High-temperature Mössbauer Studies on ^{119}Sn-Enriched Caesium Tin(II) Chlorides and Bromides

Stephen J. Clark and John D. Donaldson
Department of Chemistry, Brunel University, Uxbridge, London UB8 3PH, UK

Variable-temperature Mössbauer studies have been carried out on ^{119}Sn-enriched samples of $CsSnBr_3$, Cs_4SnBr_6, $CsSnCl_3$ and Cs_4SnCl_6. Significant changes found in the chemical isomer shift and quadrupole splitting or linewidth parameters with temperature are compared with changes in electrical conductivity. In each case the shift decreases with increasing temperature over a range of temperatures to a value which coincides with a minimum in the linewidth and with maximum conductivity. The changes observed are consistent with the direct population of solid-state bands by the non-bonding electrons on the tin(II) and with the changes expected from orbital-matching arguments.

Non-bonding electron pairs in tin(II) compounds generally lead to distorted structures in which the most common environment for the tin atom is a distorted six-co-ordinated structure with three short and three long bonds.[1] Recent examples of structure determinations showing distorted tin(II) environments include those of $[C_5H_{12}N][SnBr_3]$ and $NH_4Br{\cdot}NH_4SnBr_3{\cdot}H_2O$,[2] $[Sn_3(OH)_4][NO_3]_2$ [3] and Sn_4OF_6.[4] The distorting effects of the non-bonding electrons can, however, be totally removed by delocalization into solid-state bands in high-symmetry structures such as $CsSnBr_3$.[5]

We have previously studied the phases in the system $CsBr$–$SnBr_2$ and shown that two compounds with unusual properties,[6] *viz* $CsSnBr_3$ and Cs_4SnBr_6, can be obtained. Both of these caesium tin bromides are black materials in which the tin(II) atoms at ambient temperatures are surrounded by a regular octahedron of bromide ions. Both materials are characterized by relatively high electrical conductivity and anomalously low ^{119}Sn Mössbauer isomer shifts.[7] The compound $CsSnBr_3$ has a slight tetragonal distortion below room temperature which is removed at about 300 K. It is also known to undergo a reversible colour change from black to red near 400 K which is not accompanied by a structural change, and this has therefore been ascribed to electronic changes in the band structure of the solid. The room-temperature modifications of the corresponding chlorides are insulators and have no intense colour. At ambient temperatures $CsSnCl_3$ is a white monoclinic phase which transforms to a yellow high-temperature perovskite modification above 373 K.[8] The compound Cs_4SnCl_6 is a light green material which is said to be isostructural with its bromide.

Variable-temperature Mössbauer spectroscopy has often been used to identify changes in the electronic environment of the Mössbauer nucleus at phase transitions and to provide information on the Debye temperatures of solids.[9] In previous work we described how the Mössbauer parameters,[7] the optical spectra and electrical conductivity of $CsSnBr_3$ are related to a minor phase transition near 303 K.[10] Others have recently examined these systems and obtained similar results including evidence for other transitions at lower temperatures.[11] We now describe the high-temperature ^{119m}Sn-enriched Mössbauer spectra and electrical conductivity data for $Cs^{119}SnX_3$ and $Cs_4{}^{119}SnX_6$ (X = Br or Cl) with particular reference to changes occurring near the transition temperatures to their cubic forms.

Experimental

Since it proved impossible to obtain satisfactory results with samples prepared from natural tin (8.5% ^{119}Sn) the caesium tin halides were prepared using $^{119}SnX_2$ which had been synthesized from ^{119}Sn metal powder. The $^{119}SnX_2$ was dissolved in boiling ethane-1,2-diol and a solution of CsX in ethane-1,2-diol was added in the appropriate ratio to yield $Cs^{119}SnX_3$ or $Cs_4{}^{119}SnX_6$. The syntheses were carried out under an atmosphere of oxygen-free nitrogen and a trace of the parent acid (HX; X = Br or Cl) was added to the initial solution to suppress hydrolysis. On slow cooling of the solutions the products crystallized out, were filtered off, and washed with the minimum of cold water and diethyl ether. The samples were then powdered, dried, and stored *in vacuo* over P_2O_5. Sample compositions were checked by comparison of their X-ray powder patterns with previously published data.

Electrical conductivity measurements were made on pelleted polycrystalline samples using the apparatus described previously.[10] Mössbauer data were collected on samples containing equivalent weights of ^{119}Sn enclosed in polytetrafluoroethylene holders under nitrogen and mounted in the tube furnace. The spectra were recorded over the temperature range 80–425 K (± 1.0 K), by accumulating counts over a period of 5 h at each temperature using a Cryophysics MS-102 Mössbauer spectrometer with a $Ca^{119m}SnO_3$ source.

In the harmonic oscillator approximation of the Debye model the recoil-free fraction, f, is related to the recoil energy of the Mössbauer nucleus, E_R, by equation (1) where E_R =

$$f = \exp\left\{\frac{-6E_R}{k\theta_D}\left[\frac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} \frac{x\mathrm{d}x}{e^x - 1}\right]\right\} \qquad (1)$$

4.18×10^{-22} J for ^{119}Sn, θ_D is the Debye temperature and $<x^2>$ is the component of the mean-square vibrational amplitude in the direction of the X-ray. At the high-temperature limit, when $T \geqslant (\theta_D/2)$, then equation (2) applies. Since f is

$$f = \exp\left(\frac{-6E_R}{k{\theta_D}^2}\right)T \qquad (2)$$

directly proportional to the area (a) under the Mössbauer spectral areas, a plot of ln a against T was used to obtain the characteristic Mössbauer temperatures, θ_M, of the bromides (Table 1), but because the chloride spectra were quadrupole

Table 1 Room-temperature electrical conductivities and Mössbauer parameters for caesium tin(II) halides at 80 K and $CsSnBr_3$ at 295 and 418 K

Compound	Conductivity,[a] σ/S cm^{-1}	Mössbauer parameters (mm s^{-1}) at 80 K[b] $\delta(\pm 0.01)$	$\Delta E_Q(\pm 0.01)$	$\Gamma(\pm 0.01)$	θ_M[a]/K
Cs_4SnBr_6	7.3×10^{-7}	4.09	0	0.90	89.4
$CsSnBr_3$		3.97	0	0.84	
at 295 K	9.3×10^{-4}	3.89	0	0.77	163
at 418 K		0.23	0	1.38	
Cs_4SnCl_6	1.5×10^{-8}	3.85	0.89		–
$CsSnCl_3$[a]	4.1×10^{-8}	3.63	0.87	–	–

[a] This work. [b] Relative to $CaSnO_3$. Data not from this work taken from ref. 6.

Table 2 Relationship between Mössbauer isomer shift data and bond lengths for some typical tin(II) compounds[12]

Compound	Average bond length (Å)	δ/mm s^{-1} (± 0.03)
$Co(SnF_3)_2 \cdot 6H_2O$	2.05	3.16
NH_4SnF_3	2.08	3.25
$NaSn_2F_5$	2.12	3.32
Sn_3F_8	2.17	3.82
$CsSnCl_3$ (monoclinic)	2.52	3.64
$KCl \cdot KSnCl_3 \cdot H_2O$	2.57	3.70
$SnCl_2$	2.74	4.12
$Ca[Sn(MeCO_2)_3]_2$	2.14	2.97
$K[Sn(ClCH_2CO_2)_3]$	2.16	3.11
$K_2Sn_2[CH_2CO_2 \cdot CO_2]_3 \cdot H_2O$	2.19	3.15
$SnSO_4$	2.26	3.95

split at low temperatures and their resolution was relatively poor, θ_M for these compounds were not calculated.

The 80 K Mössbauer parameters for the caesium tin halides obtained previously[6] are listed in Table 1 along with conductivity data and θ_M values obtained in this work. The 295 and 418 K Mössbauer data for $CsSnBr_3$ are given for comparison. The new variable-temperature conductivity and Mössbauer data are contained in Figs. 1–4.

Results and Discussion

In Mössbauer studies of tin(II) compounds in which the tin is bonded to only one type of ligand atom, there is usually a close relationship between increase in chemical isomer shift and increase in the lengths of the tin to nearest-neighbour bonds as illustrated in Table 2 for tin compounds bonded to fluorine, chloride and oxygen.[12] This relationship is to be expected because an increase in bond length is equivalent to an increase in the electrostatic character of the bonding and a movement of the shift towards the value of the isolated Sn^{2+} ($5s^2$) ion. In the absence of phase changes and/or solid-state band-population effects, an increase in temperature should result in an increase in tin–ligand bond lengths and thus to an increase in isomer shift. The second-order Doppler shift for these phases would be of the order of $+3 \times 10^{-4}$ mm s^{-1} K^{-1} at high temperatures; this could account for a total increase in shift of $+0.15$ mm s^{-1} over the temperature range studied. The variable-temperature Mössbauer data for the compounds studied in this work, however, all show anomalous relationships between shift and temperature over specific temperature ranges which cannot be accounted for by lattice expansion, changes in electrostatic character of the bonding or second-order Doppler shift.

For $CsSnBr_3$ (Fig. 1) the Mössbauer isomer shift has values of 4.14 and 3.89 mm s^{-1} at 4.2 and 323 K respectively, and over the same range the linewidth narrows from 1.0 to 0.77 mm s^{-1}. We have interpreted these changes in terms of a model involving direct population of solid-state bands by the non-bonding electrons in tin and which requires the highest possible symmetry for the tin site.[1] As the Mössbauer parameters tend to minima, the conductivity, σ, tends to a maximum at a temperature below which the material behaves as a semiconductor, but above which temperature it is pseudo-metallic. Over the range of pseudo-metallic behaviour the isomer shift and linewidth behave as would be expected up to 418 K, in that the shift increases as the lattice expands because of the greater electrostatic character in the tin bonding while the linewidth increases through vibrational broadening. Above 418 K the tin(II) Mössbauer resonance line disappears and is replaced by a resonance at 0.23 mm s^{-1} in the tin(IV) part of the spectrum and there is also a colour change from black to bright red. When the sample is recooled, the tin(IV) resonance line decreases in intensity, the tin(II) line reappears and the black colour is restored. The conductivity and Mössbauer data for Cs_4SnBr_6, Fig. 2, show behaviour similar to that of the tribromide. Although the conductivity of Cs_4SnBr_6 is lower, the minimum in the Mössbauer linewidth and isomer shift again coincides with the maximum conductivity at 373 K.

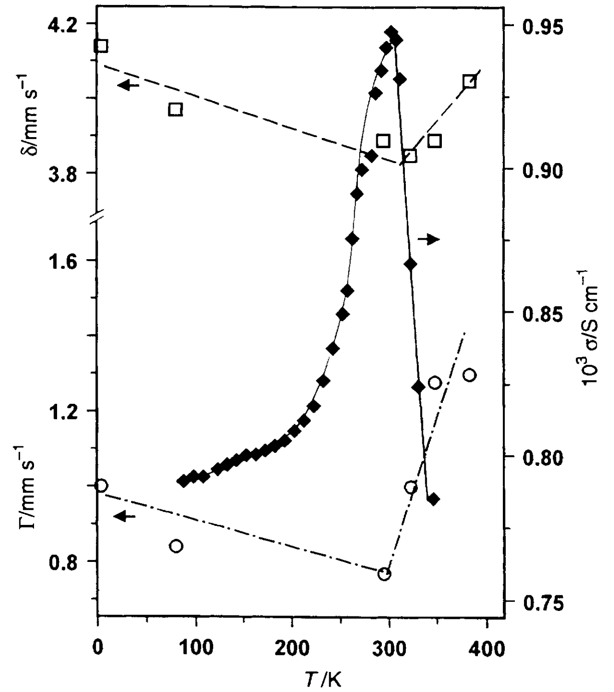

Fig. 1 Variation of Mössbauer isomer shift (δ) and linewidth (Γ) and electrical conductivity with temperature for $CsSnBr_3$

The Mössbauer and electrical conductivity data for $CsSnCl_3$, Fig. 3, are consistent with the known monclinic to cubic phases change and measurements made by other authors well below the transition temperature.[13] The conductivity behaviour of the cubic phase with temperature is similar to that of $CsSnBr_3$, showing pseudo-metallic conduction, but only over a narrow temperature range. Although the crystallographic phase transition occurs at 373 K, the Mössbauer data, decrease in shift (loss of s-electron density) and quadrupole splitting in

Fig. 3 show that the tin(II) environment changes rapidly from about 300 K. Above 373 K the linewidth shows the expected vibrational broadening from 1.41 to 1.52 mm s^{-1}; at 348 K the linewidth is 1.80 mm s^{-1} consistent with an unresolved quadrupole splitting. Fig. 4 shows that, apart from the absence of a crystallographic phase change, the behaviour of Cs_4SnCl_6 is similar to that of $CsSnCl_3$ with anomalous Mössbauer shifts between 300 and 400 K which are paralleled by decreases in quadrupole splitting associated with an increasingly high-symmetry tin environment. Although it has been suggested[6] that Cs_4SnCl_6 is isostructural with Cs_4SnBr_6, this can only be true for the high-symmetry phase.

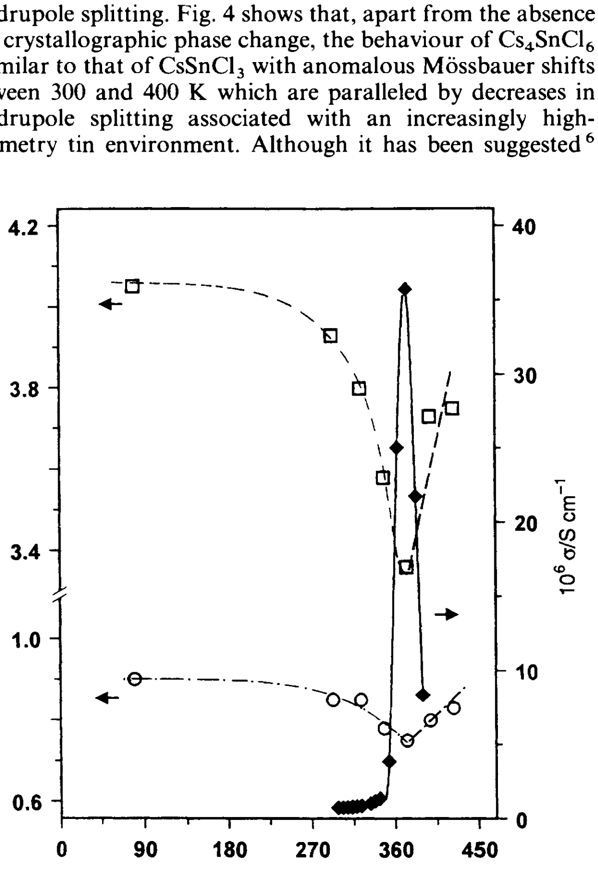

Fig. 2 Variation of Mössbauer isomer shift (δ) and linewidth (Γ) and electrical conductivity with temperature for Cs_4SnBr_6

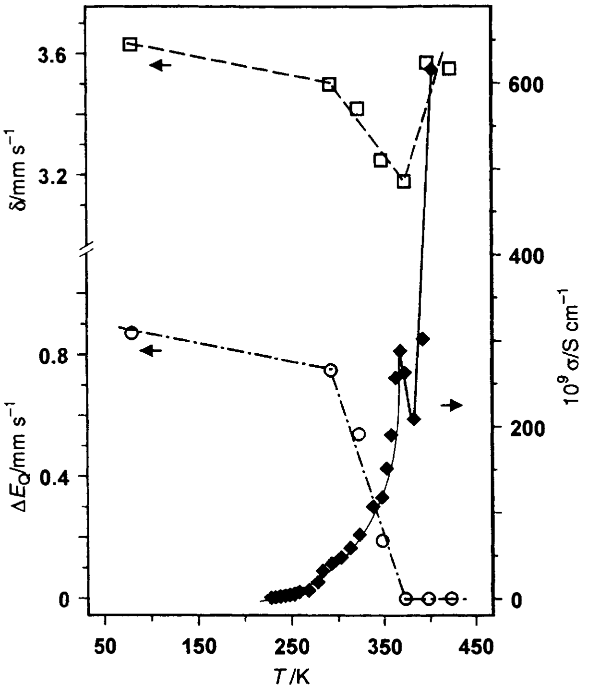

Fig. 3 Variation of Mössbauer isomer shift (δ) and quadrupole splitting (ΔE_Q) and electrical conductivity with temperature for $CsSnCl_3$

Electronic Structures.—At ambient temperatures $CsSnBr_3$ has the ideal perovskite structure in which the tin(II) lies at the centre of a regular octahedron of bromide ions and this high-symmetry environment around the tin is reflected in the narrow Mössbauer linewidth (0.77 mm s^{-1} at 80 K). The isomer shift is, however, much lower than that expected for a compound containing isolated spherical Sn^{2+} ions,[14] and we have interpreted this loss of s-electron density to the involvement of the tin 5s electrons in solid-state bands formed by the overlap of empty bromine d orbitals. The loss of s-electron density is, thus, explained by the direct population of these bands by the tin(II) non-bonding electron pair.[10,15]

We have used conductivity data and electronic spectra to deduce the band structure of $CsSnBr_3$ shown by the density-of-states (N_E) diagram in Fig. 5.[10] If we examine a projection of the tin 5s and bromine d orbitals in $CsSnBr_3$ it can be seen how such a delocalized empty band system can arise from the mutual overlap of empty bromine t_2 orbitals (Fig. 6).

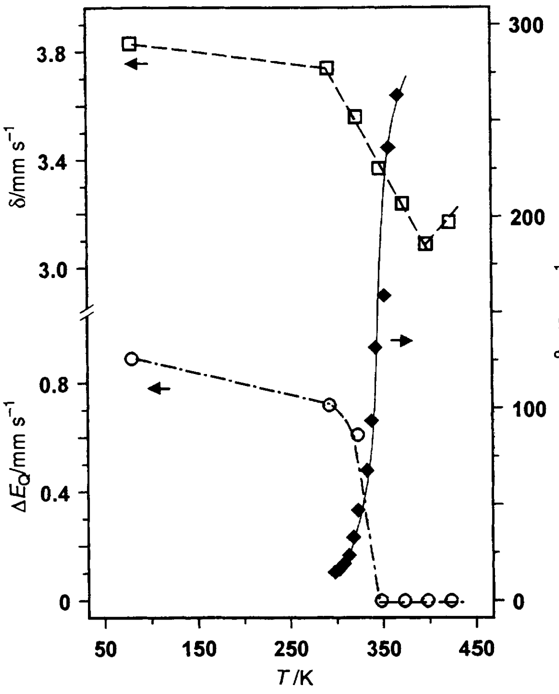

Fig. 4 Variation of Mössbauer isomer shift (δ) and quadrupole splitting (ΔE_Q) and electrical conductivity with temperature for Cs_4SnCl_6

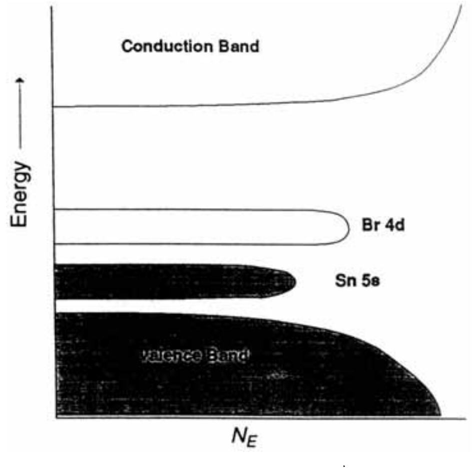

Fig. 5 Energy-level diagram for $CsSnBr_3$; eV ≈ 1.60 × 10^{-19} J

Calculation of the size of the $5s^2$ orbital on the tin atom leads to the conclusion that there will be an overlap between this orbital and the empty bromine 4d orbitals.[14] It is then possible for the distortive effects of the non-bonding 5s orbital to be reduced by the direct population of the solid-state band by the non-bonding tin electron pair. The undistorted perovskite structure becomes favoured once direct population is possible because the mutual overlap of the bromine 4d orbitals is greatest in such a structure, and this in turn permits maximum transfer of electron density from the potentially distorting non-bonding tin orbital. This electronic model is consistent with the electrical conductivity, optical and other properties of a wide range of main-group element halides with the main-group element in a high-symmetry environment.[16]

The variable-temperature Mössbauer and conductivity data for $CsSnBr_3$ are consistent with the direct population of solid-state band model because the loss of tin s-electron density indicated by the Mössbauer shift data is paralleled by an increase in conductivity up to 303 K. The minimum in Mössbauer linewidth also occurs at about this temperature, suggesting that maximum conductivity is associated with the most symmetrical tin environment. The extent of delocalization of the tin non-bonding electron density into solid-state bands for $CsSnBr_3$ must be sufficient to remove the distorting effects of the non-bonding electron pair. The decrease in conductivity and increase in both Mössbauer shift and linewidth above 295 K suggests that the ideal band-overlap conditions between the tin ns^2 level and the empty potential valence bromine d bands must occur at around 300 K. The changes above the phase transition, decrease in conductivity and increase in isomer shift, indicate a relocalization of 5s electron density onto tin.

The loss of the tin(II) resonance line near 400 K must be associated with the changes in the optical spectra previously observed.[10] At this temperature, therefore, the tin(II) non-bonding electrons are totally transferred into the band structure thus giving a pseudo-tin(IV) electronic environment to the tin nucleus. Increasing temperature has two effects on the solid-state band system, *viz.*: (1) lattice expansion is tending to increase the energy gap between the donor and acceptor bands, and (2) the extra energy provided to the system increases the ability of the donor electrons to populate the acceptor band. It is clear that the latter effect becomes more important in $CsSnBr_3$ at about 400 K. Depopulation of this band, however, does occur on cooling. The high value for θ_M is consistent with the lack of vibrational freedom that would be expected from a tin atom strongly held at the centre of an undistorted octahedral bromide environment by the constraints of the perovskite lattice and the solid-state bonding effects which favour the undistorted structure.

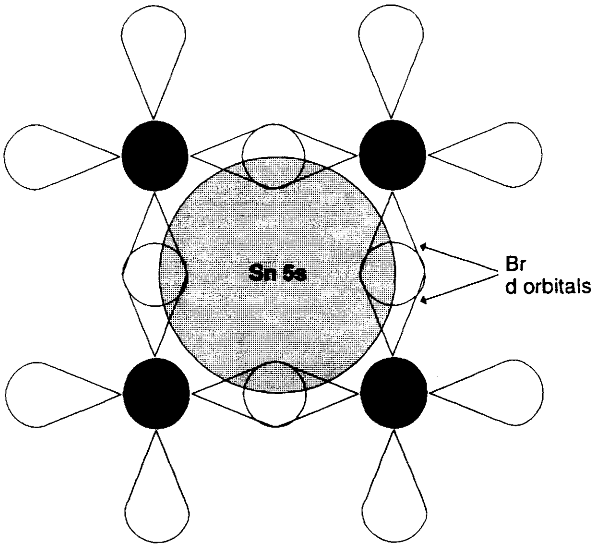

Fig. 6 Relative positions of Sn s- and Br d-orbitals in $CsSnBr_3$

The variable-temperature Mössbauer and conductivity data for Cs_4SnBr_6 are similar to those for $CsSnBr_3$ and can be explained on the same model with the maximum overlap of the ns^2 level with the potential bromine valence level occurring at about 370 K. The actual value of the conductivities for Cs_4SnBr_6 are three orders of magnitude lower than for $CsSnBr_3$ but this would be expected from the longer Sn–Br distances (3.08 compared with 2.90 Å in $CsSnBr_3$) and with the lower tin : bromine ratio in Cs_4SnBr_6. The lower value of θ_M would also be consistent with these differences. The narrower range over which the change in conductivity occurs may be explained in terms of a narrower temperature range over which the donor ability of the tin(II) non-bonding electron pair and the acceptor ability of the bromide d band are geometrically favourable.

For $CsSnCl_3$ the variable-temperature Mössbauer and conductivity data must be interpreted in terms of a monoclinic phase at low temperatures and a perovskite phase above 373 K. The data for the high-temperature phase can be interpreted in terms of the direct-population model with the non-bonding electron-pair electrons being partly delocalized into an empty three-dimensional chlorine d band. The very much smaller electrical conductivities must be due to a less-efficient overlap of the chlorine orbitals to form conduction bands. The monoclinic form of $CsSnCl_3$ contains distorted-pyramidal $SnCl_3^-$ ions and this asymmetry is reflected in a quadrupole splitting of the Mössbauer spectrum. The shift and quadrupole splitting do not change significantly until the onset of the changes which start about 300 K and lead to the formation of the cubic modification. The discontinuity in the electrical conductivity around the phase transition suggests that the structural change may be of a complex nature similar to those found in $CsPbCl_3$,[17] $CsPbBr_3$[18] and $CsSnBr_3$[19] in which the phase change to cubic occurs through a succession of transitions.

The Cs_4SnCl_6 data must also be interpreted in terms of (1) a low-temperature modification, which has very low conductivity and Mössbauer parameters that hardly change with temperature up to about 275 K and (2) a modification with a higher-symmetry tin environment, presumably isostructural with Cs_4SnBr_6, and with variable-temperature Mössbauer and conductivity data similar to those of the cubic perovskite form of $CsSnCl_3$.

The unusual electronic structures of these compounds are emphasized by the decrease of the Mössbauer isomer shifts of their low-temperature forms (shown in Figs. 1–4) with increasing temperature. This behaviour is contrary to that of most other tin(II) compounds, which show an increase in Mössbauer isomer shift with increasing bond length.

The different behaviour of the chlorides and bromides can be explained in terms of orbital-energy-matching arguments (Fig. 7).[20] In compounds containing SnF_3^- the non-bonding electron pair on tin(II) has high 5p character because 5s–5p orbital mixing offers no energy advantage and the bond orbitals between tin and fluorine must have high tin 5s character. This means that the non-bonding electron pair on tin atoms in

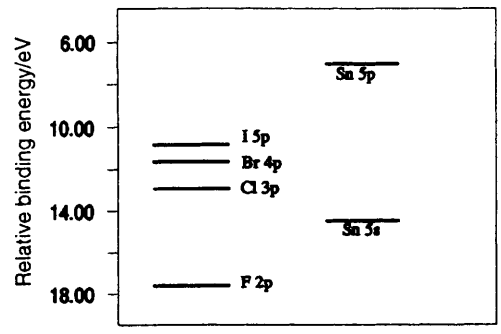

Fig. 7 Relative binding energies of halides and tin atomic orbitals

fluorides is highly directional and stereochemically active. For Sn–Cl and Sn–Br environments, however, 5s–5p mixing should be energetically favourable and this would increase the p character in the order Sn–Br > Sn–Cl ≫ Sn–F. Consequently the s character of the non-bonding electron pair on the tin in bromides will be higher than in chlorides making easier the formation of high-symmetry structures by direct population of solid-state bands. Poorer band overlap in the chlorides studied could also arise in the acceptor band because the size of the cubic cell is principally determined by the size of the caesium ions so that the overlap in three dimensions of the chlorine d orbitals is much less than that of the bromine ions and hence the band formed is much less accessible.

In compounds which contain SnX_6 octahedra the tendency is for the tin(II) environment to distort to accommodate directional non-bonding electron pairs[1] unless, as in the caesium tin halides studied in this work, there are solid-state bands available to delocalize the electron density and remove the distortion.

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