3.164	3.622			2.431	93.8	3.04	3.15	3.18
Sb6	2.417	2.420	2.461	3.590	3.629	3.692	3.794		2.415	96.3	3.08	3.24	3.30
Sb7	2.430	2.504	2.520	3.105	3.161	3.643			2.437	93.3	3.00	3.13	3.13
Sb8	2.398	2.523	2.564	3.135	3.168	3.684	3.899		2.442	93.3	2.96	3.13	3.09
Sb9	2.417	2.450	2.639	2.976	3.520	4.000	4.182		2.448	91.0	3.01	3.04	3.05
Sb10	2.426	2.517	2.608	3.082	3.191	3.709			2.462	94.0	2.78	3.15	2.92
Sb11	2.424	2.478	2.516	3.007	3.557	3.614			2.432	93.8	3.03	3.15	3.18
Sb12	2.425	2.465	2.553	3.030	3.568	3.671	4.115		2.439	94.7	2.94	3.18	3.12
Sb13	2.419	2.422	2.461	3.405	3.566	3.617	3.971		2.412	96.5	3.08	3.25	3.33
Sb14	2.406	2.544	2.562	3.088	3.107	3.742	3.860		2.445	93.7	2.93	3.14	3.06
$(NH_4)SbS_2$ (Volk, Bickert, Kolmer & Schäfer, 1979)													
Sb1	2.395	2.420	2.685	2.926	4.057				2.442	96.0	2.86	3.23	3.07
Sb2	2.415	2.425	2.629	2.910	4.020	4.038	4.081		2.436	93.8	2.99	3.15	3.13
$(NH_4)_2Sb_4S_7$ (Dittmar & Schäfer, 1977*a*)													
Sb1	2.395	2.497	2.510	3.477	3.501	3.886			2.446	95.6	2.85	3.22	3.04
Sb2	2.465	2.507	2.525	3.037	3.193	3.697			2.449	90.8	3.01	3.03	3.04
Sb3	2.443	2.479	2.520	3.114	3.251	3.568			2.438	91.0	3.09	3.04	3.14
Sb4	2.403	2.448	2.477	3.485	3.597	3.752	4.020		2.424	95.2	3.04	3.20	3.23
$(CH_3NH_3)_2Sb_8S_{13}$ (Wang & Liebau, 1994*a*)													
Sb1	2.446	2.454	2.526	3.042	3.293	3.681	3.821		2.429	90.1	3.21	3.00	3.22
Sb2	2.465	2.504	2.564	3.062	3.100	3.803	3.884		2.454	91.8	2.93	3.07	3.00
Sb3	2.463	2.497	2.502	3.037	3.470	3.749	3.933		2.446	94.8	2.88	3.18	3.05
Sb4	2.410	2.554	2.656	2.855	3.278	3.621	3.989		2.457	93.2	2.85	3.12	2.96
Sb5	2.392	2.490	2.497	3.480	3.602	3.721	3.794		2.436	95.2	2.94	3.20	3.12
Sb6	2.433	2.499	2.530	2.997	3.252	3.651	3.747		2.433	92.3	3.08	3.09	3.17
Sb7	2.444	2.450	2.457	3.309	3.529	3.690	4.013	4.155	2.425	91.7	3.17	3.07	3.24
Sb8	2.429	2.450	2.488	3.282	3.529	4.113	4.161		2.433	91.2	3.13	3.05	3.17
$TlSbS_2$ (Rey, Jumas, Olivier-Fourcade & Philippot, 1983)													
Sb1	2.405	2.448	2.602	2.961	3.690	4.018			2.438	94.8	2.94	3.18	3.11
Sb2	2.433	2.456	2.710	2.812	3.702	3.839	3.967		2.453	92.2	2.92	3.08	3.00
$TlSb_3S_5$ (Gostojic, Nowacki & Engel, 1982)													
Sb1	2.429	2.468	2.568	3.067	3.273	3.492	3.985		2.437	95.5	2.92	3.21	3.12
Sb2	2.438	2.519	2.635	2.849	3.167	3.646	4.025		2.449	90.6	3.02	3.02	3.05
Sb3	2.448	2.490	2.605	3.001	3.343	3.718	4.185		2.460	92.1	2.87	3.08	2.95
$TlSb_5S_8$ (Engel, 1980)													
Sb1	2.441	2.636	2.737	2.745	2.764	3.447	3.710		2.442	90.6	3.08	3.02	3.11
Sb2	2.465	2.515	2.595	2.995	3.369	3.537	3.795		2.467	95.0	2.71	3.19	2.88
Sb3	2.464	2.498	2.634	2.875	3.673	3.801	3.834	4.057	2.467	91.9	2.83	3.07	2.89
Sb4	2.489	2.512	2.552	2.949	2.981	3.674	3.695		2.441	90.2	3.10	3.01	3.11
Sb5	2.429	2.500	2.533	3.070	3.172	3.585	3.796		2.434	94.8	2.97	3.18	3.15
Sb6	2.405	2.520	2.647	2.896	3.202	3.536	3.689		2.442	92.1	3.01	3.08	3.09
Sb7	2.416	2.467	2.527	3.196	3.424	3.570	3.861		2.433	92.3	3.08	3.09	3.17

Table 1 (*cont.*)

(*a*) [$Sb^{III}S_n$] and [$Sb^{III}Se_n$] groups plotted in Figs. 1 and 3

Central atoms	Bond lengths D_{ij} (Å)								$^{for}_{i}r_o$ (Å)	$\tilde{\alpha}_i$ (°)	$^{for}_{cal}V_i$ [equation (6)]	$^{eff}V(\tilde{\alpha}_i)$ [equation (8)]	$^{eff}V(\tilde{\alpha}_i, D_{ij})$ [equation (9)]
$TlSb_3S_8$ (Engel, 1980)													
Sb8	2.474	2.481	2.500	3.102	3.351	3.703	3.867		2.444	95.8	2.85	3.22	3.05
Sb9	2.433	2.466	2.498	3.202	3.612	3.880	3.981	4.027	2.437	91.6	3.08	3.06	3.14
Sb10	2.447	2.514	2.702	2.844	3.188	3.396	3.617	4.130	2.454	90.6	2.98	3.02	3.00
Tl_3SbS_3 (Rey, Jumas, Olivier-Fourcade & Philippot, 1984)													
Sb1	2.430	2.430	2.430	3.601	3.601	3.601			2.415	99.2	2.96	3.35	3.30
$Ca_2Sb_2S_5$ (Cordier & Schäfer, 1981)													
Sb1	2.428	2.528	2.540	3.138	3.154	3.726	4.133		2.450	88.2	3.11	2.93	3.05
Sb2	2.442	2.457	2.465	3.240	3.287	3.476			2.421	96.3	3.02	3.24	3.25
$SrSb_4S_7.6H_2O$ (Cordier, Schäfer & Schwidetzky, 1984)													
Sb1	2.414	2.530	2.541	3.196	3.220	3.735	3.834		2.450	93.7	2.89	3.14	3.02
Sb2	2.405	2.470	2.480	3.234	3.648	4.013	4.122		2.428	94.6	3.03	3.18	3.20
Sb3	2.472	2.495	2.534	3.106	3.111	3.743	3.831		2.448	92.4	2.95	3.09	3.04
Sb4	2.432	2.570	2.681	2.819	3.125	3.636	3.704		2.461	93.0	2.83	3.12	2.94
$Sr_2Sb_2S_5.15H_2O$ (Cordier, Schäfer & Schwidetzky, 1985)													
Sb1	2.383	2.405	2.496	4.027					2.423	98.7	2.91	3.33	3.22
$BaSb_2S_4$ (Cordier, Schwidetzky & Schäfer, 1984)													
Sb1	2.450	2.456	2.468	3.298	3.478	3.613	4.116		2.431	96.3	2.93	3.24	3.16
Sb2	2.402	2.511	2.551	3.004	3.424	3.477	3.964		2.435	91.6	3.09	3.06	3.16
Sb3	2.488	2.603	2.695	2.718	2.985	3.679	3.770		2.467	87.0	3.01	2.88	2.92
Sb4	2.421	2.501	2.693	2.843	3.376	3.750	3.932	4.146	2.455	92.7	2.86	3.10	2.98
$Ba_8Sb_6S_{17}$ (Dörrscheidt & Schäfer, 1981)													
Sb1	2.399	2.433	2.443	3.291	4.064				2.411	95.9	3.11	3.23	3.34
Sb2	2.391	2.434	2.469	3.171	3.276				2.402	95.7	3.20	3.22	3.43
Sb3	2.412	2.415	2.450	3.336	3.841				2.412	95.8	3.11	3.22	3.33
Sb4*	2.356	2.413	2.425	3.304	3.704				2.383	94.6			
Sb5*	2.394	2.413	2.637	2.708	3.225	3.889			2.392	90.3			
Sb6	2.405	2.423	2.423	3.282	3.591				2.400	95.9	3.21	3.23	3.44
Sb_2Se_3 (Voutsas, Papazoglou, Rentzeperis & Siapkas, 1985)													
Sb1	2.664	2.678	2.678	3.215	3.215	3.247	3.739		2.593	89.9	3.00	3.00	3.00
Sb2	2.588	2.803	2.803	3.007	3.007	3.486	3.486		2.596	90.1	2.97	3.00	2.98
$Na_3(Sb_2O_3)_3[SbSe_3].0.5Sb(OH)_3$ (Kluger & Pertlik, 1985)													
Sb1	2.481	2.481	2.481						2.481	106.1	3.23	3.62	3.88
$KSbSe_2$ (Dittmar & Schäfer, 1977*b*)													
Sb1	2.531	2.553	2.804	3.072	3.949				2.574	92.6	3.04	3.10	3.14
Sb2	2.548	2.563	2.807	2.988	3.940	4.019	4.090		2.571	93.5	3.02	3.13	3.15
$K_3(Sb_2O_3)_3[SbSe_3].3H_2O$ (Wang & Liebau, 1995)													
Sb1	2.523	2.523	2.523						2.523	104.3	2.96	3.55	3.48
$RbSb_3Se_5$ (Sheldrick & Häusler, 1988*a*)													
Sb1	2.535	2.607	2.635	3.345	3.427	3.869	3.973		2.556	98.0	2.96	3.31	3.24
Sb2	2.560	2.569	2.756	3.055	3.459	3.728	3.909		2.562	93.5	3.10	3.13	3.23
Sb3	2.584	2.604	2.729	3.103	3.486	3.836	4.051		2.583	93.7	2.92	3.14	3.05
$BaSb_2Se_4$ (Cordier & Schäfer, 1979)													
Sb1	2.579	2.586	2.601	3.413	3.493	3.652			2.559	97.5	2.95	3.29	3.22
Sb2	2.558	2.653	2.848	2.919	3.307	3.850	3.952		2.584	94.0	2.89	3.15	3.04
Sb3	2.550	2.665	2.673	3.098	3.297	3.506	4.051		2.562	94.1	3.07	3.16	3.22
Sb4	2.610	2.703	2.805	2.848	3.124	3.717	3.916		2.584	88.5	3.14	2.94	3.09
$[Ba(en)_2]_3[SbSe_3]_2$ (König, Eisenmann & Schäfer, 1984)													
Sb1	2.548	2.548	2.548						2.548	101.7	2.87	3.45	3.28

(*b*) [$Sb^{V}X_4$] tetrahedral groups used in Fig. 1

Central atoms	Individual bond lengths D_{ij} (Å)				Average D_{ij} (Å)	Individual bond angles X—Sb—X α_i (°)	Average α_i (°)
$(NH_4)_3SbS_4$ (Graf & Schäfer, 1976)							
Sb	2.35	2.35	2.35	2.35	2.35	109.5 (6×)	109.5
K_3SbS_4 (Graf & Schäfer, 1976)							
Sb	2.32	2.32	2.32	2.32	2.32	109.5 (6×)	109.5
Na_3SbS_4 (Graf & Schäfer, 1976)							
Sb	2.32	2.32	2.32	2.32	2.32	109.5 (6×)	109.5
$Na_3SbS_4.9H_2O$ (Mereiter & Preisinger, 1979)							
Sb	2.326	2.330	2.330	2.330	2.329	108.4 (3×) 110.5 (3×)	109.5
$Na_3SbS_4.9D_2O$ (Mereiter & Preisinger, 1979)							
Sb	2.331	2.320	2.320	2.320	2.326	108.7 (3×) 110.3 (3×)	109.5
Average					2.329		109.5
K_3SbSe_4 (Eisenmann & Zagler, 1989)							
Sb	2.473	2.475	2.475	2.475	2.475	109.4 (3×) 109.6 (3×)	109.5
Na_3SbSe_4 (Eisenmann & Zagler, 1989)							
Sb	2.459	2.459	2.459	2.459	2.459	109.5 (6×)	109.5
Average					2.467		109.5

* Excluded since both the Sb atoms and the S atom connecting them have abnormally high displacement parameters.

Table 2. *Values of bond-valence parameters P and Q of (5), calculated by minimization of (7), and P′ and Q′ derived by minimization of (10).*

N = number of $[SbX_n]$ polyhedra used. Numbers in parentheses are standard deviations in the last significant digit.

Bond	N	Q(Å)	P(Å)	R	Q'(Å)	P'(Å)
Sb^{III}—S	76	2.455(3)	0.28(2)	0.79	2.455(2)	0.04(2)
	135	2.464(3)	0.38(5)	0.60	2.463(3)	0.10(5)
Sb^{III}—Se	14	2.592(5)	0.30(4)	0.90	2.593(6)	0.06(4)

The respective P and Q values were derived by minimization of

$$\sum_{i=1}^{N}({}^{\text{for}}V_{Sb^{III}} - {}^{\text{for}}_{\text{cal}}V_i)^2 = \sum_{i=1}^{N}\{3 - \sum_j \exp[(P\cos\bar{\alpha}_i + Q - D_{ij})/b]\}^2, \quad (7)$$

where N is the number of $[Sb^{III}X_n]$ polyhedra ($N = 76$ for $X = S$, $N = 14$ for $X = Se$), ${}^{\text{for}}V_{Sb^{III}} = +3$ v.u. and $b = 0.37$ Å. The resulting values of P and Q are listed in Table 2. Valences ${}^{\text{for}}_{\text{cal}}V_i$ of Sb^{III} calculated with these P and Q values and (6) vary between +2.71 and +3.21 v.u. for $X = S$ and between +2.87 and +3.23 v.u. for $X = Se$, with mean deviations of 0.083 (2.8%) and 0.077 v.u. (2.6%), respectively (Table 1*a*).

Considering that several of the polyhedra with high α_i values used for the analyses (Fig. 1, Table 1) are from structures that are very similar [cetineite-type structures (Wang & Liebau, 1994*b*)] and exhibit problems with regard to valence compensation between nearest neighbours, we repeated the statistical analysis with a set of 135 $[Sb^{III}S_n]$ polyhedra having $\bar{\alpha}_i \leq 99°$. Most of these data were extracted from the Inorganic Crystal Structure Database ICSD, others were added from more recently published and unpublished structures. The corresponding P and Q values are also given in Table 2. Although in this extended data set the restrictions mentioned in the previous chapter with regard to the chemical composition of the compounds have been dropped, the results confirm that ${}^{\text{for}}_i r_o$ is correlated with $\bar{\alpha}_i$, although with a lower value of the correlation coefficient R which is 0.60 compared with $R = 0.79$ for the smaller set of 76 polyhedra.

Consequently, the calculated valence, ${}^{\text{for}}_{\text{cal}}V(D_{ij}, \bar{\alpha}_i)$, of Sb^{III} in thio and seleno compounds is a function of both bond lengths and angles rather than solely of bond lengths, as assumed in the present BVC.

Instead of correlating ${}^{\text{for}}_i r_o$ with D_{ij} and $\bar{\alpha}_i$ using the constant value $b = 0.37$ Å, one could consider to analyse the data by varying b and keeping r_o constant, *i.e.* ${}^{\text{for}}V(D_{ij}, b)$. Using the data sets of Table 1 the best fit is obtained with $r_o = 2.371$ and $b = 0.5415$ Å (mean deviation 0.072 v.u., 2.4%) for 76 $[Sb^{III}S_n]$ and $r_o = 2.516$ and $b = 0.4982$ Å (mean deviation 0.077 v.u., 2.6%) for 14 $[Sb^{III}Se_n]$ polyhedra, respectively.

In fact, both treatments led to almost the same mean deviations of ${}^{\text{for}}_{\text{cal}}V_{Sb^{III}}$ from ${}^{\text{for}}V_{Sb^{III}} = +3$. Since at present no straightforward interpretation of b in terms of physical or chemical parameters seems to be available, whereas the bond angles α_i are structural data which can be linked to the electronic structure of the Sb^{III} atoms (see next paragraph), we prefer to treat r_o as variable and dependent on $\bar{\alpha}_i$.

4. Interpretation

4.1. *The role of the lone-electron pair of* Sb^{III}

The general observation that the bond lengths (A—X) are correlated with bond angles X—A—X in $[AX_n]$ polyhedra, in which A is a 'cation' having one or several lone-electron pairs (LEP), is usually explained by the stereochemical influence of the LEP (*e.g.* Galy, Meunier, Andersson & Aström, 1975; Trömel, 1980). Brown (1974) already observed a correlation between individual bond angles X—A—X and the average of the bond valences of the two defining A—X bonds. Since trivalent antimony has a LEP, it seems reasonable to assume that in $[Sb^{III}X_n]$ polyhedra the LEP of Sb^{III} are responsible for the correlation between ${}^{\text{for}}_i r_o$ and $\cos\bar{\alpha}_i$ documented in Fig. 1 and described by (5).

If the three 5*p* bonding electron pairs and the 5*s* LEP of Sb^{III} in ψ-$[SbX_3]$ tetrahedra are assumed to be fully sp^3 hybridized, then the average bond angle $\bar{\alpha}_i$ would be 109.5°. In the actual crystal structures the average angles $\bar{\alpha}_i$ are less than 109.5° due to the repulsion between the LEP and the three bonding electron pairs. The nearer the LEP to the Sb nucleus the stronger the repulsion and the smaller the $\bar{\alpha}_i$ angles (Fig. 2).

From Table 1(*a*) it can be seen that each of the known $[SbX_n]$ polyhedra with rather large $\bar{\alpha}_i$ values has three short Sb—X bonds of equal length (these polyhedra have in fact trigonal symmetry) and no complementing 'anions' within $D_{ij} \leq 4.2$ Å. Consequently, for these polyhedra (4) reduces to

$${}^{\text{for}}_i r_o = b\ln({}^{\text{for}}V_{Sb^{III}}/3) + D_{ij} = D_{ij}$$

Fig. 1 shows that for both $X = S$ and Se, $D_{ij}[Sb^{III}$—$X]$ approaches $D_{ij}[Sb^{V}$—$X]$ (Table 1*b*) as $\bar{\alpha}_i$ approaches 109.5°. This suggests that the progressive retraction of

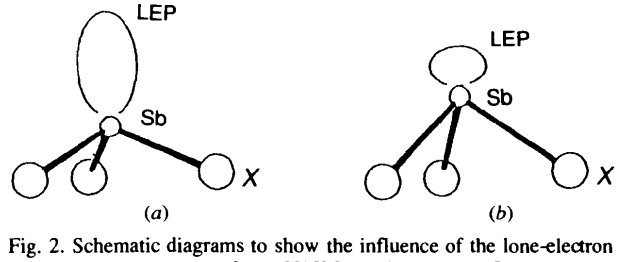

Fig. 2. Schematic diagrams to show the influence of the lone-electron pair on the geometry of a ψ-$[SbX_3]$ tetrahedron: (*a*) $\bar{\alpha}_i \approx 110°$ and (*b*) $\bar{\alpha}_i \approx 90°$.

the LEP from the Sb nucleus should be considered as a continuous change of the 'actual' valence of Sb^{III} from +3 to +5, the latter value being reached at complete dissociation of the LEP.

4.2. *Reflections on atomic valence*

Profound discussions of the term valence shall not be attempted here. Instead, we shall restrict ourselves to two specific properties of atoms in a compound.

(1) The *formal valence* ${}^{for}V$ or *oxidation number* is the number of fictitious positive or negative charges of an atom in a compound if the compound is assumed to be composed of ions and if the formal valence of hydrogen is assumed to be 1. It is usually an integer derived formally from the stoichiometry of the compound.

(2) As the *actual valence* ${}^{act}V$ of an atom in a compound we consider the number of electrons the atom transfers in time average to its neighbours (electron acquisition is considered a negative transfer). Since in a compound electrons are only partially transferred from one atom to another, actual valences will generally be non-integer.

Although accurate determination of the actual valence may be extremely difficult it is, nevertheless, the property that describes the chemical state of an atom in a compound most realistically. Any theoretical or experimental method to determine ${}^{act}V$ should, therefore, be welcome. In the following paragraph an empirical procedure to derive at least an estimate of ${}^{act}V$ for antimony in thio- and selenoantimonates(III) is developed.

4.3. *Determination of an effective valence*

The calculation of ${}^{for}V_i$ for Sb^{III} with the aid of (6) and the P and Q values from Table 2 is based on the assumptions that $V_{Sb^{III}} = +3$ v.u., the valences of the other 'cations' and 'anions' in the structure are also equal to their formal integer valences and that $b = 0.37$ Å. The calculated values ${}^{for}_{cal}V_i$, therefore, scatter around +3, the formal oxidation number of Sb^{III} (Table 1*a*).

The correlation between ${}^{for}_{i}r_o$ and $\cos\bar{\alpha}_i$ (Fig. 1) and its interpretation as a consequence of a continuous change of the actual valence of Sb offers a possibility to scale the atomic valence of Sb^{III} such that an *effective bond valence* ${}^{eff}s$ and an *effective atomic valence* ${}^{eff}V$ are derived which are reasonable estimates of the actual valences ${}^{act}s$ and ${}^{act}V$, respectively.

If the values of ${}^{eff}s$ and ${}^{eff}V$ are obtained from the average bond angles, $\bar{\alpha}_i$, of individual polyhedra, then they are defined for individual polyhedra. Therefore, their full symbols are ${}^{eff}s(\bar{\alpha}_i)$ and ${}^{eff}V(\bar{\alpha}_i)$.

To scale ${}^{eff}V(\bar{\alpha}_i)$, two 'end-member' cases are considered.

(1) $\bar{\alpha}_i = 90°$: The majority of $[Sb^{III}X_n]$ polyhedra have $\bar{\alpha}_i$ values slightly larger than 90°, while only very few have $\bar{\alpha}_i < 90°$ (Fig. 1). This is considered to imply that the smallest retraction of the LEP from the Sb^{III} nucleus is approached in $[Sb^{III}X_n]$ polyhedra having $\bar{\alpha}_i = 90°$. We therefore consider that it is reasonable to assume ${}^{eff}V_{Sb^{III}}(\bar{\alpha}_i) = {}^{for}V_{Sb^{III}} = +3$ v.u. for such polyhedra.

(2) $\bar{\alpha}_i = 109.5°$: From Fig. 1 it has been deduced that $D_{ij}[Sb^{III}—X]$ approaches $D_{ij}[Sb^{V}—X]$ as $\bar{\alpha}_i$ approaches 109.5°. This is interpreted as indicating that at $\bar{\alpha}_i = 109.5°$ corresponding $Sb^{III}—X$ and $Sb^{V}—X$ bonds are of equal effective valence. Since in a ψ-$[Sb^{III}X_3]$ tetrahedron with $\bar{\alpha}_i \approx 109.5°$ there are only three $Sb^{III}—X$ bonds of non-negligible strength (Table 1*a*), it is reasonable to assume that for such polyhedra ${}^{eff}V_{Sb^{III}}(\bar{\alpha}_i) = 3/4\,{}^{eff}V_{Sb^{V}} = 3/4\,{}^{for}V_{Sb^{V}} = 3.75$ v.u.

As a first approximation it is suggested that for other values of $\bar{\alpha}_i$, the effective atomic valence ${}^{eff}V(\bar{\alpha}_i)$ of antimony in a $[Sb^{III}X_n]$ polyhedron can be obtained by linear interpolation according to

$$\begin{aligned} {}^{eff}V_{Sb^{III}}(\bar{\alpha}_i) &= 3 + [(3.75 - 3)/(109.5 - 90)](\bar{\alpha}_i - 90) \\ &= 3[1 + 0.0128(\bar{\alpha}_i - 90)]. \end{aligned} \tag{8}$$

This equation, which does not explicitly contain the experimental bond lengths D_{ij}, allows the estimation of the actual valence of Sb^{III} from $\bar{\alpha}_i$, the average of the three experimental bond angles of the ψ-$[SbX_3]$ tetrahedra for both X = S and Se. The values of ${}^{eff}V_{Sb^{III}}(\bar{\alpha}_i)$ calculated with (8) are given in Table 1(*a*).

Effective bond valences for *individual bonds*, ${}^{eff}s(\bar{\alpha}_i, D_{ij})$ and their corresponding effective atomic valences ${}^{eff}V(\bar{\alpha}_i, D_{ij})$ can be derived from

$$\begin{aligned} {}^{eff}V(\bar{\alpha}_i, D_{ij}) &= \sum_j {}^{eff}s(\bar{\alpha}_i, D_{ij}) \\ &= \sum_j \exp[(P' \cos\bar{\alpha}_i + Q' - D_{ij})/b], \end{aligned} \tag{9}$$

which has the same form as (6). The parameters P' and Q' have been derived by minimization of

$$\begin{aligned} &\sum_{i=1}^{N}[{}^{eff}V_{Sb^{III}}(\bar{\alpha}_i) - \sum_j {}^{eff}s(\bar{\alpha}_i, D_{ij})]^2 \\ &\quad = \sum_{i=1}^{N}\{3[1 + 0.0128(\bar{\alpha}_i - 90)] \\ &\qquad - \sum_j \exp[(P' \cos\bar{\alpha}_i + Q' - D_{ij})/b]\}^2 \end{aligned} \tag{10}$$

by analogy with (7).

The values of P' and Q', for both data sets of $[Sb^{III}S_n]$ polyhedra, are given in Table 2. The fact that for the smaller data set $P' \approx 0$ indicates that the influence of α_i on the bond-valence parameter r_o has been properly taken into account by the procedure of scaling ${}^{eff}V(\bar{\alpha}_i)$ of Sb^{III}. The higher value of $P' = 0.10$ Å for the larger data set is probably due to the drop of restrictions with regard to cations other than Sb^{III}.

The ${}^{eff}_{cal}V(\bar{\alpha}_i, D_{ij})$ values of Sb^{III}, calculated with (9) with P' and Q' values of Table 2, are found to vary

between +2.88 and +3.80 v.u. for the 76 $[Sb^{III}S_n]$ and between +2.98 and +3.88 v.u. for the 14 $[Sb^{III}Se_n]$ polyhedra, with standard deviations of 0.11 and 0.12 v.u., respectively (Table 1*a*, Fig. 3).

5. Discussion

(1) The assumptions made in the current BVC, in particular the supposition that s_{ij} depends only on the bond length D_{ij} and the restriction to the use of formal valences ${}^{for}V$, seem to be rather crude. Therefore, the fact that the application of the current BVC has been so successful in interpreting crystal structures is more surprising than the observation that in some cases s_{ij} depends on both bond lengths and angles, and that occasional considerable deviation of a calculated atomic valence from the integer formal valence may be a reality and reflects the true non-integer chemical valence state of an atom.

An error of bond length ΔD introduces a relative error of bond valence $(\Delta s)/s = (\Delta D)/b = (\Delta D)/0.37$ through (2). As long as experimentally determined D_{ij} were only accurate to within 0.05 Å, deviations of calculated valences from integer values of ${}^{for}V$ were in most cases within the limit of error $(0.05/0.37 = 13.5\%)$. Since nowadays D_{ij} are generally determined to an accuracy of much better than 0.05 Å, it is to be expected that deviations from the integer value ${}^{for}V$ can, with a high degree of confidence, be correlated to chemical effects, such as the influence of LEP.

(2) For the case of Sb^{III}—S and Sb^{III}—Se bonds, we have shown that the bond valence s_{ij} and the atomic valence V_i not only depend on bond lengths D_{ij}, but also on bond angles $\bar{\alpha}_i$ (6 and 9). Since this correlation is caused by the influence of the LEP of Sb^{III}, it should be expected that corresponding correlations also exist for the other cations with LEP and that similar improvements to the present BVC will have to be made at least for compounds containing such LEP cations.

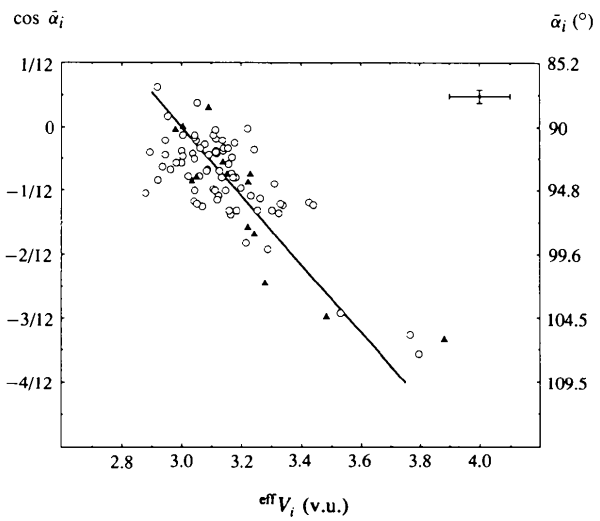

Fig. 3. Correlation between the effective valence ${}^{eff}V(\bar{\alpha}_i, D_{ij})$ of Sb^{III} calculated from (9) and $\cos\bar{\alpha}_i$. ○ – $[Sb^{III}S_n]$ groups and ▲ – $[Sb^{III}Se_n]$ groups. The solid line corresponds to (8). The error bars inserted in the upper right corner of the plot have been derived from the upper limits of the experimental errors of D_{ij} and α_i.

(3) According to the electroneutrality principle any excess (deficiency) of the calculated valence ${}_{cal}V$ of a 'cation' over its integer value ${}^{for}V$ is compensated either by a deficiency (excess) of ${}_{cal}V$ of some other 'cations' or, more likely, by an excess (deficiency) of ${}_{cal}V$ of some of the 'anions' over their integer ${}^{for}V$ and *vice versa*. Such compensation does not necessarily have to take place between neighbouring 'ions' of opposite valence, but can be achieved within second or even higher coordination spheres. This holds for ${}^{eff}V$ as well as for ${}^{for}V$.

(4) The non-integer values of the effective atomic valences, ${}^{eff}V(\bar{\alpha}_i)$ and ${}^{eff}V(\bar{\alpha}_i, D_{ij})$, calculated using (8) and (9), respectively, are only estimates of the actual valence ${}^{act}V$ because: (*a*) the assignment of ${}^{eff}V_{Sb^{III}}(\bar{\alpha}_i) = +3.75$ v.u. to polyhedra with $\bar{\alpha}_i = 109.5°$, and of ${}^{eff}V_{Sb^{III}}(\bar{\alpha}_i) = +3$ v.u. to polyhedra with $\bar{\alpha}_i = 90°$ is somewhat artificial, and there is no theoretical reason to assume that the correlation between ${}^{eff}V(\bar{\alpha}_i)$ and $\bar{\alpha}_i$ has to be described by a linear interpolation, as proposed in (8). The linear interpolation is suggested because no other reliable correlation can be justified at present. (*b*) The influence of the LEP of the anions (X = S, Se) on ${}^{for}_{i}r_o$ and, consequently, on the atomic valence has not been taken into consideration. (*c*) The individual bond lengths D_{ij} have not been taken into consideration in the calculation of ${}^{eff}V(\bar{\alpha}_i)$.

(5) Although ${}^{eff}V(\bar{\alpha}_i)$ and ${}^{eff}V(\bar{\alpha}_i, D_{ij})$ for Sb^{III} are only approximations of the corresponding actual valence ${}^{act}V$, their values certainly come much nearer to it than the assumption that ${}^{act}V_{Sb^{III}} = {}^{for}V_{Sb^{III}} = +3$.

(6) In Fig. 4 values of ${}^{121}Sb$ Mössbauer isomer shifts δ reported in the literature are plotted *versus* the $\cos\bar{\alpha}_i$ values of the corresponding $[SbS_n]$ polyhedra. Although only eight data points are available, the correlation shown in Fig. 4 for the Mössbauer data is formally the same as that shown in Fig. 1 for the structural data. Since δ is an approximate measure of the number of valence *s*-electrons of the Sb absorber at the nucleus and is, therefore, correlated with the actual valence state of the Sb atom in the $[SbS_n]$ polyhedron, Mössbauer spectroscopy confirms the interpretation of, and strengthens the conclusions drawn from, the correlation between ${}^{eff}V_{Sb^{III}}$ and $\bar{\alpha}_i$ deduced in previous sections.

(7) The ${}^{eff}V$ value derived with (8) or (9) for the Sb^{III} atoms of one crystallographic site (Wyckoff position) of a thio- or selenoantimonate describes the valence state of each individual Sb atom occupying the site. It should not be considered to be the result of averaging over Sb atoms of different oxidation numbers occupying the same site. This is in agreement with ${}^{121}Sb$ and ${}^{119}Sn$ Mössbauer spectroscopic studies of Smith *et al.* (1992) on $Ba(Sn_{1-x}Sb_x)O_3$ perovskites. From the observation of a

single absorption peak for both ^{119}Sn and ^{121}Sb these authors conclude that there is no static disproportionation into Sn^{II} and Sn^{IV} or Sb^{III} and Sb^{V}, even on the characteristic time scale ($\tau < 10^{-8}$ s) of a Mössbauer experiment. Their tabulated isomer shift values, however, suggest that Sn and Sb both have non-integer effective valences, $+(4-\epsilon_1)$ and $+(5-\epsilon_2)$, respectively, with $\epsilon_1, \epsilon_2 \approx 0.15$, rather than Sn alone, as suggested by Smith *et al.* (1992).

6. Prospects

6.1. *Phases with lone-pair cations*

In this paper it has been proven for Sb^{III} that the bond valence is not only correlated with bond length but also with bond angles. Similar studies of structures containing other lone-pair cations such as Tl^{I}, Ge^{II}, Sn^{II}, Pb^{II}, As^{III}, Bi^{III}, Se^{IV} and Te^{IV} and other anions such as Hal^{-I}, O^{-II}, Te^{-II} and N^{-III} are necessary in order (*a*) to prove whether the present BVC has to be modified to include bond angle correlations for LEP cations in general, and (*b*) if so, to develop for those LEP cations empirical equations which correspond to (5) to (10) developed for Sb^{III}.

Since the procedures to calculate effective valences of Sb^{III} by application of (8) and (9) are only rather crude approximations, a more accurate method has to be developed to scale the bond valences derived from crystal structure data to actual valences for Sb^{III}, as well as for other LEP cations. This can perhaps be achieved with the help of Mössbauer and X-ray absorption spectroscopy, measurements of magnetic susceptibilities and band gap calculations.

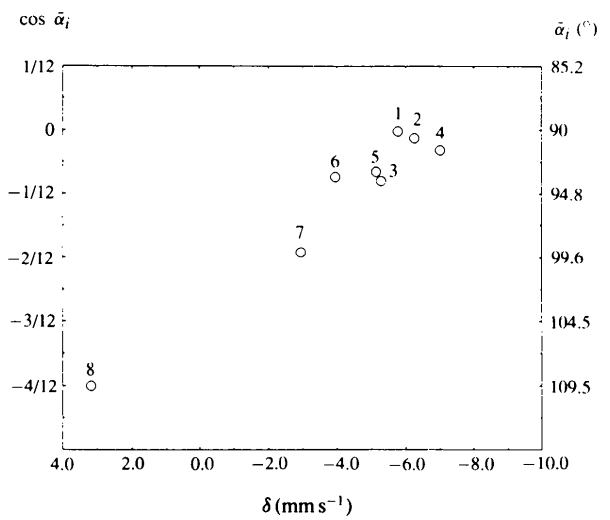

Fig. 4. Correlation between the ^{121}Sb Mössbauer isomer shift δ (relative to InSb) and $\cos\bar{\alpha}_i$. If several symmetry-independent Sb sites correspond to only one δ value due to insufficient experimental resolution, an averaged $\bar{\alpha}_i$ value is plotted. Mössbauer data are from 1: Jumas, Olivier-Fourcade, Ibanez & Philippot (1986); 2–7: Olivier-Fourcade, Jumas, Rey, Philippot & Maurin (1985); 8: Long & Bowen (1970). For structure data see Table 1. 1 = Sb_2S_3, 2 = $TlSb_3S_5$ *B*, 3 = $TlSb_3S_5$ *A*, 4 = $TlSb_5S_8$ *B*, 5 = $TlSb_5S_8$ *A*, 6 = $TlSbS_2$, 7 = Tl_3SbS_3, 8 = $Na_3SbS_4.9H_2O$. The error bars are smaller than the plotted symbols.

6.2. *Phases with transition element cations*

It has been shown that in oxides containing transition element cations with d^0, d^4 and d^9 electron configurations, such as Cu^{II}, Cr^{II}, Mn^{III}, Ti^{IV}, Nb^{V} and W^{VI} which have irregular coordination due to electronic distortions, there are considerable deviations from the equal valence rule (*e.g.* Brown, 1992; O'Keeffe, 1992). This rule states that the atomic valence is distributed as equally as possible among the bonds between like pairs of atoms. It is these cations which, in addition to angular distortions of their coordination, have a remarkable tendency to form mixed-valence compounds. Therefore, studies should be made to test whether the influence of bond angles on bond valences has also to be taken into account for such cations.

6.3. *Applications*

Since the electric properties of high-temperature superconductors are closely linked to the presence of elements such as Tl, Cu, Sn, Pb and Bi, an extension of the bond-valence concept should help to understand the role of these elements in superconductors.

Compounds containing lone-pair cations have a remarkable tendency to form structures that are commensurately (superstructures) or incommensurately modulated. The extended bond-valence concept may shed light on the correlation between modulation character, distribution of effective bond valences and electric properties (ferroelectricity, semiconductivity, superconductivity) of such phases.

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