

The Electronic Structure of CsSnBr₃ and Related Trihalides; Studies Using XPS and Band Theory

D. E. PARRY AND M. J. TRICKER*

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, SY23 1NE, Wales

AND J. D. DONALDSON

Department of Chemistry, Chelsea College, University of London, Manresa Road, London SW3 6LX, England

Received July 21, 1978

The electronic structure of the cubic phase of crystalline CsSnBr₃ has been investigated using X-ray photoelectron spectroscopy and a semiempirical energy band structure calculation. The observed semimetallic behaviour of this system and some similar crystalline trihalides in the cubic phase is related to the presence of a triply degenerate R_{15} energy level in the calculated conduction band. The nonmetallic behaviour of the cubic phase of CsSnCl₃ may be accounted for by consideration of the spin-orbit splitting of this R_{15} level.

Introduction

Recently a range of crystalline solids, of composition CsSnX₃ (with X = Cl, Br, or I; mixed trihalides are also known), has become of great interest (1, 2) because it exhibits an interesting variety of electronic properties. A most intriguing observation is that the simple cubic (perovskite) phases of some of these compounds are black semimetals. Typical of these black materials is CsSnBr₃ which is cubic¹ between temperatures of -100 and 350°C and has a room temperature resistivity of 20 ohms cm (2). In contrast the known monoclinic crystalline modifications of these trihalides are

nonconducting (2). In the simple cubic perovskite structure the Sn(II) atoms are in regular octahedral sites implying that the expected stereochemical activity of the lone-pair electrons is suppressed. In the monoclinic phases the Sn atoms have the more usual distorted environments. Qualitative attempts have been made to relate such differences in short-range order to the observed electronic properties of the crystals (3). In the quantitative theoretical study reported here it has been discovered that these properties are, in contrast, sensitive to the nature of the long-range crystalline order (translational symmetry) as manifested by characteristic degeneracies in the energy-band structure at certain symmetry points of the Brillouin zone of the simple cubic lattice.

A semiempirical energy-band calculation has been carried through to gain insight into the details of the CsSnBr₃ band structure, in

* Present address: Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh, EH14 4AS, Scotland.

¹ NQR data (2) indicate that there might be a small tetragonal distortion below 19°C.

particular the positions within the band structure of the several degeneracies that should occur at symmetry points and on symmetry lines of the simple cubic lattice Brillouin zone. In addition the valence-band density of states of CsSnBr_3 has been studied at room temperature using X-ray photoelectron spectroscopy (XPS) and the data were compared with calculated results.

Experimental

Photoelectron spectra were recorded on an AEI ES200A instrument using $\text{MgK}\alpha$ X radiation. Samples were prepared by pressing (at 10–20 tons in.^{-2}) freshly ground chips of melt-grown CsSnBr_3 single crystals (4). After scraping of its surface the sample was mounted in electrical contact with a probe and immediately placed within the spectrometer.

Wide-scan spectra revealed the presence of Cs, Sn, and Br together with signals associated with the 1s levels of carbon and oxygen present as surface contamination. From the intensities of these 1s signals and using the known ratios between valence and core-level cross sections (5) it is estimated that no feature due to contaminants in the valence spectrum will have a peak height more than 3% of the peak marked A in Fig. 2a. Contamination did increase over a period of some hours but the increase was negligible over the period in which the valence spectra

were recorded. High-resolution spectra of the Sn 3d doublet exhibited sharp (FWHM = 1.8 eV) symmetrical peaks, indicating that no significant decomposition of the surface had occurred. Because the sample was a conductor charging effects were expected to be absent; this was confirmed by application of a DC bias to the sample and observation of the consequent shift in photoelectron kinetic energy.

Figure 2a shows the digitally accumulated valence-band spectrum of CsSnBr_3 , after subtraction of the $\text{MgK}\alpha_{3,4}$ satellite spectra and a linear background by a standard procedure (6). The position of the Fermi level was determined by observing the position of the Fermi level in the spectrum of a platinum foil in electrical contact with the sample.

Theoretical

The valence-electron energy-band structure and density of states of cubic CsSnBr_3 have been calculated using a recently developed, semiempirical, linear combination of atomic orbitals (LCAO) method (7). All significant overlap integrals between the atomic-orbital basis functions are evaluated without approximation and the diagonal Fock-matrix elements are calculated from valence-state ionization energies (VSIE) and Madelung potentials, with short-range modifications to these point-charge potentials taking the Mataga–Nishimoto form as in previous applications (7, 8). Off-diagonal Fock matrix elements are calculated according to an overlap-dependent formula. Matrix elements between Bloch orbitals at any given point in the Brillouin zone may then be calculated using the above atomic-orbital matrix elements.

All the constituent elements of CsSnBr_3 are much heavier than those encountered in previous applications and their VSIEs and valence atomic orbitals are correspondingly less precisely known. In addition the Cs

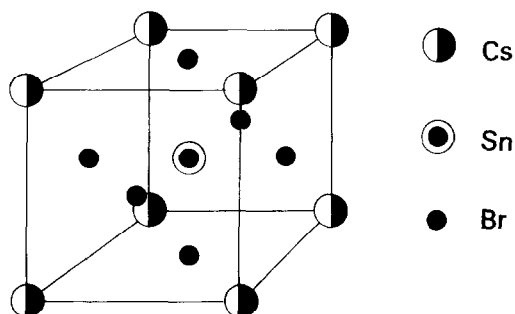


FIG. 1. Unit cube of CsSnBr_3 in the simple cubic (perovskite) phase.

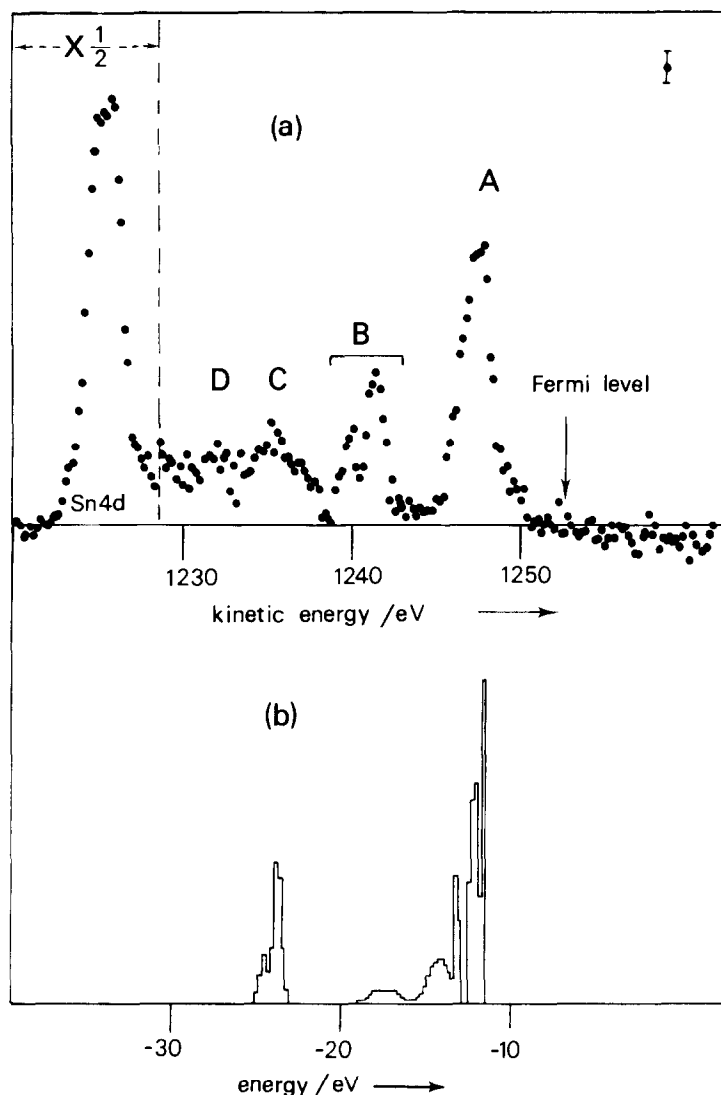


FIG. 2. (a) Photoelectron spectrum of CsSnBr₃ (see text) after refinement due to subtraction of satellite-component spectra and a linear background (6). (b) Density of states histogram calculated from the energy-band structure of Fig. 3.

valence orbitals are very diffuse and their inclusion in the basis set is unlikely to improve the calculation significantly; indeed their inclusion might well come near to making the basis set overcomplete, so Cs 6s and 6p orbitals were excluded. The Cs 5s and 5p and the Sn 4d orbitals have energies comparable to those of the basis set but were also excluded because their compact struc-

ture implies that they would not participate significantly in the bonding of CsSnBr₃. The fixed basis set used thus consists of Sn 5s and 5p and Br 4s and 4p valence orbitals, which for the calculation of overlap integrals were represented by normalized Slater-type orbitals (STO) with the exponents of Burns (9). These exponents, together with atomic charge-dependent VSIEs calculated from

the data of Sichel and Whitehead (10), are given in Table I.

Self-consistency in this band-structure calculation was achieved when the atomic-charges input to calculate VSIEs and Madelung potentials agreed with their output (calculated using Mulliken gross-orbital populations) to within a chosen tolerance, here $3 \times 10^{-4} e$ (7). The population analysis requires in principle summation over all occupied crystal orbitals i.e., over all occupied bands at each allowed value of \mathbf{k} in the Brillouin zone. For computational economy in this reduced basis-set calculation the population analysis was performed at only one point in the zone, the Baldereschi (11) mean-value point $\mathbf{k} = (2\pi/a)(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, a being the repeat distance of the simple cubic lattice. The probability of incompletely filled bands in a semimetal in principle makes the population analysis much more difficult, but as this method is approximate the "full band" mean-value point has been retained. Semimetals are usually characterized by *small* pockets of electrons and holes in otherwise empty and full bands, respectively, so the Baldereschi point is still acceptable. Certainly it would be hard to justify a more complicated population analysis in this calculation.

Omission of the Cs atomic orbitals from the basis set accords well with chemical intuition in implying that the crystal contains Cs^+ ions. Exploratory calculations including

trial Cs 6s orbitals in the basis yielded self-consistent Cs atomic charges that were reassuringly close to $+|e|$. Therefore the band structure may be regarded as that of an extended complex anion, a lattice of $[\text{SnBr}_3]_n^{n-}$, coexisting with a lattice of isolated Cs^+ cations. The latter enter the band-structure calculation through the calculation of the lattice potentials at the Sn and Br sites. Iteration to self-consistency yielded acceptable Sn and Br configurations and atomic charges (q);

$$\begin{aligned} \text{Sn } 5s^{1.78} 5p^{2.32}, & \quad q = -0.10|e|, \\ \text{Br } 4s^{1.90} 4p^{5.40}, & \quad q = -0.30|e|. \end{aligned}$$

The band structure calculated by using this electron distribution is shown in Fig. 3 for various symmetry points and lines of the Brillouin zone, labeled conventionally (12). With 26 valence electrons in the unit cell the Fermi level appears to be positioned between the R_{15} and M_5 levels ca. 0 eV. No attempt has been made to calculate its position accurately because the energies of these higher "conduction" bands in this region are not expected to be particularly reliable; this M_5 level is the highest energy M_5 level and its wave function is therefore completely determined by orthogonality to the wave functions of the lower energy M_5 levels. Similar arguments apply to the R_{15} level. More generally energies of the empty bands, and therefore the Fermi level, cannot be reliably predicted with only 3 out of the 16 bands in this band structure unfilled. However, what may be deduced with confidence is that there is, at or near the Fermi level, an R_{15} triply degenerate level which appears to ensure some form of metallic behavior for cubic CsSnBr_3 . This will be discussed in the next section.

TABLE I

CHARGE (q)-DEPENDENT VSIEs (10) AND STO EXPONENTS (9) USED FOR THE TIN AND BROMINE ORBITALS

Orbital	VSIE (eV)	Exponent
Sn 5s	$14.090 + 4.297q$	1.92
Sn 5p	$8.978 + 4.297q$	1.25
Br 4s	$23.475 + 8.823q$	2.8875
Br 4p	$12.474 + 8.823q$	2.05

Discussion and Conclusion

The XPS valence-band studies provide additional evidence for the semimetallic

nature of cubic CsSnBr_3 . No charging effects were detected and the Fermi level was found to be at an energy where the observed density of states (DOS) was very small. A valence-band DOS histogram was calculated (7) from the band structure and is shown in Fig. 2b. The calculated DOS at energies above -12 eV was too small to plot but naturally is not zero. The theoretical position of the Fermi level was not considered reliable enough to be used in aligning the theoretical and experimental spectra, but it is clear that the two main peaks in the histogram correlate well with the experimental peaks A and C. Some weak structure in the histogram between -14 and -18 eV cannot be compared with the experimental spectrum because the latter exhibits the strong doublet B which may be confidently assigned to the Cs $5p$ doublet which the calculation does not reproduce (vide supra). The peak area ratio of this doublet, the magnitude and sign of the spin-orbit splitting (13), and the binding energy (13, 14) of the doublet all confirm this assignment for feature B. The linewidth of each doublet component peak is comparable to that observed for the Sn $3d$ doublet, indicating insignificant delocalization of the Cs $5p$ orbitals in this crystal and therefore justifying their omission from the basis set of the calculation. In passing it may be noted that because this crystal has a center of inversion no spin-orbit splitting (15) in this calculated band structure near -18 eV may be expected.

There is relatively more uncertainty in the experimental DOS near C because the $\text{MgK}\alpha_3, \alpha_4$ satellite spectrum of the intense Sn $4d$ peak has been subtracted (6) in this region. No definite identification of a Cs $5s$ peak can be made but the very weak structure at D may be due to this. (Signals from valence s orbitals tend to be weak in XPS.) Examination of the crystal orbitals calculated at various points in the Brillouin zone confirms that Br $4s$ orbitals contribute mainly to the peak at -24 eV which would

explain the weakness of feature C. There is naturally a preponderance of bromine character in the histogram, especially in the peak regions, consistent with 21.9 of the 26 electrons in each unit cell being in bromine gross-orbital populations. In contrast the tin valence-orbital character is more widely distributed over the calculated density of states consistent with the tin atoms having a coordination number of 6 compared to one of 2 for the bromine atoms. It is interesting to find that an intuitively attractive initial assumption, that the valence electron structure of the crystal is essentially that of a bonded lattice of tin and bromine atoms stabilized by a lattice of cesium cations, has enabled a useful description of the electronic structure of the crystal to be obtained.

The band structure shown in Fig. 3 indicates that the semimetallic properties of the cubic phase may originate in the band degeneracy at either the R or M points on the Brillouin zone surface. However, it is essential to investigate whether the omission of certain interactions from this calculation, in particular spin-orbit coupling, invalidates this prediction. Before doing so, it should be recognized that a small change in the parameters employed in the semiempirical calculation could reverse the ordering of the closely spaced M_1 and M_5 levels from that shown in Fig. 4a to that in Fig. 4b. As the two Σ_1 bands will not cross, the band structure of Fig. 4b will not provide a guarantee of semimetallic behavior. So although Fig. 4a may give the correct picture near M , it is the degeneracy at R that appears to ensure that the cubic phase will be semimetallic.

The band structures of cubic CsSnCl_3 and CsSnI_3 should not differ significantly from that of CsSnBr_3 , so an apparent paradox is presented by the nonmetallic properties of yellow cubic CsSnCl_3 . It is unlikely that the latter compound lies on the insulating side of a Mott transition, for it has a smaller unit cell than the other trihalides. Therefore band theory should be appropriate to describe this

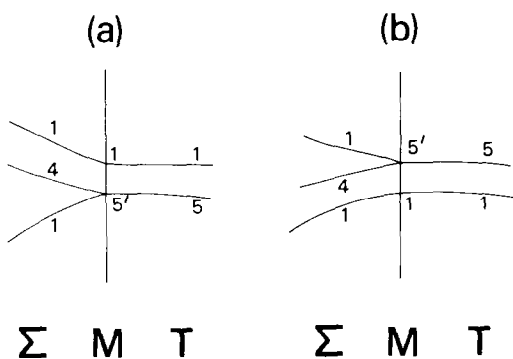


FIG. 4. Two possibilities for the non relativistic conduction-band structure near the M symmetry points.

system and a possible mechanism for lifting the degeneracy at the R_{15} level must be found to permit the formation of a band gap. The only such mechanism that can result in such level splitting is the relativistic spin-orbit coupling interaction, neglected in the simple calculation above. This interaction splits the triply degenerate R_{15} level into nondegenerate R_{6^-} and doubly degenerate R_{8^-} levels (15), resulting in two possibilities for the band structure near R shown in Figs. 5a and b. In Fig. 5a the double degeneracy of R_{8^-} still guarantees semimetallic behavior, while in Fig. 5b, it is quite possible that the separation of R_{6^-} and R_{8^-} may be large

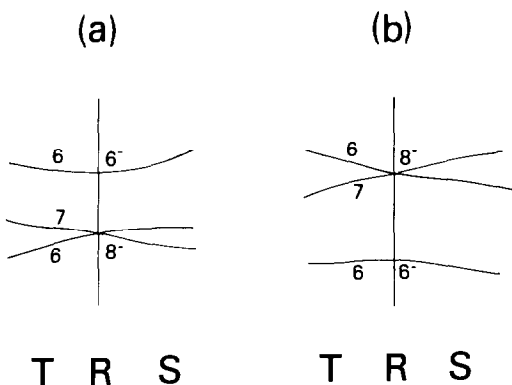


FIG. 5. Possible modifications near the Fermi level to the nonrelativistic band structure of Fig. 3 due to spin-orbit coupling, near the R symmetry points on the Brillouin zone surface.

enough to prevent overlap of the valence and conduction bands anywhere in the Brillouin zone, which would correspond to the non-metallic behavior of cubic CsSnCl₃. Either case could hold for cubic CsSnBr₃ and CsSnI₃, overlapping valence and conduction bands being possible in both Figs. 5a and b. If the cubic phase of CsSnBr₃ does distort slightly to tetragonal symmetry (2) below 19°C this will split the R_{8^-} level in a relativistic band structure (15). As this crystal below 19°C is still a black semimetal one might deduce, if Fig. 5a were correct, that in the cubic phase the Fermi level does not lie at the R_{8^-} level but is positioned, by the fine details of the overlap of the valence and conduction bands, elsewhere in the Brillouin zone.

To conclude, the semimetallic properties of some cesium tin trihalides appear to originate in their possession of the highly symmetric simple cubic Bravais lattice. Consequently their nonrelativistic band structures will exhibit degenerate R_{15} levels near the Fermi level. This symmetry due to long-range order is not sufficient to ensure that such crystals are semimetallic because the detailed nature of the spin-orbit splitting of the R_{15} level is also important. Interestingly the properties of the mixed trihalides tally with these proposals. Black semimetallic cubic CsSnBr₂I may be regarded as intermediate between the tribromide and triiodide, while CsSnBr₂Cl is cubic, red, and a poor conductor (1, 2). Given good nonrelativistic wave functions from a band structure calculation, perturbation theory could be used to investigate the spin-orbit splittings quantitatively, but as this range of crystalline trihalides exhibits such an interesting variety of electronic properties it is surely an excellent candidate for study using one of the relativistic band-structure methods that are now established. Such a study is in any case essential if the detailed optical properties (16) of these compounds are to be elucidated.

Acknowledgment

We thank Dr. Stephen Evans for much helpful advice and assistance in obtaining the photoelectron spectra.

References

1. J. BARRETT, S. R. A. BIRD, J. D. DONALDSON, AND J. SILVER, *J. Chem. Soc. A*, 3105 (1971).
2. D. E. SCAIFE, P. F. WELLER, AND W. G. FISHER, *J. Solid State Chem.* **9**, 308 (1974).
3. J. D. DONALDSON AND J. SILVER, *Inorg. Nucl. Chem. Lett.* **10**, 537 (1974).
4. R. H. ANDREWS, J. D. DONALDSON, J. SILVER, AND E. A. D. WHITE, *J. Mater. Sci.* **10**, 1449 (1975).
5. J. H. SCOFIELD, *J. Electron Spectrosc.* **8**, 129 (1976).
6. J. M. ADAMS, S. EVANS, AND J. M. THOMAS, *J. Phys. C: Solid St. Phys.* **6**, L382 (1973).
7. D. E. PARRY, *J. Chem. Soc. Faraday Trans. 2* **73**, 774 (1977).
8. D. E. PARRY, *Chem. Phys. Lett.* **46**, 605 (1977).
9. G. BURNS, *J. Chem. Phys.* **41**, 1521 (1964).
10. J. M. SICHEL AND M. A. WHITEHEAD, *Theor. Chim. Acta* **7**, 32 (1967).
11. A. BALDERESCHI, *Phys. Rev. B* **7**, 5212 (1973).
12. L. P. BOUCKAERT, R. SMOLUCHOWSKI, AND E. WIGNER, *Phys. Rev.* **50**, 58 (1936).
13. W. LOTZ, *J. Opt. Sci. Amer.* **60**, 206 (1970).
14. K. SIEGBAHN, C. NORDLING, A. FAHLMAN, R. NORDBERG, K. HAMRIN, J. HEDMAN, C. JOHANSSON, T. BERGMARK, S. E. KARLSSON, I. LINDGREN, AND B. LINDBERG, "ESCA, Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist & Wiksells, Stockholm (1967).
15. R. J. ELLIOTT, *Phys. Rev.* **96**, 280 (1954).
16. S. J. CLARK, J. D. DONALDSON, AND C. D. FLINT, unpublished work.