Fig. 1. The trichromate ion.
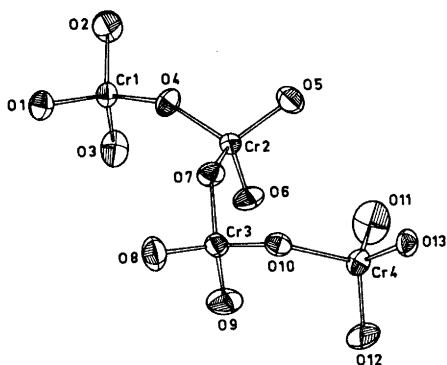

Fig. 2. The tetrachromate ion.

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Comments on the Use of InSb as Standard for ^{121}Sb Mössbauer Spectroscopy

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The Mössbauer chemical shift (δ) is a function of the total s electron density at the relevant nucleus. The observed variations in δ values for different chemical environments result from changes in the population of the valence orbitals. The orbitals of p and d character affect δ by virtue of their shielding properties. The δ value for a given compound is only meaningful when referred to a standard. The choice of such a standard is not arbitrary — it must fulfil certain requirements. The most important of these are good reproducibility and maximum accuracy in the determination of its δ value. The latter condition precludes compounds which possess unresolved quadrupole and/or magnetic interactions or a large line-width.

For ^{121}Sb Mössbauer spectroscopy InSb, which satisfies the above requirements, is widely accepted as a standard. The environments of both kinds of atoms in InSb are of T_d symmetry as a consequence of its ZnS zinc blende type crystal structure. Hence, there is no quadrupole interaction in this compound. An additional feature favouring the selection of InSb as a standard is its highly covalent nature. This is a direct result of the close proximity of In to Sb in the Periodic System and the average electron to atom ratio of four. These features have led a number of investigators to postulate $5s^1 5p^3$ as the outer electronic configuration for Sb in InSb. It does not necessarily follow, however, that four tetrahedral covalent bonds between the In and Sb atoms imply an sp^3 hybridization or 25 % s character per bond as has been inferred by, e.g., Refs. 1, 2. In fact, the differences in s and p orbital electronegativities in the actual molecule cause an electron flow towards or away from the ligands; cf., e.g., Refs. 3 — 5. Theoretical calculations [6] and electron spin resonance data [7] appear to be compatible with the assumption of zero charge on the atoms in InSb.

In order to assess the bonding properties of InSb it is useful to make comparisons with the isostructural compounds AlSb and GaSb. It is quite common to estimate degrees of covalence from electronegativity differences. However, ambiguity arises because Pauling's [8] electronegativity scale gives the order of increasing covalence as AlSb < GaSb < InSb, whereas GaSb would be the more covalent compound according to Allred-Rochow's [9] scale. The latter deduction is, for example, supported by the LCAO-MO calculations for AlSb, GaSb, and InSb by Coulson et al.[10] and the values obtained for their fractional ionic characters by Phillips and Van Vechten. [11] On the other hand, two kinds of experimental evidence, viz. the values for the band gap energy (ΔE_g) and the ^{121}Sb Mössbauer chemical shift (δ), do indicate that the correct order of covalence is AlSb < GaSb < InSb.[12-15] A plot of δ (at 78 K, relative to InSb) versus ΔE_g (extrapolated to 0 K) is shown in Fig. 1, where the experimental data are taken from Refs. 13, 15. (It would have been more appropriate to employ δ values taken at ~ 0 K, but unfortunately these do not appear to be available.)
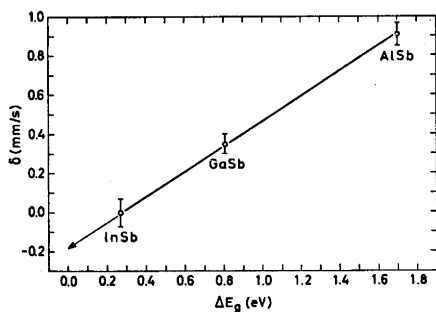

Fig. 1. Correlation between ^{121}Sb Mössbauer chemical shift and band gap energy for AlSb, GaSb, and InSb.

The parameters δ and ΔE_g are both governed by details of the electronic band structure of the compounds, and hence there must be a correlation between them. Schematically, ΔE_g is the energy gap between the valence and conduction bands, while δ depends on the energy separation of the bonding bands of a_1 and t_2 symmetry. The proportionality between δ and ΔE_g suggests that the $5s$ population on Sb remains virtually constant in these

compounds and that the variation in δ is due to the expansion of the Sb $5p$ atomic orbitals into the t_2 "molecular orbitals". Extrapolation to $\Delta E_g = 0$ gives a δ value of -0.2 ± 0.1 mm/s. This figure is proposed as the ^{121}Sb Mössbauer chemical shift for an ideal covalent antimony compound with tetrahedral coordination. The significance of this value is in permitting direct comparisons between ^{121}Sb and ^{119}Sn Mössbauer chemical shifts, since the ^{119}Sn Mössbauer reference compound is α-Sn ($\Delta E_g = 0.08$ eV at 0 K[12]) which is isostructural with the hypothetical Sb compound. On the other hand, the closeness of -0.2 ± 0.1 to zero emphasizes the suitability of InSb as a reference compound.

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