



Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Absolute core-level binding energy shifts between atom and solid: The Born–Haber cycle revisited for free nanoscale metal clusters

M. Tchaplyguine^{a,*}, S. Peredkov^{c,1}, A. Rosso^b, I. Bradeanu^b, G. Öhrwall^b, S. Legendre^b, S. Sorensen^c, N. Mårtensson^{a,b}, S. Svensson^b, O. Björneholm^b

^a MAX-lab, Lund University, Box 118, Lund, Sweden

^b Department of Physics, Uppsala University, Box 530, Uppsala, Sweden

^c Department of Synchrotron Radiation Research, Lund University, Box 118, Lund, Sweden

ARTICLE INFO

Article history:

Available online 16 May 2008

PACS:

61.46.-w

61.46.Bc

36.40.-c

79.60.-i

Keywords:

Nanoscale clusters

Electronic structure

Electron spectroscopy

ABSTRACT

Core-level binding energy shifts between the free atom and corresponding large clusters, the latter closely approximating the infinite solid, have been experimentally derived for several elemental metals. The cluster core-level binding energies in question have been determined relative to the *vacuum level* using synchrotron-based photoelectron spectroscopy. As expected, the experimental shift values show reasonable agreement with those calculated using the thermochemical Born–Haber cycle approach. The largest uncertainty factors defining the discrepancies between the experiment and the model, such as the difference in the multiplet structure of free atoms and the solid, the in some cases indirectly established cluster work functions, and the metal solvation energy, are discussed.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

From the early days of electron spectroscopy, studies of the core-level energy change from a free atom to the corresponding solid, the so-called *core-level shift*, have been of principal importance [1–5]. It has been established that for bulk *metals* the core-level energy decreases by several eV relative to the free-atom value. The main factors which cause this difference are: (1) a fundamental change in the electronic structure in the solid metal giving rise to a strong metallic bonding in the initial state, (2) complete screening of the local vacancy created in the core shell of a solid-constituent atom. This screening – due to the mobility of the delocalized valence electrons – is one of the manifestations of metallic electronic structure in solid metals which can be observed in a core-level photoelectron spectroscopy experiment.

When it became possible to obtain the core-level energies for the elemental solid *metals*, theoretical methods of various levels of complexity were developed deriving core-level binding energies for free atoms from those of the corresponding solids [2–5].

The main practical motivation to these theoretical efforts was the difficulty to obtain the free-atom energies experimentally due to considerably lower sample density of metal-atom vapour possible to produce preserving high-vacuum conditions. One of the most fruitful theoretical methods for calculating the core-level shifts was based on the thermochemical approach: implementing a Born–Haber cycle to describe the core-ionization process [5,6] (see below). The success of this method can be assigned not only to its simplicity, but also to the fact that the expression provides a link between some microscopic and macroscopic properties such as the core and *valence* ionization energies for free metal atoms, and solid metal cohesive energies. The metal work function, a quantity often known inaccurately, was eliminated from the final expression. The method allows calculating core-level shifts for the bulk-metal energy referenced to the *Fermi edge*—a conventional way to *measure* solid-sample core-level energies experimentally, and not to the *vacuum level*, the default for free atoms.

Recent progress in core-level photoelectron spectroscopy (XPS) of *free* nanoscale clusters has made it possible to measure the core-level energies for elemental non-supported solids relative to the same zero level as for free atoms – the vacuum level [7–9]. These experiments [7–9] have confirmed the expected solid-like electronic structure of the metal clusters under investigation, and thus justified a Born–Haber cycle construction for them in the same way

* Corresponding author.

E-mail address: maxim@maxlab.lu.se (M. Tchaplyguine).

¹ Present address: BESSY, Berlin, Germany.

as for the “infinite” metallic samples. Indeed, it has been shown that the core-level energies of the infinite solids, when recalculated to the vacuum level, were very close to the cluster energies. In all cases under discussion in the present work, the difference between the cluster and the infinite solid core-level energies has not exceeded 0.2 eV, what is below 10% of the corresponding atom-to-bulk shifts for all metals in question. In this sense 90% of the change from a free atom to a bulk metal is completed. It has been demonstrated that the free-cluster core-level electron binding energy differs from that of an infinite metallic sample in the same way as the valence ionization energy [10,11,7]: it is inversely proportional to the radius of the cluster or, in other terms, to a cubic root out of the number of atoms in the cluster. Using this relationship one can estimate the average number (N) of atoms per cluster in our experiments as several thousand atoms. An increase in the cluster size (N) by an order of magnitude would mean further lowering of the cluster energy by only 5% of the atom-to-bulk energy shift. All these considerations justify treatment of the clusters under discussion as objects closely approximating solid metals. The possibility to directly and accurately measure the cluster work function W_{cluster} in the same photoelectron spectroscopy experiment as the core-level energies – and relative to the same zero level – is of special importance when comparing our experimental results with the Born–Haber cycle calculation.

This work presents the core-level spectra of tin and bismuth clusters, not reported earlier, as well as Born–Haber cycle related analyses of the data recently obtained by us on sodium [7], lead [9], and potassium clusters [9].

2. Experimental

With the advent of the third generation synchrotron facilities producing intense tunable X-ray radiation in a wide energy range it became possible to apply core-level electron spectroscopy to *free* nanoparticles [12–14]. A complementary step in the instrumentation development, which allowed going from model-systems, like clusters of inert gases [13–14] or simple molecules [15,16,17], to much more practically and fundamentally interesting *metallic* nanoscale clusters was made when gas-aggregation cluster sources started being used in electron spectroscopy experiments [18–20]. Gas-aggregation sources are known to produce a distribution of cluster sizes in the beam [21,22]. However, the analysis of the binding energy size-dependence in the regime of large cluster production (thousand of atoms per cluster and more) shows that the size-related energy spread is often below the inherent, lifetime-defined widths of the spectral features [8]. Thus this spread is – as a rule – just a minor contribution to the total width due to various, cluster-specific and instrumental broadening factors [8].

In the present work the gas-aggregation cluster source described in details in Ref. [23] has been used to produce metal clusters from several parent bulk metals. Briefly, a magnetron gun or a furnace was placed inside a liquid-nitrogen-cooled cryostat. The metal-atom vapour was produced by the magnetron sputtering process or by evaporation from the furnace in inert gas atmosphere at the gas input pressures of a few mbar. The magnetron-based source was used in the core-level electron spectroscopy experiments with tin, bismuth, and lead. Lower melting point metals – sodium and potassium – were vaporized in the furnace. A beam of metal clusters coming out from the cryostat was crossed by the horizontally polarized synchrotron light of the I411 beamline at MAX-lab in Lund, Sweden. The electrons ejected as the result of the core-ionization process have been analyzed by a Scienta R4000 electron spectrometer, fixed at 90° to the polarization plane of the radiation and to the horizontal cluster beam. Typical total resolu-

tion in the experiments, defined by the beamline monochromator bandwidth and by the spectrometer instrumental broadening, has been below 100 meV, and in the best cases, used for the resolution-sensitive issues, below 50 meV. All elements in question have been probed by ionizing their outer-most core-levels, taking the advantage of the energy range with the highest flux for the beamline radiation (around 100 eV), where also the monochromator resolution is close to its highest.

The signal intensity has been very much dependent on the type of the parent metal, influenced by the sputtering rate/evaporation efficiency, gas dynamics in the cryostat, core-level ionization cross-section in the photon energy regions in question, chosen resolution, etc. For the sputtering-based source there is still much dedicated development to do. For example, each metal demands specific conditions: a compromise between discharge power on the one hand and limited heat conductivity of the sputtered targets on the other hand has to be found. Higher power should in principle give higher metal vapour concentrations, but for the low-melting-point metals like lead and tin, and for the low-heat-conductance metals like bismuth, the powers have been far below those used for copper and silver in our previous studies [24]. In spite of all limitations the recorded core-level spectra have been of a sufficient intensity to reliably fit them and establish the absolute energy values using the argon 3s line and the inelastic loss features appearing in the photoelectron spectra due to the presence of free argon atoms in the cluster beam.

3. Born–Haber cycle

The Born–Haber cycle for metallic solids is constructed utilizing two main assumptions to model the final core-ionized state: (1) The complete metallic screening which implies that an itinerant electron is associated to the atom with a core-hole. In other words it means the equivalence of the core-ionized state of a bulk metal built out of the element with the nuclear charge Z , and the same bulk metal with a dissolved in it $Z + 1$ -element single-atom impurity; (2) The so-called $Z + 1$ approximation stating the equivalence of a core-ionized free-atom state of a Z -element and a valence-ionized state of a $Z + 1$ element [25]. The creation of the core hole represents a reduction of the negative charge in the inner parts of the atom, and the effect of this upon the valence electrons is approximated by a corresponding increase of the positive nuclear charge.

It is worth underlining here again that the core-level shift δE should be calculated using the solid energy measured relative to the vacuum level, since this is the quantity experimentally determined for clusters. In deriving the expression for the Born–Haber cycle one can start from, for example, the free atom (Fig. 1). The direction up in energy in the cycle is the core-level ionization, increasing the energy by $E_{\text{core,atom}}$ (step 1). A core-ionized atomic state of a Z -atom is then approximated by a valence-ionized state of an atom with the nuclear charge $Z + 1$ (step 2). Neutralization of this $Z + 1$ ion demands an energy equal to the ionization potential of a $Z + 1$ free neutral atom – $IP_{Z+1,a}$. This neutralizing (step 3) decreases the energy. Formation of the solid from $Z + 1$ atoms (step 4) decreases the energy per atom by a quantity equal to the cohesive energy of the $Z + 1$ metal. Dissolving a bound $Z + 1$ atom in the Z -metal (step 5) costs the solvation energy $E_{\text{solv},Z+1}$ known approximately from the studies of low-concentration binary metal alloys. By following this pathway of the cycle, a single neutral $Z + 1$ atom dissolved in the bulk Z -metal is obtained. The same chemical state can be reached via an alternative pathway of the cycle, also starting from the free Z -atom. The first step on this pathway is forming the Z -element solid from free atoms (step 1 in Fig. 1), for which the Z -element cohesive energy per atom – $E_{\text{coh},Z}$ is gained. Then follows the bulk-metal core

Download English Version:

<https://daneshyari.com/en/article/5396821>

Download Persian Version:

<https://daneshyari.com/article/5396821>

[Daneshyari.com](https://daneshyari.com)