Evidence of 'Mixed-valency' Character in the *X*-Ray Photoelectron Spectra of α-Diantimony Tetraoxide and Barium Bismuth Trioxide

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X-Ray photoelectron spectra of the metal(III)–metal(V) oxides α-Sb_2O_4 and $BaBiO_3$ are reported. Indications of 'mixed-valency' character in the metal core-electron spectra could be found only after careful pretreatment of the samples *in situ*. Under normal conditions both compounds appear to have surface phases containing just the lower oxidation state.

A 'MIXED-VALENCY' compound is one in which an element (usually a metallic element) occurs in more than one formal oxidation state.[1] *X*-Ray photoelectron (*X*-p.e.) spectroscopy is at first sight an attractive technique for investigating such compounds since in general one expects to observe separate core-level signals for the different oxidation states, and perhaps obtain useful information concerning the distribution of valence electron density. In this field, *X*-p.e. spectroscopy has the advantage over other relevant techniques (such as Mössbauer spectroscopy) in that all the elements except hydrogen are within its scope of study. But it has, at the same time, the disadvantage of being essentially a surface technique: it samples only a thin surface layer (commonly 20 Å or less in thickness) of a solid material. When the aim is to gain information about the bulk material great care is clearly necessary to ensure a clean sample surface, a surface free of adsorbed contaminants and of phases with compositions unrepresentative of the bulk.

Invariably, only two oxidation states (A and B, say) can co-exist in a solid and, at the simplest level of approximation,[2] the separation of the two sets of core p.e. signals expected should be as in equation (1) where

$$I_A - I_B = (E_B - E_A) + e(V_B - V_A) \qquad (1)$$

I denotes the ionisation energy (binding energy) for a particular core electron species, *E* the orbital energy of this core subshell were the atom transported adiabatically from the solid into the gas phase, and *V* the lattice potential at the site of the atom. The two oxidation states usually have quite different lattice sites, and so the difference in site potential energies, $e(V_A - V_B)$, is an important ingredient of the chemical-shift effect.

A variety of mixed-valency solids have been studied by *X*-p.e. spectroscopy [3-6] and the expected doubling of the metal core signals is usually observed. Occasionally, however, this doublet structure is surprisingly absent. The celebrated example is Pb_3O_4 where, in spite of the lead(II) and lead(IV) atoms having radically different crystallographic sites (the oxygen co-ordination numbers being three and six, respectively), one observes a single set of $4f_{\frac{5}{2}},4f_{\frac{7}{2}}$ p.e. bands, and these are no broader than the $4f$ bands of PbO and PbO_2.[5] This disconcerting result has been attributed to (more or less) exact compensation of the 'intrinsic' or local term in equation (1) by the lattice-potential term, the difference in site potential energies of the lead(II) and lead(IV) species.[5,7,8] However, one cannot usually rule out the possibility, in such a case, that the observation of just one set of metal core p.e. signals is due to an untypical surface phase containing only one oxidation state. (In the particular case of Pb_3O_4 the surface might have the composition PbO, for example.) An alternative interpretation along these lines is by no means fanciful. Mixed-valency materials involving a relatively unfamiliar oxidation state, unless freshly prepared, frequently have only the more stable oxidation state at the surface. A well documented case is that of the antimony(III)–antimony(V) compound Cs_2SbCl_6 [4,9] which, under normal conditions, decomposes fairly rapidly at the surface to a purely antimony(III) phase. Certainly, a knowledge of such effects would engender suspicion if the 'accidental' cancellation of the local- and lattice-potential terms in equation (1) were invoked too often.

We explore this point, albeit in a limited way, with an investigation by *X*-p.e. spectroscopy of the oxides α-Sb_2O_4 and $BaBiO_3$. Both materials belong (like Pb_3O_4) to class I of the scheme for mixed-valency compounds due to Robin and Day:[1] that is, in each case the metal(III) and metal(V) atoms occupy crystallographically quite different lattice sites.

EXPERIMENTAL

The samples of α-Sb_2O_4 and $BaBiO_3$ used in this study were powders that had been the objects of previous structure determinations by diffraction techniques.[10,11]

The *X*-p.e. spectra were recorded with a modified A.E.I. ES 200B electron spectrometer using Mg-$K_{\alpha_{1,2}}$ ($h\nu$ 1 254 eV) †

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† Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 Torr = (101 325/760) Pa; 1 atm = 101 325 Pa.

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[11] G. Thornton and A. J. Jacobson, in preparation.

exciting radiation. The count rates obtained for the Sb 3*d* signals (Sb_2O_4) and the Bi 4*f* signals ($BaBiO_3$) were typically in the range 10^3—10^4 s^{-1}, the vacuum in the sample region being 10^{-9} Torr or better.

The samples were ' cleaned ' within an ancillary UHV chamber connected directly to the ionisation chamber (*via* a UHV gate valve) by a method that involved reproduction of the preparative conditions in an atmosphere free from water vapour and CO_2. Thus α-Sb_2O_4 and $BaBiO_3$ were heated at 750 °C for 4 and 12 h, respectively, in 1 atm of an ' air mixture ' containing 21% O_2 and 79% N_2 (Air Products Ltd.). This gas mixture was passed over activated alumina (to remove water) and admitted to the preparation chamber *via* a UHV leak valve. The heating of the samples was carried out within a radio frequency (r.f.) induction coil, the susceptor being the platinum sample holder. The oxides Sb_2O_3 and Bi_2O_3, examined for comparison purposes, were heated in a dynamic vacuum of 10^{-8} Torr for 3 h at 600 and 700 °C, respectively, prior to the *X*-p.e. measurements.

The spectra, recorded in digital form, were deconvoluted by a Fourier-transform method described elsewhere.[12] Resolution of overlapping bands was carried out by means of a Du Pont 310 analogue curve resolver.

RESULTS AND DISCUSSION

α-Sb_2O_4.—*X*-Ray diffraction demonstrates clearly that the structure of this antimony(III)–antimony(V) compound involves two quite distinct lattice sites for antimony.[13] (α-Sb_2O_4 is isomorphous with $Sb^{III}Nb^{V}O_4$.) A recent neutron-diffraction study [10] provides a complete structure determination, showing a distorted octahedral array of oxygen atoms about Sb^V and distorted square-pyramidal co-ordination about Sb^{III}. As one would therefore expect, the Mössbauer spectrum of α-Sb_2O_4 exhibits two antimony resonances.[14]

However, the antimony 3*d* region of the *X*-p.e. spectrum, obtained without special precautions shows just *one* set of symmetrical Sb $3d_{\frac{5}{2}},3d_{\frac{3}{2}}$ signals each with a half-width (full-width at half-maximum height) of 1.6 eV (Figure 1).* But, after heating the sample in ' air ' (see above) the antimony 3*d* signals broadened to a half-width of 2.3 eV and developed a discernible asymmetry. In a comparative study of Sb_2O_3 and $BaBi_{0.5}Sb_{0.5}O_3$,[15] the Sb^{III} 3*d* and Sb^V 3*d* half-widths were found to be 1.8 and 1.7 eV, respectively. It thus appears that under normal conditions α-Sb_2O_4 has an unrepresentative surface composition with only one oxidation state of antimony present. The surface layer is presumably an antimony(III) phase, probably some hydrated form of Sb_2O_3.

The Sb $3d_{\frac{3}{2}}$ signal of treated α-Sb_2O_4 was subjected to gaussian analysis, assuming two constituent elements. The best fit was obtained with component signals having the relative areas 1 : 1.6, a separation of 0.6 eV, and half-widths of 1.7 and 1.9 eV respectively. The more intense component is that corresponding to the lower ionisation energy, the antimony(III) signal, most likely. The disparate intensities of the component signals presumably reflect incomplete reconstitution of Sb^V on heating in oxygen.

An *X*-p.e. study of Sb_2O_4 has also been described by Birchall *et al.*,[16] who report evidence of mixed-valency character in the form of unusually broad Sb 3*d* signals at 77 K. Unfortunately, it is not entirely clear whether these measurements were carried out on α- or β-Sb_2O_4. (The structure of β-Sb_2O_4 is a slight modification of that of the α form.[17]) We have observed some broadening of the Sb 3*d* signals from *untreated* α-Sb_2O_4 on cooling from ambient temperature to 77 K, but this effect seems connected with the surface phase since it is not observed in the case of samples preheated in ' air '.

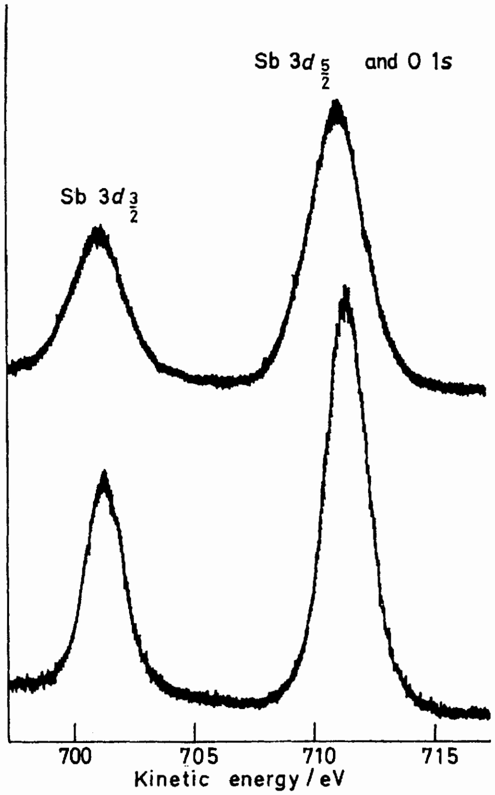

FIGURE 1 Antimony 3*d* region of the *X*-p.e. spectra of α-Sb_2O_4 (raw data). The upper trace relates to a ' clean ' sample treated with 'air,' the lower to a ' dirty ' untreated sample (see text)

An attempt was made to estimate the separation of the antimony-(III) and -(V) signals using equation (1), and assuming a point-charge model for the α-Sb_2O_4 lattice. The site potentials of the antimony-(III) and -(V) atoms were calculated by means of a computer routine due to

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* Actually attention should be confined to the form of the $3d_{\frac{3}{2}}$ p.e. signal since the $3d_{\frac{5}{2}}$ signal of antimony is overlapped by the oxygen 1*s* signal. However, the O 1*s* signal should be significantly weaker than either of the Sb 3*d* signals; indeed, in practice, there is little evidence of it and, in the case of Sb_2O_4, the $3d_{\frac{5}{2}}$ and $3d_{\frac{3}{2}}$ signals were always of a consistent line shape.

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Van Gool and Piken.[18] The antimony $3d$ orbital energies were obtained by a non-relativistic SCF method, using a computer program developed by D. F. Mayers of this university. Three sets of calculations were actually carried out assuming in turn full ionicity, half the formal ionic charges, and a quarter the formal charges. When calculating the $3d$ orbital energies for different formal charges on antimony, it was assumed that added electron density first filled the $5s$ orbital before any was accommodated in the $5p$ subshell. The results of these calculations are shown in the Table. It can be seen there that the observed Sb^{III}–Sb^{V} binding energy difference of 0.6 eV would correspond to partial ionic charges of approximately half the formal values.

Calculations of the Sb^{V}–Sb^{III} $3d$ binding-energy difference in α-Sb_2O_4 using equation (1) * (see text)

Ionic charges assumed	$-\Delta E(3d)$/eV	$e\Delta V$/eV
Formal (Sb^{3+}, Sb^{5+})	26.9	−20.3
Half formal	10.4	−10.1
Quarter formal	4.6	−5.1

* $\Delta I = -\Delta E + e\Delta V$.

$BaBiO_3$.—This bismuth(III)–bismuth(V) compound has a distorted version of the perovskite structure.[11] Both species of bismuth atom have six-co-ordinate sites, but sufficiently distorted from octahedral symmetry that the Bi^{III}–O (2.25—2.27 Å) and the Bi^{V}–O bond lengths (2.13—2.15 Å) are significantly different.

The bismuth $4f_{\frac{7}{2}}$,$4f_{\frac{5}{2}}$ p.e. signals from untreated samples of $BaBiO_3$ were simple symmetrical bands (Figure 2), like the corresponding antimony $3d$ doublet, each with a half-width of 1.6 eV. The oxygen $1s$ signal (here separately observable) consisted of three overlapping bands, indicating surface impurities such as adsorbed water and perhaps carbonate. But, after heating in oxygen, $BaBiO_3$ showed a singlet O $1s$ signal and both bismuth $4f$ signals acquired a perceptible asymmetry (Figure 2), their half-width being increased somewhat to 1.7 eV. This is significantly greater than the half-width of the bismuth(III) $4f$ signals from Bi_2O_3 (1.5 eV), but the same as the half-width observed for the bismuth(III)-antimony(V) compound $BaBi_{0.5}Sb_{0.5}O_3$ (1.7 eV).[15] (The asymmetry that develops in the bismuth $4f$ signals is not sufficiently pronounced to allow a reliable curve resolution.)

It seems likely that $BaBiO_3$ normally has a surface phase in which Bi^{III} predominates, although the evidence is not as clear cut as it is in the case of the antimony(III)–antimony(V) systems. But, then, the bismuth-(III) and -(V) sites are not as dissimilar as are the corresponding antimony sites in α-Sb_2O_4. Some might regard the case of $BaBiO_3$ as intermediate between classes I and II of the Robin and Day scheme.[1]

Conclusions.—Here then is further evidence that, unless exceptional precautions are taken in sample preparation, a mixed-valency compound may have a surface phase containing only one of the two oxidation states present in the bulk material. The particular systems investigated, α-Sb_2O_4 and $BaBiO_3$, belong to the same class as Pb_3O_4, and our results raise a doubt concerning the prevailing interpretation of X-p.e. spectroscopy data on the latter system. However, we must await the application of other surface-sensitive techniques for a clear resolution of the issue. It is all too clear, given the ambiguities that may exist concerning the surface purity of samples, that X-p.e. spectroscopy does not provide a reliable structural tool for the mixed-valency field.

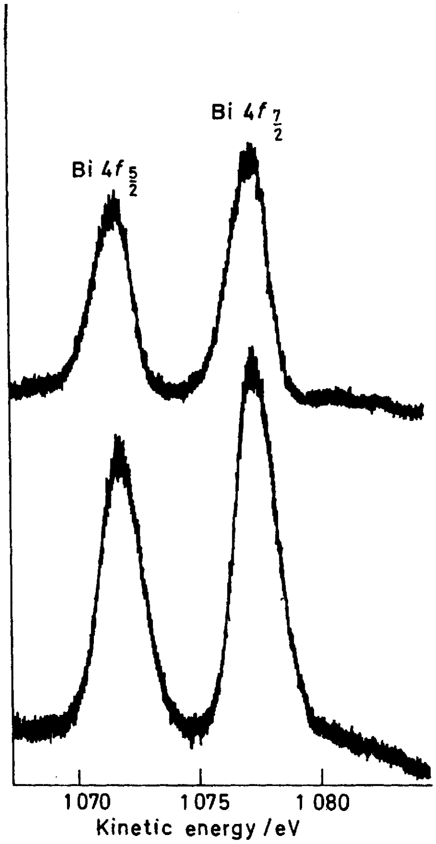

FIGURE 2 Bismuth $4f$ region of the X-p.e. spectra of $BaBiO_3$ (raw data). The upper trace corresponds to a sample preheated in 'air,' the lower to an untreated sample (see text)

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