Notes

An *X*-Ray Photoelectron Spectroscopic Study of the Surface Properties of Vanadium Antimonate and β-Antimony Tetroxide †

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X-Ray photoelectron spectroscopy shows that non-stoicheiometric rutile-type vanadium antimonates prepared by solid-state reactions between antimony(III) oxide and vanadium(V) oxide are enriched at the surface in antimony. The observations are discussed and related to the superficial enrichment in antimony which occurs in other solids with rutile-type structures but prepared by different methods. The spectra from β-antimony tetroxide containing low concentrations of vanadium are consistent with the incorporation of vanadium within the bulk and associated with the low-temperature stabilisation of this phase. The thermally induced outgrowth from ' β-antimony tetroxide ' formed by decomposition of vanadium antimonate is related to a surface reaction with vanadium(V) oxide and the subsequent development of a crystalline vanadium antimonate outgrowth.

Considerable uncertainty has, in the past,[1-6] been associated with the character of the products which may be formed in the antimony–vanadium–oxygen system. We have recently[7,8] shown that the reaction between antimony(III) oxide and vanadium(V) oxide is critically dependent on the presence of oxygen and that a rutile-type monophasic antimony-deficient vanadium antimonate of composition $VSb_{1-y}O_{4-\frac{3}{2}y}$ $(0 < y < 0.1)$ may be prepared by slowly heating equimolar quantities of the reactants in a strictly oxygen-free environment. Reactions in a limited supply of oxygen yield non-stoicheiometric vanadium antimonate containing less oxygen, $VSb_{1-y}O_{4-2y}$ $(0 < y < 0.1)$, together with small amounts of antimony tetroxide. At temperatures exceeding 800 °C the antimony tetroxide is formed as the β-polymorph which[9] may be more accurately described as a solid solution of *ca.* 5% vanadium in β-Sb_2O_4. Reactions in air give[7,8] homogeneously oxidised materials of formula $V_{1-y}Sb_{1-y}O_4$ $(0 < y < 0.1)$. We have also investigated[9] the nature of thermally induced changes in these phases and found them to be indicative of chemical reactivity and structural changes at the solid surfaces.

We have therefore examined the surface regions of the rutile-type vanadium antimonate and the solid solution of vanadium in β-antimony tetroxide by *X*-ray photoelectron spectroscopy (x.p.s.) to elucidate the surface properties of these materials.

Experimental

Monophasic antimony-deficient vanadium antimonate was prepared[8] by slowly heating to 750 °C an intimately ground mixture of antimony(III) oxide and vanadium(V) oxide in flowing dry nitrogen from which oxygen was rigorously excluded.[10] Similar experiments[8] in commercial-grade nitrogen, which is nominally oxygen free, gave non-stoicheiometric vanadium antimonate containing less oxygen, together with antimony tetroxide. Reactions performed[8] in air gave oxidised vanadium antimonate.

β-Antimony tetroxide containing *ca.* 5% vanadium was prepared[9] by heating antimony(III) oxide and vanadium(V) oxide (Sb : V = 18 : 1) in commercial nitrogen at 700 °C (24 h) and then in air at 810 °C (4 h).

The x.p.s. data were recorded in digital form with a Kratos ES300 spectrometer operating at a base pressure of *ca.* 1×10^{-8} Torr using Mg-K_α exciting radiation ($h\nu$ = 1 253.6 eV). The samples were investigated as fine powders mounted on double-sided Sellotape and examined at room temperature. Quantitative measurements were based on the Sb 4*d* and V $2p_{\frac{3}{2}}$ peaks using previously reported[11] sensitivity factors. All binding energies were referred to a value of 285 eV for the C 1*s* signal arising from carbon impurity on the sample surfaces.

Results and Discussion

Typical *X*-ray photoelectron spectra recorded from vanadium antimonate are depicted in the Figure and show that, despite overlap between the V $2p_{\frac{1}{2}}$ and the Mg-$K_{\alpha_{3,4}}$ satellite peaks from the Sb $3d_{\frac{5}{2}}$ and O 1*s* levels, the V $2p_{\frac{3}{2}}$ and Sb 4*d* peaks are well resolved and amenable for interpretation in quantitative analysis. The vanadium and antimony binding energies and the Sb : V atomic ratios recorded from the compounds are given in the Table.

Vanadium Antimonate.—The x.p.s. data show that the antimony concentration in the vanadium antimonate surfaces may be up to four times greater than the nominal bulk Sb : V ratio of unity.

It might be envisaged that the surface enrichment in antimony observed in both the oxidised and monophasic vanadium antimonates results from the accumulation of unreacted antimony(III) oxide at the surface in the first stage of the formation of a macroscopically distinguishable antimony tetroxide phase. Indeed, monolayer coverage of vanadium antimonate by such an Sb_2O_4 phase would, assuming the involvement of the minimum O–Sb–O unit with bond distances similar to those reported[12-14] for antimony oxides containing Sb^{III}, constitute a thickness of *ca.* 4 Å and would be readily detectable by x.p.s. However, the reaction between antimony(III) oxide and vanadium(V) oxide in air gives[8] a single-phase homogeneously oxidised product and the reaction in a strictly oxygen-free environment leads[8] to the

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† *Non-S.I. units employed*: Torr = (101 325/760) Pa; eV ≈ 1.60×10^{-19} J.

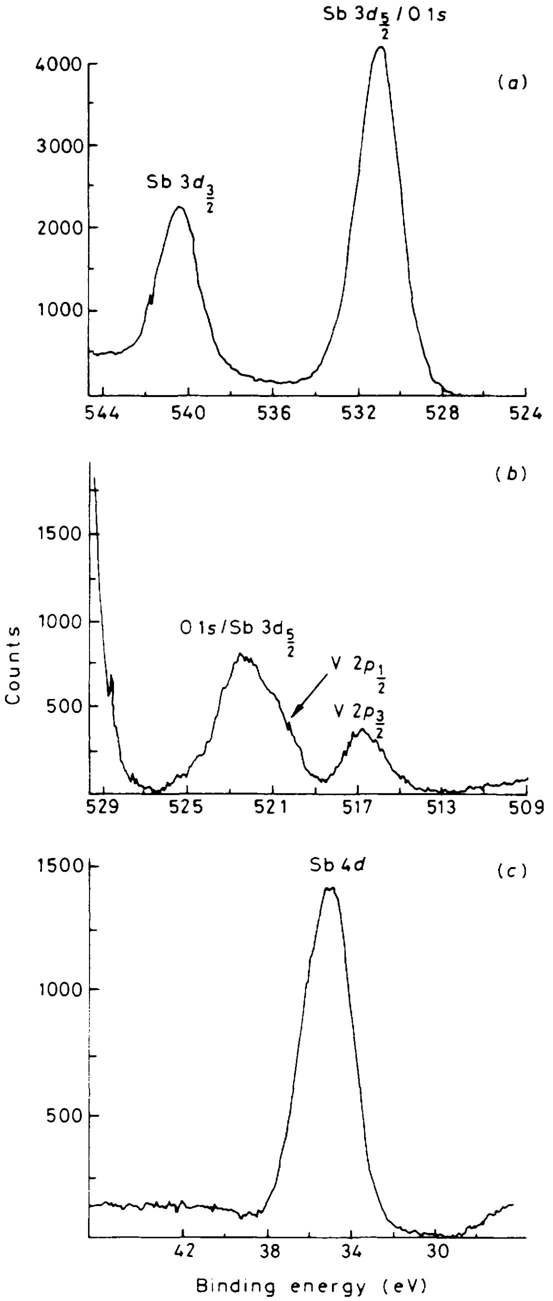

Figure. *X*-Ray photoelectron spectra recorded from vanadium antimonate; (*a*)–(*c*) are different parts of the spectrum of binding energies scanned

formation of vanadium antimonate which, although non-stoicheiometric, is monophasic. Hence neither reaction involves the formation of antimony tetroxide and, given that antimony(III) oxide sublimed during the preparation of the monophasic vanadium antimonate, it seems unreasonable to attribute the surface antimony enrichment to unreacted antimony and the formation of a discrete surface antimony oxide.

Hence the observed enrichment of the vanadium antimonate surface by antimony suggests that the surface layer undergoes substantial modification similar to that which has been proposed [15] for structurally related solid solutions containing *ca.* 4% antimony within bulk tin(IV) oxide but in which the surface antimony concentration is *ca.* 25%. Although the surface enrichment in tin–antimony oxides has been [15] associated with the preparative procedure during which the calcination of an amorphous precipitate induces nucleation and crystallisation of a bulk rutile-type tin(IV) oxide lattice and a counter migration of antimony to the surface, it must be noted that the formation of vanadium antimonate is very different and involves a solid-state reaction between two oxides to produce, without melting, a crystalline compound. Despite this difference, we suggest that it is more pertinent to recognise that both tin–antimony oxide and vanadium antimonate adopt a rutile-type structure in which the cation diffusion rates are likely to be of similar orders of magnitude and that the surface segregation of antimony ions is a reflection of their more favourable accommodation in superficial sites of lower symmetry than are offered in the bulk.

Table. Vanadium and antimony binding energies and surface com positions of phases in the vanadium–antimony–oxygen system

Compound	Atomic ratio Sb : V	Binding energies ± 0.1 eV	
		V $2p_{\frac{3}{2}}$	Sb 4*d*
$V_{1-y}Sb_{1-y}O_4$	2.63	516.6	35.2
$VSb_{1-y}O_{4-2y}$ + Sb_2O_4	4.00	516.1	35.1
$VSb_{1-y}O_{4-3y}$	1.85	516.3	35.2
β-Sb_2O_4/5% V	Vanadium not detectable		34.6
Annealed β-Sb_2O_4 formed from the decomposition of monophasic vanadium antimonate	0.51	517.4	35.2
α-Sb_2O_4			35.3
V_2O_5		517.9	

In these respects it is relevant that Mössbauer spectroscopy, which essentially examines the bulk solid, has identified Sb^V in both tin–antimony oxide [16] and vanadium antimonate.[5] Given the preference of Sb^V for six-fold octahedral co-ordination [17] it seems reasonable to associate the Mössbauer data with the accommodation of Sb^V in the bulk rutile-type vanadium antimonate lattice. However, Sb^{III} is more stable in four-fold co-ordination [17] and would therefore be more favourably accommodated in the surface of the rutile-type solid. In this respect it is unfortunate that, as in a recent x.p.s. study [15] of antimony-containing tin(IV) oxide, we have been unable unequivocally to resolve the x.p.s. spectra from the vanadium antimonates into separate contributions from Sb^{III} and Sb^V. Although the identification of Sb^{III} and Sb^V in other mixed-valence antimony compounds from the x.p.s. Sb $3d_{\frac{5}{2}}$ and $3d_{\frac{3}{2}}$ signals has been found to be difficult [18-21] and remains a matter of some uncertainty,[15,22] it is pertinent to note that the successful [18] determination of binding-energy shifts between Sb^{III} and Sb^V in cleaned and re-oxidised α-Sb_2O_4 has shown that Sb^{III} adopts the superficial sites. In this respect it is also relevant to record that a recent comprehensive investigation of antimony-containing tin(IV) oxide [23] by x.p.s., ultraviolet photoelectron spectroscopy (u.p.s.), and high-resolution electron energy-loss spectroscopy (h.r.e.e.l.s.) has confirmed the enrichment of the tin–antimony oxide surface by Sb^{III}. It therefore seems reasonable to suggest that the surfaces of the vanadium antimonates are enriched by Sb^{III}.

The nature of the superficial vanadium in vanadium antimonates may be considered in terms of the V $2p_{\frac{3}{2}}$ binding energies which, for all three materials, fall within the range 516.1—516.6 eV and are significantly lower than that recorded from vanadium(V) oxide, 517.9 eV. In this respect it is relevant that the V $2p_{\frac{3}{2}}$ binding energies recorded from V_2O_5 and V_2O_3 during other investigations [24] are, when converted to the C 1*s* reference value used in the present study, 517.3 and 516.1 eV respectively.

Although other [25] V $2p_{\frac{3}{2}}$ binding energies of 516.4 and 515.0 eV for V_2O_5 and V_2O_3 respectively are, in the absence of a suitable reference, not comparable with our data, the difference of 1.4 eV between the binding energies agrees with differences observed elsewhere.[24] It seems therefore that the V $2p_{\frac{3}{2}}$ binding energies recorded in this work from vanadium antimonates may be quite reasonably associated with the presence of superficial V^{III}. It is important to note, however, that, despite pathlengths of *ca.* 45 and 60 Å for the V $2p_{\frac{3}{2}}$ and Sb 4*d* photoelectrons respectively, the susceptibility of the vanadium antimonate surfaces to damage during argon-ion etching has precluded an assessment of the thickness of the surface layers examined in this investigation.

The biphasic product formed from the reaction between antimony(III) oxide and vanadium(V) oxide in commercial nitrogen and composed of non-stoicheiometric vanadium antimonate and antimony tetroxide gave an *X*-ray photoelectron spectrum from which a superficial Sb : V ratio of 4.00 : 1 was deduced. The apparently higher surface concentration of antimony in this material, as compared with oxidised or monophasic vanadium antimonate, is presumably a reflection of the presence of the additional antimony tetroxide phase.

β-*Antimony Tetroxide*.—The antimony tetroxide produced during the reaction between antimony(III) oxide and vanadium(V) oxide at temperatures exceeding 800 °C in oxygen-containing nitrogen is formed as the β polymorph.[9] This observation is unusual because antimony(III) oxide is normally oxidised to α-antimony tetroxide in air and only converted into the β form by a dissociative vapour-phase deposition route at 1 300 °C.[14] The detection [9] by electron-probe microanalysis of *ca.* 5% vanadium in the 'β-Sb_2O_4' hexagonal plate-type crystals has been associated with this lower temperature stabilisation of the β polymorph. The x.p.s. data recorded from the 'β-Sb_2O_4' crystals showed the surface vanadium concentration to be below the normal level of detection of *ca.* 3 cation %. The absence of significant amounts of vanadium in the surface implies that the β-antimony tetroxide structure does not result from isomerisation of the α polymorph by interfacial contact with vanadium(V) oxide as has been invoked [26] to describe the low-temperature transformation of the anatase modification of titanium(IV) oxide to the rutile form when heated in the presence of vandaium(V) oxide. Hence the low-temperature stabilisation of the β polymorph of antimony tetroxide appears to be associated with the incorporation of vanadium within the bulk lattice.

It is also pertinent to record that 'β-Sb_2O_4' containing *ca.* 5% vanadium can be produced [9] by the decomposition of monophasic vanadium antimonate at 810 °C. These hexagonal 'β-Sb_2O_4' plate-type crystals have been found [9] to give an outgrowth of a crystalline vanadium antimonate phase when heated at 670 °C for 27 h. Such a material gave an x.p.s. spectrum from which an Sb : V ratio of 0.51 : 1 was deduced and thereby indicative of an enhanced vanadium presence at the annealed surface. It seems therefore that whilst some vanadium dissolves in the α-antimony tetroxide produced by decomposition of vanadium antimonate at 810 °C causing isomerisation to the β polymorph, the remainder coats the surface of the 'β-Sb_2O_4' to give a material with a lower Sb : V ratio. It is significant that the V $2p_{\frac{3}{2}}$ binding energy resembles that recorded from vanadium(V) oxide and is different from that recorded from the vanadium antimonates. The results suggest that the vanadium coating on the β-Sb_2O_4 surface formed by decomposition of vanadium antimonate is vanadium(V) oxide which, when [9] annealed at 670 °C, reacts with antimony migrating from the β-Sb_2O_4 surface to give an outgrowth of needle-shaped vanadium antimonate crystals.

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References

1 L. W. Vernon and W. O. Milligan, *Tex. J. Sci.*, 1951, 82.
2 R. S. Roth and J. L. Waring, *Am. Mineral.*, 1963, **48**, 1348.
3 R. Renaud, *Rev. Chim. Miner.*, 1971, **8**, 633.
4 H. Schüer and W. Klemm, *Z. Anorg. Allg. Chem.*, 1973, **395**, 287.
5 T. Birchell and A. W. Sleight, *Inorg. Chem.*, 1976, **15**, 868.
6 B. Darriet, J. O. Bovin, and J. Galy, *J. Solid State Chem.*, 1976, **19**, 205.
7 F. J. Berry, M. E. Brett, and W. R. Patterson, *J. Chem. Soc., Chem. Commun.*, 1982, 695.
8 F. J. Berry, M. E. Brett, and W. R. Patterson, *J. Chem. Soc., Dalton Trans.*, 1983, 9.
9 F. J. Berry, M. E. Brett, and W. R. Patterson, *J. Chem. Soc., Dalton Trans.*, 1983, 13.
10 C. R. McIlwrick and C. S. G. Phillips, *J. Phys. E*, 1973, **6**, 1208.
11 H. Berthou and C. K. Jørgenson, *Anal. Chem.*, 1975, **47**, 482.
12 C. Svensson, *Acta Crystallogr., Sect. B*, 1974, **30**, 458.
13 R. M. Bozorth, *J. Am. Chem. Soc.*, 1923, **45**, 1621.
14 D. Rogers and A. C. Skapski, *Proc. Chem. Soc., London*, 1964, 400.
15 Y. M. Cross and D. R. Pyke, *J. Catal.*, 1979, **58**, 61.
16 F. J. Berry, P. E. Holbourn, and F. W. D. Woodhams, *J. Chem. Soc., Dalton Trans.*, 1980, 2241.
17 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.
18 A. F. Orchard and G. Thornton, *J. Chem. Soc., Dalton Trans.*, 1977, 1238.
19 P. Burroughs, A. Hamnett, and A. F. Orchard, *J. Chem. Soc., Dalton Trans.*, 1974, 565.
20 M. J. Tricker, I. Adams, and J. M. Thomas, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 633.
21 T. Birchall, J. A. Connor, and I. H. Hillier, *J. Chem. Soc., Dalton Trans.*, 1975, 2003.
22 Y. Boudeville, F. Figueras, M. Forissier, J-L. Portefaix, and J. C. Vedrine, *J. Catal.*, 1979, **58**, 52.
23 P. A. Cox, R. G. Egdell, C. Harding, W. R. Patterson, and P. J. Tavener, *Surf. Sci.*, 1982, **123**, 179.
24 S. L. T. Andersson, *J. Chem. Soc., Faraday Trans. 1*, 1979, 1356.
25 C. N. R. Rao, D. D. Sarma, S. Vasudevan, and M. S. Hegde, *Proc. R. Soc., London, Ser. A*, 1979, **367**, 239.
26 A. Vejux and P. Courtine, *J. Solid State Chem.*, 1978, **23**, 93.

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