

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231406808>

Stability of free intermetallic compound clusters: Lead/antimony and bismuth/antimony

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · MAY 1987

Impact Factor: 2.78 · DOI: 10.1021/j100294a037

CITATIONS

34

READS

12

4 AUTHORS, INCLUDING:



Klaus D. Sattler

University of Hawai'i at Mānoa

150 PUBLICATIONS 4,347 CITATIONS

SEE PROFILE

Stability of Free Intermetallic Compound Clusters: Lead/Antimony and Bismuth/Antimony

D. Schild,* R. Pflaum, K. Sattler, and E. Recknagel

Fakultät für Physik, Universität Konstanz, 7750 Konstanz, Federal Republic of Germany
(Received: June 17, 1986)

Binary compound clusters are generated by inert gas condensation of Pb, Bi, and Sb, evaporated from two separately heated crucibles. The clusters are ionized by electron impact and analyzed by time-of-flight mass spectrometry. Bismuth and lead clusters show different adsorption probabilities for Sb_4 molecules. Lead clusters dissociate the adsorbed Sb_4 tetramers symmetrically, while dissociation of antimony tetramers by bismuth clusters generates antimony monomers and trimers as well. In contrast to well-known polyanions which are stabilized in complex chemistry, isovalent *free* heteronuclear compound clusters are generated and found with enhanced stability.

Introduction

Compound clusters are a field of growing interest in immiscibles, new materials, and devices. Reactions of transition-metal clusters with hydrogen,¹ N_2 , and CO_2 were investigated in the past few years as the transition elements are the classical field for catalysis. Bimetallic clusters gain major importance in petroleum refining as they lead to a higher rate of desired reactions than pure metal clusters.³ The structure of supported bimetallic clusters was studied by EXAFS measurements.⁴ Compound clusters of semiconducting materials are used in the reactive ionized-cluster beam (RICB) deposition for the preparation of homogeneous thin films for submicrometer electronic devices.⁵ Research on the growth of binary compound clusters is fundamental for under-

standing the formation of bulk phases of compounds⁶ and alloys. Alloy clusters of Ni-Cr and Ni-Al for instance are observed to form clusters with compositions interpretable by simple statistical accretion of the atoms.⁷

Special metal clusters, known as Zintl ions and stabilized within organic solids or liquid ammonia, are subject of research since their discovery in the early 1930s. Two of the group IV (group 4)³³ Zintl ions, containing five and nine metal atoms, are isovalent to the free neutral clusters Pb_5Sb_2 and Pb_5Sb_4 and, additionally, to the ions $(\text{Pb}_2\text{Sb}_3)^+$ and $(\text{Pb}_4\text{Sb}_5)^+$, which in the present work are found with enhanced stability. Furthermore, results on adsorption, dissociative chemisorption, and fragmentation are presented.

Experimental Section

For generation of *compound clusters*, the former cluster source⁸ was modified and described in ref 9. The new source contains two ovens twisted inward and shielded from each other by tantalum cylinders and a copper wall. The ovens are boron nitride crucibles and separately resistance heated. The temperature is

(1) (a) Richtsmeier, S. C.; Parks, E. K.; Liu, K.; Pobo, L. G.; Riley, S. J. *J. Chem. Phys.* **1985**, *82*, 3659. (b) Parks, E. K.; Liu, K.; Richtsmeier, S. C.; Pobo, L. G.; Riley, S. J. *J. Chem. Phys.* **1985**, *82*, 5470. (c) Liu, K.; Parks, K.; Richtsmeier, S. C.; Pobo, L. G.; Riley, S. J. *J. Chem. Phys.* **1985**, *83*, 2882. (d) Whetten, R. L.; Cox, D. M.; Trevor, D. J.; Kaldor, A. *Phys. Rev. Lett.* **1985**, *54*, 1494. (e) Geusic, M. E.; Morse, M. D.; Smalley, R. E. *J. Chem. Phys.* **1985**, *82*, 590. (f) Phillips, J. C. *J. Chem. Phys.* **1986**, *84*, 1951.

(2) Morse, M. D.; Geusic, M. E.; Heath, J. R.; Smalley, R. E. *J. Chem. Phys.* **1985**, *83*, 2293.

(3) Sinfelt, J. H. *Sci. Am.* **1985**, *9*, 96.

(4) (a) Meitzner, G.; Via, G. H.; Lythe, F. W.; Sinfelt, J. H. *J. Chem. Phys.* **1985**, *83*, 353. (b) Meitzner, G.; Via, G. H.; Lythe, F. W.; Sinfelt, J. H. *J. Chem. Phys.* **1985**, *83*, 4793.

(5) Takagi, T. *JARECT 13, Semiconductor Technologies*, Nishizawa, J., Ed.; Ohmsha, Japan, 1984, p 323.

(6) (a) Martin, T. P. *J. Chem. Phys.* **1984**, *80*, 170. (b) Martin, T. P. *J. Chem. Phys.* **1985**, *83*, 78. (c) Saito, Y.; Mihima, K.; Noda, T. *Jpn. J. Appl. Phys.* **1983**, *22*, L179.

(7) Rohlfing, E. A.; Cox, D. M.; Petkovic-Luton, R.; Kaldor, A. *J. Phys. Chem.* **1984**, *88*, 6227.

(8) Sattler, K.; Mühlbach, J.; Recknagel, E. *Phys. Rev. Lett.* **1980**, *45*, 821.

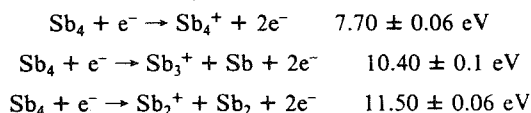
(9) Sattler, K. *Z. Phys. D.* **1986**, *3*, 223.

measured by thermocouples at the bottom of each crucible. The vapors condense in a helium atmosphere at 80 K. This temperature is defined by the liquid N₂ cooled copper walls of the condensation cell. The helium pressure (typical 50 Pa) is measured directly by a piezoelectric differential manometer. Cluster source and mass spectrometer are separated by a differentially pumped section. The cluster beam passes through a 1-mm orifice into the high vacuum chamber of the mass spectrometer. A quartz monitor located 10 cm above the cluster source is used to measure the intensity of the neutral cluster beam. The film thickness on the monitor typically grows at a rate of 1 Å/s.

Mass analysis is performed by time-of-flight mass spectrometry. Ionization of the clusters is accomplished by electron impact with electron energies E_i between 8 (low) and 80 eV (high). The voltage applied to the cathode of the electron gun is adjusted by a potentiometer symmetrically to the tip of the cathode in order to minimize the offset of the electron energy. The half-width of the energy of the electrons due to the thermal distribution was determined to be smaller than 1 eV. We apply a double pulse technique, which provides ionization within a field free region.¹⁰ Extracted from the ionizing zone, the clusters are accelerated by 3 kV and enter the field free region of the drift tube (length 2 m). At the end of the tube they are postaccelerated by 7 kV and impinge on a copper plate inducing secondary electron emission. These electrons are accelerated toward the first dynode of an electron multiplier. The time differences between the starting pulse of the ion extraction lens and the stop signals from the detector are stored in a multichannel analyzer.

Results and Discussion

Bi-Sb Clusters. Bismuth and antimony are isovalent, with three p electrons in the highest occupied states, and show unlimited miscibility in the bulk phase diagram.¹¹ However, evaporation of pure bismuth produces mainly monomers and dimers whereas antimony vapor consists of more than 95% Sb₄ molecules at the oven temperatures applied.¹² Consequently, condensation of bismuth vapor generates Bi_n clusters of all sizes,¹³ whereas for antimony only Sb_{4n} clusters are created (Figure 1). For antimony, the ionization potential and lowest appearance potentials of the fragments have been reported¹⁴ to be



For antimony clusters, all lines observed are within the Sb_{4n} sequence indicating that fragmentation does not influence the mass spectrum at 9 eV (Figure 1). For bismuth clusters a recent study shows that the intensity of the bismuth tetramer is not affected by fragmentation of larger clusters at electron energies below 10.5 eV.¹³ Therefore, a mass spectrum of small Bi-Sb cluster ions is recorded with an electron energy of 9 eV in order to avoid fragmentation.

We consider the adsorbed fraction of Sb_{4n} ($n = 1, 2, \dots$) on bismuth clusters after simultaneous quenching of Bi (crucible temperature $T = 980$ K) and Sb ($T = 860$ K) vapors in helium and concentrate on the adsorption probability of Sb₄. As adsorbed Sb_m ($m \neq 4n$) appear as well as adsorbed Sb_{4n} (Figure 1b), the adsorption probability $P_A(n)$ of Sb₄ on Bi_n clusters is defined as

$$P_A(n) = \frac{\sum_{k=1}^4 I(\text{Bi}_n\text{Sb}_k^+)}{\sum_{k=0}^4 I(\text{Bi}_n\text{Sb}_k^+)} \quad (1)$$

P_A is found to depend on the bismuth cluster size and takes low values for the bismuth dimer and pentamer (Figure 2). This can

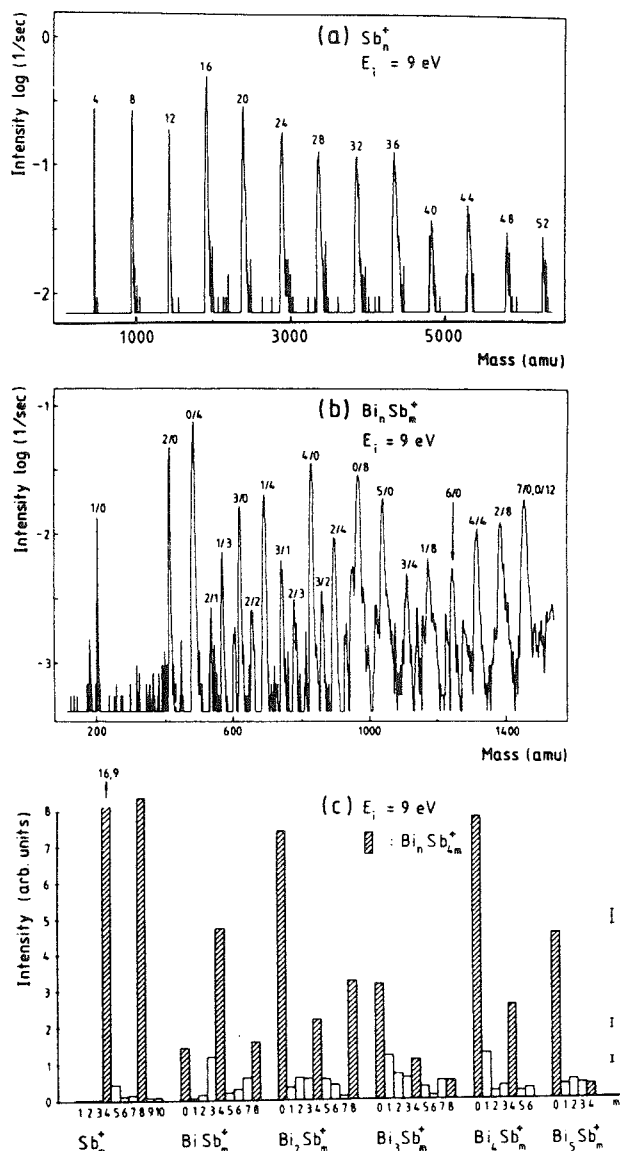


Figure 1. (a) Mass spectrum of antimony clusters. The Sb_{4n} sequence reflects that antimony evaporates mainly as tetramers. The spectrum was recorded at $E_i = 9$ eV with an oven temperature of 860 K. (b) Mass spectrum ($T(\text{Bi}) = 980$ K, $T(\text{Sb}) = 860$ K) and histogram (c) of (Bi_nSb_m)⁺ clusters at $E_i = 9$ eV. The bars denote the integrated cluster line intensities. They are arranged in groups with a fixed number of bismuth atoms contained in the clusters. On the right side of the bars of Bi_n⁺ the abundances of the (Bi_nSb_m)⁺ clusters with increasing m are plotted. Statistical error bars are noted on the right margin.

be understood by considering pure bismuth cluster spectra where Bi₆⁺ and Bi₉⁺ ions¹³ are less abundant indicating less stability for these clusters sizes. Adsorption of Sb₄ tetramers on Bi_n results in clusters containing $4 + n$ isovalent atoms, such that the low values of $P_A(n)$ observed for $n = 2$ and 5 confirm low stability also for compound clusters Bi_nSb₄ containing six or nine atoms.

The dissociation probability $P_{Dx}(n)$ of Sb₄ tetramers on Bi_n clusters, which is defined as

$$P_{Dx}(n) = I(\text{Bi}_n\text{Sb}_x^+) / \sum_{k=1}^4 I(\text{Bi}_n\text{Sb}_k^+) \quad x = 1, 2, 3 \quad (2)$$

is plotted in Figure 2. All three dissociation channels are populated to about 20%. In contrast to the Bi_nSb and Bi_nSb₂ clusters, Bi_nSb₃ clusters are increased from $n = 1$. This can be understood from the generation of Bi_{4-x}Sb_x tetramers by dissociation, which is found with enhanced probability for all three channels.

At high electron impact energies fragmentation enhances the lines of exceptionally stable Bi-Sb compound cluster ions (Figure 3). For pure bismuth¹⁵ and antimony^{9,16} clusters this leads to

(10) Pflaum, R.; Sattler, K.; Recknagel, E. *Phys. Rev. B* **1986**, *33*, 1522.

(11) Hultgren, R.; Desai, P. D.; Hawkins, D. T.; Gleiser, M.; Kelly, K. K. *Selected Values of the Thermodynamic Properties of Binary Alloys*; American Society for Metals: Metals Park, OH, 1973.

(12) Mühlbach, J.; Pfau, P.; Recknagel, E.; Sattler, K. *Surf. Sci.* **1981**, *106*, 18.

(13) Walstedt, R. E.; Bell, R. F. *Phys. Rev. A* **1986**, *33*, 2830.

(14) Cabaud, B.; Hoareau, A.; Nounou, P.; Uzan, R. *Int. J. Mass Spectrom.* **1973**, *11*, 157.

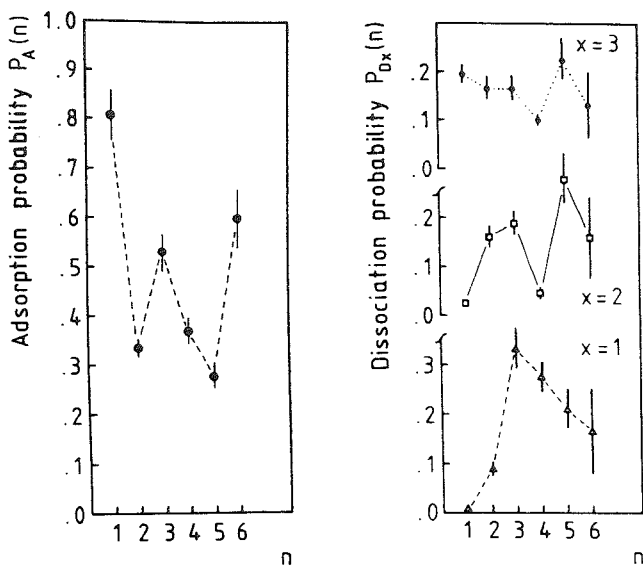


Figure 2. Adsorption probability $P_A(n)$ and dissociation probability $P_D(n)$ of Sb_4 molecules on Bi_n clusters. Tetramers show their comparative stability and inertness. Data are taken from the mass spectrum shown in Figure 1.

enhanced abundances of cluster ions containing 3, 4, 5, or 7 atoms. Analogous anomalies are found for Bi-Sb compound cluster ions, independent of their stoichiometry. This coincidence for pure and mixed cluster ions can be understood from the similarity of the covalent atomic radii (difference less than 8%¹⁷), in addition to the isovalency. Within different fragment cluster ions containing an equal number of atoms, the relative abundances are found to decrease with decreasing fraction of Sb atoms contained in the compound clusters. For instance, the relative abundances of tetramer ions decrease from the $(\text{BiSb}_3)^+$ to the $(\text{Bi}_3\text{Sb})^+$ ion (Figure 3). This is explained by a systematic decrease of the dissociation energies from Sb_4 to Bi_4 ¹⁸ (Sb_4 , 9.04 ± 0.15 eV; BiSb_3 , 8.27 ± 0.11 eV; Bi_2Sb_2 , 7.52 ± 0.08 eV; Bi_3Sb , 6.82 ± 0.06 eV; Bi_4 , 6.03 ± 0.08 eV).

The enhanced abundances of the $\text{Bi}_n\text{Sb}_{n-m}^+$ ions ($m = 0-n$) consisting of 3, 5, and 7 atoms could be explained by the even electron rule which states that clusters containing an even number of electrons show enhanced stability. Therefore cluster ions containing an even number of electrons should be enhanced by fragmentation.¹⁹ However, Bi-Sb tetramer ions are found to be enhanced by fragmentation though they are containing an odd number of electrons. On the other hand, $(\text{Bi}_n\text{Sb}_m)^+$ cluster ions containing nine atoms are not enhanced by fragmentation (Figure 3). This means they are not particularly stable though they are provided with an even number of electrons. The same is found for pure $(\text{Bi}_9)^+$ cluster ions.¹⁵ To explain the different cluster stabilities it is necessary not only to consider the number of electrons but also geometric and electronic structural properties.

Pb-Sb Clusters. Condensation of Pb (1070 K) and Sb (810 K) vapors generates high intensities for Pb_nSb_m compound clusters (Figure 4). Bare lead clusters are almost not observed in the size range for $n < 7$. In addition to $(\text{Pb}_n\text{Sb}_4)^+$, $(\text{Pb}_n\text{Sb}_2)^+$ cluster ions are observed with high intensities exceeding the $(\text{Pb}_n\text{Sb}_4)^+$ lines for $n > 7$. To decide whether the only origin of the $(\text{Pb}_n\text{Sb}_2)^+$ clusters is dissociative chemisorption in the condensation cell or if this is superimposed by fragmentation following electron impact, mass spectra with different electron energies are recorded and taken into account.

At high electron impact energies, two stable cluster ions are

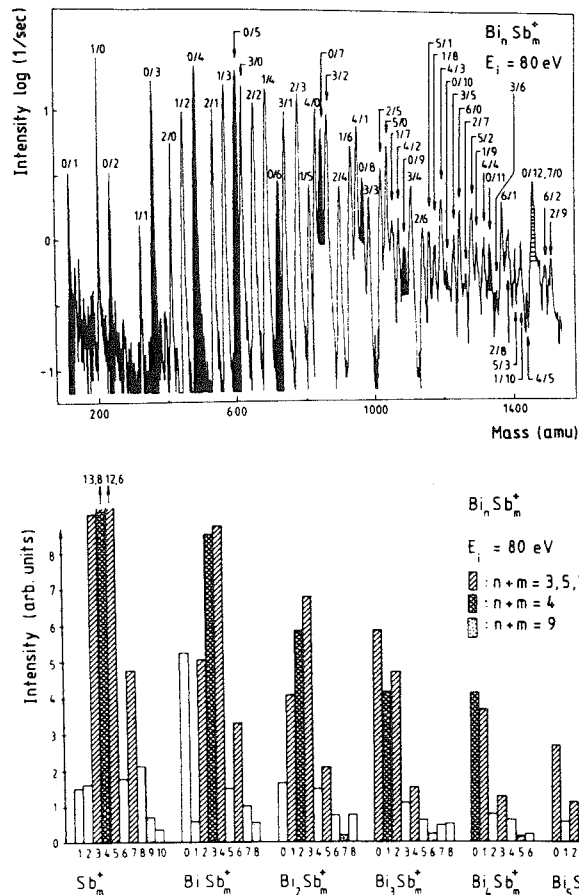


Figure 3. Mass spectrum of Bi-Sb clusters at $E_i = 80$ eV with corresponding histogram. In the mass spectrum pure antimony lines are colored black for clearness. The hatched peak of Bi_7^+ or Sb_{12}^+ marks the end of unequivocal mass resolution. Arrangement and notation in the histogram is the same as in Figure 1.

preferably observed: $(\text{Pb}_2\text{Sb}_3)^+$ and $(\text{Pb}_4\text{Sb}_5)^+$, Figure 5 shows their relative abundances depending on electron energy and condensation parameters. Their relative intensities increase strongly from low electron energies. With enhanced oven temperatures, i.e. with enhanced abundance of large clusters,²⁰ the relative abundances are increased and the ion signal of $(\text{Pb}_4\text{Sb}_5)^+$ finally exceeds the $(\text{Pb}_2\text{Sb}_3)^+$ signal. The abundance of the two ions reaches more than 15% of the total ion signal. This confirms not only a high stability of these two cluster ions but also that they originate from fragmentation of many different parent clusters.

Suggested structures of these particularly stable cluster ions are displayed in Figure 6. They correspond to the structures reported for the Pb_5^{2-} and Pb_9^{4-} polyanions.^{21,22} Substitution of m lead atoms by antimony from the anions leads to Pb_3Sb_2 ($m = 2$), $(\text{Pb}_2\text{Sb}_3)^+$ ($m = 3$), Pb_5Sb_4 ($m = 4$), and $(\text{Pb}_4\text{Sb}_5)^+$ ($m = 5$) clusters, respectively. This does not change the number of atoms and valence electrons contained in the clusters. The free Pb_3Sb_2 and $(\text{Pb}_2\text{Sb}_3)^+$ clusters are isovalent with the Pb_5^{2-} and Sn_5^{2-} anions²¹ and with the cation Bi_5^{3+} maintained in the solid state and in solution.^{23,24} The Pb_5Sb_4 and $(\text{Pb}_4\text{Sb}_5)^+$ clusters are isovalent to the nido series $(\text{Sn}_{9-x}\text{Ge}_x)^{4-}$, $(\text{Sn}_{9-x}\text{Pb}_x)^{4-}$ ($x = 0-9$),^{25,26}

(20) Pfau, P.; Sattler, K.; Mühlbach, J.; Pflaum, R.; Recknagel, E. *J. Phys. F* 1982, 12, 2131.

(21) (a) Edwards, P. A.; Corbett, J. D. *Inorg. Chem.* 1977, 16, 903. (b) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, 1984; pp 454 ff, 678 ff.

(22) Lohr, L. L. *Inorg. Chem.* 1981, 20, 4229.

(23) (a) Burns, R. C.; Gillespie, R. J.; Luk, W.-C. *Inorg. Chem.* 1978, 17, 3596. (b) Burns, R. C.; Gillespie, R. J.; Barnes, J. A.; McGlinchey, M. J. *Inorg. Chem.* 1982, 21, 799.

(24) (a) Corbett, J. D. *Prog. Inorg. Chem.* 1976, 21, 129. (b) Hershaft, A.; Corbett, J. D. *Inorg. Chem.* 1963, 2, 979. (c) Friedmann, R. M.; Corbett, J. D. *Inorg. Chim. Acta* 1973, 7, 525.

(15) Mühlbach, J.; Pfau, P.; Sattler, K.; Recknagel, E. *Z. Phys. B* 1982, 47, 233.

(16) Pfau, P.; Sattler, K.; Mühlbach, J.; Recknagel, E. *Phys. Rev. Lett.* 1982, 91, 316.

(17) Adams, D. M. *Inorganic Solids*; Wiley: New York, 1974, p 227.

(18) Kohl, F. J.; Carlson, K. D. *J. Am. Chem. Soc.* 1968, 90, 4814.

(19) Martin, T. P. *J. Chem. Phys.* 1984, 81, 4426.

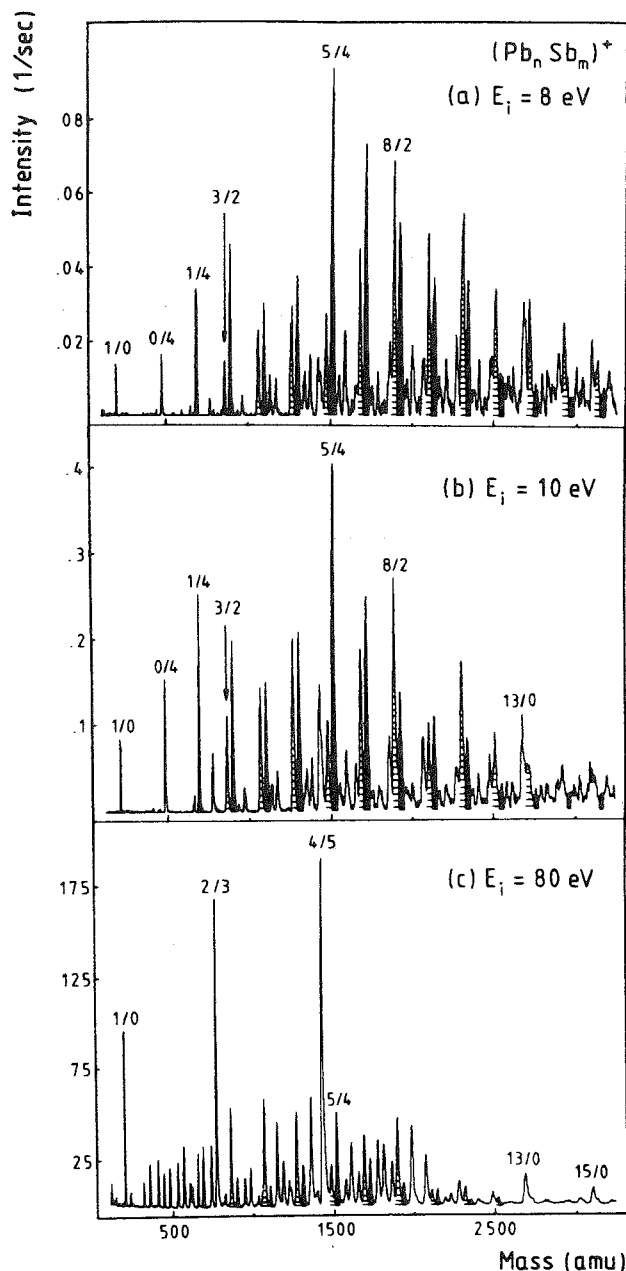


Figure 4. Mass spectra of $(\text{Pb}_n\text{Sb}_m)^+$ clusters ($T(\text{Pb}) = 1070 \text{ K}$, $T(\text{Sb}) = 810 \text{ K}$) recorded at 8 (a), 10 (b), and 80 eV (c). Filled peaks in (a) and (b) correspond to $(\text{Pb}_n\text{Sb}_4)^+$ clusters. In addition, the peaks of $(\text{Pb}_n\text{Sb}_2)^+$ clusters are hatched. The dissociation of antimony tetramers is enhanced from Pb_3Sb_2 on (a). The strongest line in the spectra (a,b) is the Pb_5Sb_4 cluster. At $E_i = 10 \text{ eV}$ the intensities of small $(\text{Pb}_n\text{Sb}_2)^+$ and $(\text{Pb}_n\text{Sb}_4)^+$ clusters are increased in comparison to the mass spectrum at 8 eV. Within the mass spectrum at 80 eV the strongest lines correspond to the stable $(\text{Pb}_2\text{Sb}_3)^+$ and $(\text{Pb}_4\text{Sb}_5)^+$ cluster ions which are preferably produced by fragmentation. As a consequence the lines of larger compound clusters are diminished leading to the accentuation of the Pb_{13}^+ and Pb_{15}^+ lines.

isovalent to the TiSn_8^{5-} anion,^{22,25} and isoelectronic to the Bi_9^{5-} cation.^{22,24} The enhanced stability of Pb_3Sb_2 is confirmed by the fact that Pb_3 dissociates the Sb_4 molecule five times more effectively than Pb_2 , while the adsorption probability is observed to be the same for the lead dimer and trimer, as is shown below.

(25) Rudolph, R. W.; Wilson, W. L.; Taylor, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 2480.

(26) (a) Rudolph, R. W.; Wilson, W. L.; Parker, F.; Taylor, R. C.; Young, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 4629. (b) Belin, C. H. E.; Corbett, J. D.; Cisar, A. J. *Am. Chem. Soc.* **1977**, *99*, 7163. (c) Corbett, J. D.; Edwards, P. A. *J. Am. Chem. Soc.* **1977**, *99*, 3313. (d) Zintl, E.; Kaiser, H. Z. *Anorg. Chem.* **1933**, *211*, 113.

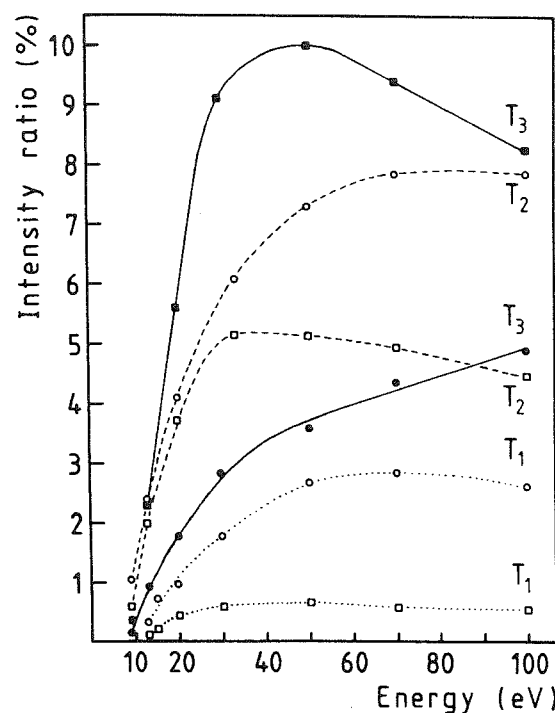


Figure 5. Dependence of the relative abundances of the $(\text{Pb}_2\text{Sb}_3)^+$ (O, ●) and $(\text{Pb}_4\text{Sb}_5)^+$ (□, ■) ions on oven temperature and electron energy (T_1) $T(\text{Pb}) = 820 \text{ K}$, $T(\text{Sb}) = 570 \text{ K}$; (T_2) $T(\text{Pb}) = 926 \text{ K}$, $T(\text{Sb}) = 573 \text{ K}$; (T_3) $T(\text{Pb}) = 1080 \text{ K}$, $T(\text{Sb}) = 598 \text{ K}$.

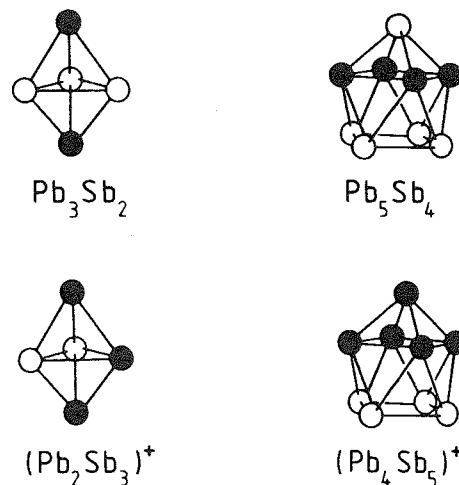


Figure 6. Suggested structures of Pb_3Sb_2 , $(\text{Pb}_2\text{Sb}_3)^+$, Pb_5Sb_4 , and $(\text{Pb}_4\text{Sb}_5)^+$ (Pb, O; Sb, ●). The positions of the Pb and Sb atoms are chosen according to their valency. For the ions, the electron is assumed to be removed from a pentavalent Sb atom.

The stability of the Pb_5Sb_4 cluster is reflected by its high abundance at $E_i = 8 \text{ eV}$ (Figure 4) and by the fact that even at $E_i = 80 \text{ eV}$ the $(\text{Pb}_5\text{Sb}_4)^+$ line appears as a maximum within the $(\text{Pb}_n\text{Sb}_4)^+$ cluster ions (Figure 4). Larger compound clusters as well as clusters corresponding to the Pb_7^{3-} polyanion,²⁷ however, are not found to be particularly stable.

The exceptional stability of the $(\text{Pb}_2\text{Sb}_3)^+$ and $(\text{Pb}_4\text{Sb}_5)^+$ ions makes them sensitive indicators for electron impact induced fragmentation. At $E_i = 80 \text{ eV}$ the integral intensity of the $(\text{Pb}_2\text{Sb}_3)^+$ and $(\text{Pb}_4\text{Sb}_5)^+$ lines are 6.7% and 9.4% of the total ion signal whereas at $E_i = 8 \text{ eV}$ their fraction is only 0.13% and 0.65%, respectively. This reveals that fragmentation decreases strongly with decreasing electron energy E_i such that it cannot be the main

(27) (a) Adolphson, D. G.; Corbett, J. D.; Merryman, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 7234. (b) Corbett, J. D.; Adolphson, D. C.; Merryman, D. J.; Edwards, P. A.; Armatis, F. J. *J. Am. Chem. Soc.* **1975**, *97*, 6267.

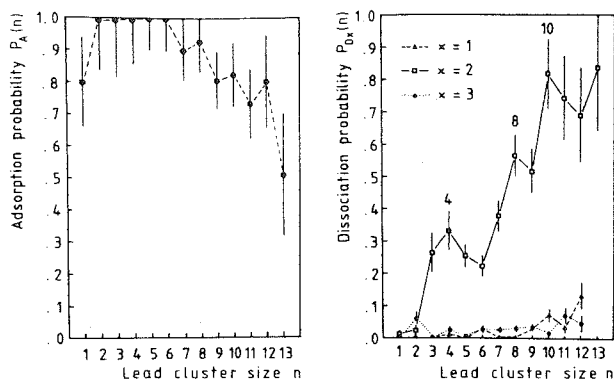


Figure 7. Adsorption probability $P_A(n)$ and dissociation probability $P_{Dx}(n)$ of Sb tetramers on Pb_n clusters. Small lead clusters react completely with antimony. The dissociation rate increases with the lead cluster size. The data are taken from the Pb-Sb mass spectrum at 8 eV shown in Figure 4.

reason for the $(Pb_nSb_2)^+$ lines which are found to be comparable or even higher than the corresponding $(Pb_nSb_4)^+$ lines. This implies that the adsorption process of Sb_4 tetramers on lead clusters is accompanied by dissociative chemisorption.

Like in the Bi-Sb system, P_A and P_{Dx} are defined in analogy to eq 1 and 2 and are found to depend on the lead cluster size. P_A takes the maximal value of unity for $n = 2$ to 6, i.e. no Pb_n^+ ions are detected in this size range. P_{D2} grows from the lead trimer on and takes a relative maximum for the lead tetramer (Figure 7). Dissociation of antimony tetramers is found to occur mainly symmetrically, although symmetric and asymmetric dissociation of free Sb_4 molecules requires almost the same energy¹⁴ (Sb_3-Sb , $E_D^\circ = 2.88 \pm 0.23$ eV; Sb_2-Sb_2 , $E_D^\circ = 2.86 \pm 0.12$ eV). However, symmetric dissociation of the chemisorbed Sb_4 molecule results in a compound cluster containing an even number of electrons, such that all electrons can be used in covalent bonds. In this case, experimental results are in coincidence with the even electron rule.

An increase in electron energy from 8 to 10 eV (Figure 4) shifts the size distribution of the $(Pb_nSb_m)^+$ compound clusters to smaller n . This shift is caused by two effects which arise from the fact that the ionization potentials decrease with increasing cluster size. The work functions of metal clusters can be described in terms of a model for small metallic drops:²⁸ $W(R) = W_{bulk} + 5.40/R$ (\AA) eV, where W_{bulk} denotes the value of the bulk work function of the metal and R (\AA) the radius of the metallic drops. The predicted decrease was confirmed experimentally.^{29,30} For a fixed

electron energy, it causes (a) a decreased ionization efficiency for small clusters when the electron energy is chosen close to the ionization threshold, but also (b) an increase in electronic excess energy which enhances the fragmentation probability of larger clusters.

At 10 eV, the lines of the fragment ions $(Pb_2Sb_3)^+$ and $(Pb_4Sb_5)^+$ already represent a fraction of 0.84% and 2.1% of the overall cluster intensity, respectively, indicating fragmentation to be enhanced. As the Sb_2 ($E_D^\circ = 3.12 \pm 0.12$ eV¹⁴) and $PbSb$ ($E_D^\circ = 1.63 \pm 0.1$ eV³¹) bonds are stronger than the Pb_2 ($E_D^\circ = 0.8$ eV)³² bond, lead atom evaporation is the most probable fragmentation process. It consumes less energy than fragmentation leading to $(Pb_2Sb_3)^+$ and $(Pb_4Sb_5)^+$ which involves the rupture of Sb-Sb and Pb-Sb bonds, too. Evaporation of lead atoms from $(Pb_nSb_4)^+$ and $(Pb_nSb_2)^+$ clusters would shift the size distribution to smaller n without enhancing the lines of Sb_m^+ fragments ($m = 1, 2, 3, 5$), which is observed in Figure 4.

Conclusions

The adsorption probability of Sb_4 on Bi_n is found to be much lower than that of Sb_4 on Pb_n clusters. This is confirmed by the fact that the antimony vapor pressure was even higher in the Bi-Sb measurements than for Pb-Sb investigations where the adsorption probability for Pb_2 to Pb_6 is observed to be 100%.

On fragmentation, the homonuclear Bi-Sb cluster ions are found to be stable at the same cluster sizes as the pure bismuth or antimony cluster ions. In contrast, fragmentation of Pb-Sb cluster ions exhibits solely two compound cluster ions. These are isovalent to the Pb_5^{2-} and Pb_9^{4-} polyanions showing that structure and electronic configuration are more decisive for cluster stability than atomic composition.

Acknowledgment. The authors thank D. Kreisle for helpful discussions. The Deutsche Forschungsgemeinschaft is acknowledged for financial support.

Registry No. Pb, 7439-92-1; Bi, 7440-69-9; Sb, 7440-36-0; Bi_nSb_m , 11104-41-9; Pb_nSb_m , 106160-94-5.

(29) Kappes, M. M.; Schär, M.; Radi, P.; Schumacher, E. *J. Chem. Phys.* **1986**, *84*, 1863.

(30) Saito, Y.; Yamauchi, K.; Mihama, K.; Noda, T. *Jpn. J. Appl. Phys.* **1982**, *21*, L396.

(31) Zmbov, K. F.; Neubert, A.; Ihle, H. R. *Z. Naturforsch. A* **1981**, *36A*, 913.

(32) Gingerich, K. A.; Locke, D. L.; Miller, F. J. *J. Chem. Phys.* **1976**, *64*, 4027.

(33) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)

(28) Wood, D. M. *Phys. Rev. Lett.* **1981**, *46*, 749.