Transition from a Bloch-Wilson to a free-electron density of states in Zn_n^- clusters

Oleg Kostko and Gert Wrigge
Fakultät für Physik, Universität Freiburg, Stefan-Meier-Straße 21, D-79104 Freiburg, Germany

Ori Cheshnovsky
School of Chemistry, The Sackler Faculty of Exact Sciences, Tel-Aviv University, 69978 Israel

Bernd v. Issendorff[a)]
Fakultät für Physik, Universität Freiburg, Stefan-Meier-Straße 21, D-79104 Freiburg, Germany

(Received 31 August 2005; accepted 26 October 2005; published online 13 December 2005)

We present photoelectron spectroscopy studies on Zn_n^- in the size range of $n=3-117$. We show that zinc clusters exhibit a distinct transition in their electronic structure as a function of size. At small sizes (up to $n=18$) the clusters follow the Bloch-Wilson picture of the development of a metal from closed-shell atoms, exhibiting a gradual decrease of the gap between the fully occupied *s* band and the empty *p* band. For large sizes ($n \gtrsim 32$) the band overlap allows the valence electrons to fully delocalize. This leads to an almost perfect free-electron density of states, as is demonstrated by discussing the spectra in the light of standard free-electron models and by comparison to the results obtained on sodium clusters. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2138689]

The Bloch-Wilson model provides a simplistic yet appealing description of the phenomena of metal to insulator transitions (MIT) for numerous systems in the condensed phase. It is based on the assumption that when a very dilute gas is gradually compressed, each atomic level develops into a narrow range of more or less delocalized states, which grows in width as the distance between the atoms decreases. In many systems, such as the bivalent metals, the evolving bands are either completely full or empty. The formation of a partially filled band, a necessary condition for the metallic state, occurs beyond a critical density at which the highest full band and the lowest empty band overlap. Similar arguments have been applied to the case of the MIT in clusters.[1] Here, while the density of atoms in the cluster is basically constant, it is the average number of nearest neighbors which causes the band broadening. So in this case there can be a critical cluster size at which the band gap closes. It should be stressed that for finite-size clusters the term "bands" refers to groups of discrete levels derived from atomic levels, while "band-gap closure" refers to a situation in which the energy gap between these bands is equal to the average level separation within each group. This is what we are referring to when using in the following the simplifying terms "band," "band gap," and "band-gap closure."

For many years mercury was considered the archetype material for such a MIT in bivalent metal clusters; many experimental[2] and theoretical[3] studies have therefore focused on the size-dependent properties of mercury clusters as indicators for the Bloch-Wilson path to MIT. In 1998 the concept of band-gap closure was directly verified by Cheshnovsky and coworkers in photoelectron spectroscopy (PES) studies of negatively charged mercury clusters.[4,5] In mercury the gap between the fully occupied *s* band and the empty *p* band[6] decreases gradually and monotonously from 3.6 eV in Hg_3 to 0.25 eV in Hg_{250}; it can be extrapolated to close completely around size $n=450\pm50$.

The PES experimental studies of Thomas *et al.*[7] on Mg_n^- have shown a distinctively different size-dependent evolution of the band gap in a bivalent metal. Already in Mg_8 the *s-p* band gap has shrunk to 0.4 eV; it closes completely at size $n=16-18$. All larger clusters in the size range studied by PES ($n=3-35$) seem to exhibit no significant gap at all, except sizes 20 and 35, which are electronically closed shell in the free-electron model. Thomas *et al.* also discussed the mass spectra of Mg cluster anions up to size $n=74$, which exhibit strong maxima at all electronically closed-shell sizes. Diederich *et al.*[8] have discussed similar mass distributions of positively charged Mg clusters. Here again all major magic numbers could be explained within standard free-electron models; for the explanation of minor magic numbers a modified shell model had to be employed. All this data has demonstrated that magnesium clusters exhibit an early transition from a nonmetallic material to a metal with a rather free-electron-like electronic structure. Evidence for a similar behavior of zinc clusters was already obtained by Katakuse *et al.*, who observed electronic magic numbers in mass spectra of both cationic and anionic zinc clusters.[9]

As we will show, zinc clusters exhibit the most comprehensive MIT observed in clusters so far. The small clusters exhibit Bloch-Wilson band gaps which are significantly larger than those of magnesium clusters. The large clusters exhibit a surprisingly clear free-electron density of states, similar to that of clusters of the "free-electron" metal sodium. This general structure of the density of states is especially important, because the appearance of gaps due to electronic shell closing does not exclude a strongly perturbed

[a)]Electronic mail: bernd.von.issendorff@uni-freiburg.de

electronic shell structure, as has been shown recently for the case of noble-metal clusters.[10]

The experimental setup is the same as in recent PES studies.[10,11] For the cluster production two different methods are used. All but the smallest clusters are produced by a gas aggregation source. Inside a liquid-nitrogen-cooled tube a magnetron discharge sputters zinc atoms into a mixture of helium and argon having a pressure of about 1 mbar, which leads to the formation of both positively and negatively charged clusters. After expansion into the vacuum the clusters enter a rf octupole ion guide. A liquid-nitrogen-cooled copper shield around the octupole allows thermalization of the clusters to about 100 K. As the gas aggregation source fails to produce clusters smaller than Zn_{13}^- with sufficient intensity (except sizes 3 and 4), for the production of the smallest clusters a technique based on the approach of Thomas *et al.*[7] is used. These clusters are produced without buffer gas by simple laser ablation from a piece of zinc mounted close to the acceleration ion optics, using fairly strong laser pulses (100 mJ, 532 nm, 0.5 mm beam diameter); as here no thermalization is used, they can be assumed to be hot. The cluster ions produced by either technique are inserted into a high-resolution double-reflectron time-of-flight mass spectrometer, mass selected, decelerated, and irradiated by an ArF excimer laser ($h\nu=6.42$ eV). The kinetic-energy distribution of the emitted electrons is measured by a magnetic bottle-type time-of-flight electron spectrometer with an energy resolution of about $E/dE=40$. It has been calibrated by measuring the known spectrum of Pt^-, which leads to an error of the energy axis of less than 60 meV. In most cases the photoelectron spectra have been averaged over 30 000 laser shots.

In Fig. 1 we present the spectra of Zn_n^- for $n=3-20$. All the spectra are cut at a binding energy (BE) of 5 eV due to the appearance of two-photon effects (photoelectron spectra of the neutralized zinc clusters) at higher BEs for all but the smallest sizes. This phenomenon is out of the scope of our discussion. In most of the spectra one can observe a single peak at low binding energy, which indicates the highest occupied single electron state in the cluster, and a group of peaks at higher binding energy, which in zeroth order represent electron states with more negative total energies. As in the case of mercury[4] or magnesium[7] the uppermost peak is assumed to be the lowest *p*-band state, which is occupied by the single additional electron of the cluster anion, and all other peaks to be *s*-band states. The differences between the two highest peaks in the spectra therefore represent to a good approximation the excitation band gaps of the corresponding neutral clusters (in the geometry of the anions), as discussed thoroughly in Refs. 1 and 4.

Based on the relatively high intensity of the uppermost peak at size $n=18$ we believe that here more than one electron is occupying the highest state in the spectrum; so we define $n=18$ as the size at which the Bloch-Wilson band gap closes for the first time. As details of the electronic structure strongly depend on the cluster geometry, one cannot expect the Bloch-Wilson gap to be zero for all larger sizes. Indeed all sizes between $n=19$ and $n=32$ exhibit a gap again. Larger clusters have no or only small band gaps, except for some

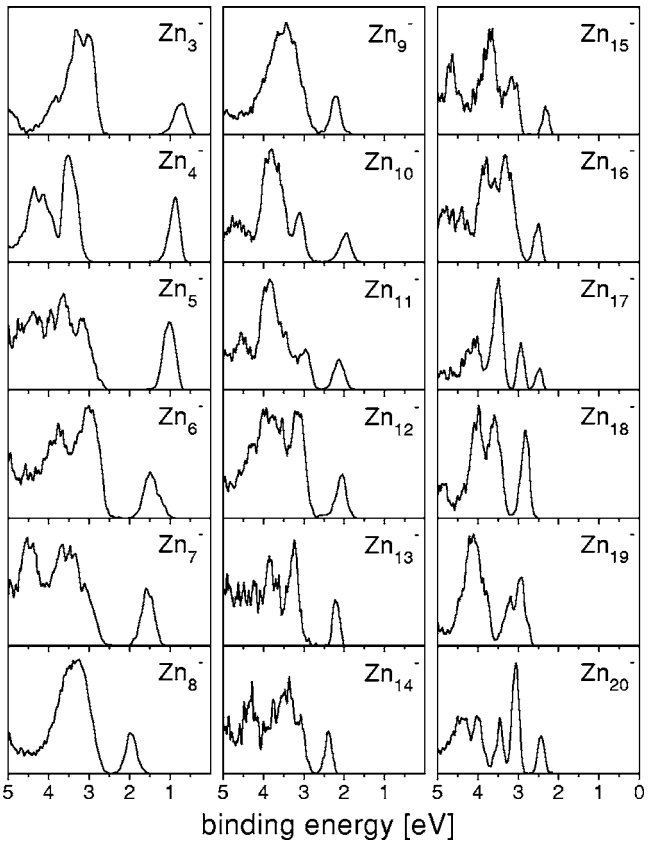

FIG. 1. Photoelectron spectra of size-selected zinc cluster anions Zn_n^- with $n=3-20$ measured at a photon energy of 6.42 eV. Note the band gap between the uppermost (lowest binding energy) level and lower-lying levels, which strongly decreases with size.

special cases which will be discussed below. In order to give an overview of all the measured data, in Fig. 2(a) we present the energies of the two lowest BE peaks in the spectra of $Zn_n^-(n=3-117)$ as a function of cluster size. More precisely we plot the data as a function of $n^{-1/3}$, which is proportional to the inverse cluster radius and therefore to the classical cluster charging energy.[12] For comparison we include here the values of $Hg_n^-(n=3-250)$, which have been published earlier.[4,5]

One can see that the electron affinities (the binding energy of the uppermost peak) of mercury and zinc clusters happen to be almost identical. This is not true for the position of the second peak (the onset of the "*s* band," the set of *s*-orbital-derived states); due to the larger band gap these states exhibit consistently higher binding energies in the case of mercury. Surprisingly in both cases the position of these states do not show a significant size dependence; obviously the size-dependent decrease of the band gap happens to cancel out the respective increase of the electron affinity. Due to their different energy positions the *s*-band onsets of zinc and mercury meet the electron affinity curve at different sizes, which means that the band gap closes at different sizes. This can be seen clearly in Fig. 2(b), which shows the extracted energy difference between the two uppermost states: while in zinc the band gap closes at size 18 for the first time and has an extrapolated general gap closing around size 40, for mercury the closure of the band gap can be extrapolated to occur

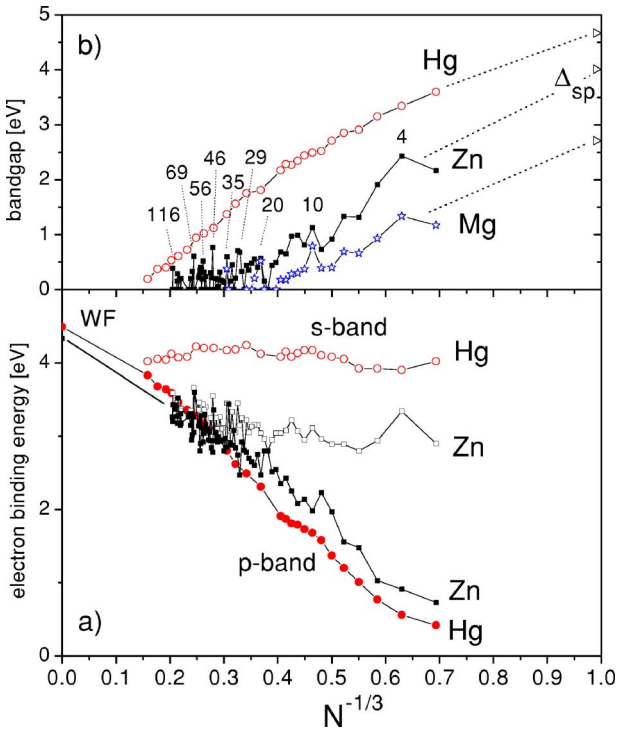

FIG. 2. (a) Energy positions of the two uppermost states visible in the photoelectron spectra of Hg_n^- and Zn_n^- clusters as a function of size. (b) Band gaps as derived from graph (a). For comparison the data for Mg_n^- (Ref. 7) is shown as well. Additionally the lowest excitation energies ($^1S_0 \rightarrow {}^3P_0$) of the respective atoms have been inserted; the lines serve to guide the eye.

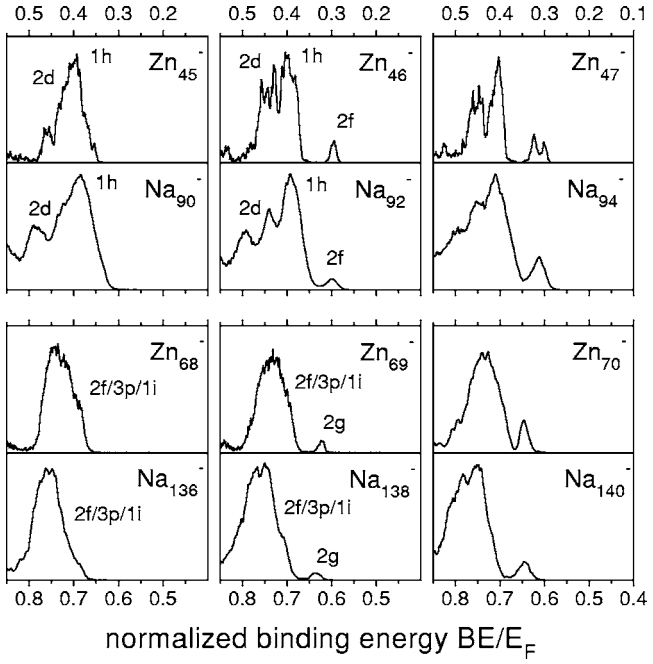

FIG. 3. Photoelectron spectra of size-selected zinc cluster anions Zn_n^- with $n=45-70$ measured at a photon energy of 6.42 eV. For comparison the spectra of sodium cluster anions with the same number of valence electrons are shown (measured at a photon energy of 4.02 eV). The energy axes of the spectra have been normalized by the Fermi energies of the bulk materials (9.43 and 3.15 eV for zinc and sodium, respectively) and shifted in order to align the visible structures. Note the close resemblance of the spectra in most cases. Electron shell quantum numbers have been tentatively assigned to the visible bands.

at $n=450\pm50$. Note that in both metals the band gaps shrink gradually as a function of the cluster size, as anticipated from the Bloch-Wilson model. In zinc this holds only up to size 18. In a transition region up to about size 32 the band gap is present again, while at higher cluster sizes it reappears only occasionally. In mercury the Bloch-Wilson picture holds all the way to the largest cluster measured, $n=250$. For comparison we include in Fig. 2(b) the band gaps of magnesium clusters, as obtained by Thomas *et al.*[7] Note that zinc and magnesium show a somewhat similar behavior but that zinc exhibits consistently larger band gaps for all sizes.

So zinc clusters clearly exhibit a shrinking Bloch-Wilson band gap for small clusters, which closes at a certain size; for larger sizes consequently delocalized electrons and maybe even a more or less free-electron-like density of states (DOS) can be expected. The rest of our discussion is therefore devoted to the characterization of the PES of larger zinc clusters in terms of the nearly-free-electron model. As can be seen in Fig. 2, there are large band gaps appearing at the cluster sizes 20, 29, 35, 46, 56, 69, and 116, corresponding to 41, 59, 71, 93, 113, 139, and 233 electrons. In the free-electron model these electron numbers lead to a closed-shell structure with one extra electron, which has to occupy the next higher shell (angular momentum eigenstate).[13] In a 41-electron cluster, for example, all shells are filled up to the $2p$ shell; the one additional electron occupies the $1g$ shell, which leads to a significant band gap in the PES.[11,14] It is quite instructive to compare the density of states as obtained for these larger zinc clusters with that of sodium clusters, which can be considered as the best representatives of free-electron metal clusters.[13] In Fig. 3 the spectra of the "magic" zinc clusters and neighboring sizes are compared to the PES of sodium clusters with the same number of electrons. The energy axes of the spectra have been normalized by the Fermi energies of the materials (as calculated from their bulk density), because in ideal free-electron metal clusters the energy differences between the electronic shells should be proportional to the total valence bandwidth. In order to facilitate the comparison of the visible structures the axes of the zinc spectra have been additionally shifted by a value of 0.3, which accounts for the smaller normalized electron affinity of the zinc clusters. One can observe a strong similarity between the scaled DOS of the two materials. Obviously in the case of 93 electrons (closing of the $1h$ shell, opening of $2f$) and 138 electrons (closing of $3p$, opening of $2g$) the respective sizes of the band gap and the widths of the uppermost filled shell are very comparable. This means not only that in zinc clusters of this size the electrons occupy delocalized states (the angular momentum eigenstates) but also that the effective electron mass is already close to the free-electron one, as only in this case the valence bandwidth is equal to the simple free-electron bulk Fermi energy.

One difference between zinc and sodium is that for the next larger sizes shown (where the new shell is occupied by three electrons) in the case of sodium at the position of the new shell one observes a peak of roughly three times the intensity than in the spectra of the smaller sizes, while in some cases of zinc clusters (e.g., at size $n=47$) the new shell splits up. This can be explained by a stronger electron-ion

core interaction in the case of zinc, which leads to a slightly stronger perturbation of the angular momentum eigenstates. One should mention that in a few cases this perturbation even produces significant band gaps for electronically nonmagic clusters, with a concomitant enhanced stability of the clusters (e.g., at $n=71$ and $n=102$). Nevertheless these spectra (as well as most of the others which have been measured in the size range up to $n=117$ but cannot be shown here) demonstrate that the larger zinc clusters exhibit a density of states fully consistent with a slightly perturbed free-electron structure.

Finally a remark can be made concerning the different behavior of the materials discussed: in Fig. 2(b) one can observe that smaller zinc clusters consistently exhibit band gaps larger than those of magnesium clusters but smaller than those of mercury clusters. In the Bloch-Wilson model the band gap is directly related to the atomic *s*-*p* energy difference in the atoms, which increases monotonically from Mg through Zn to Hg. To test this correlation we have included the atomic $^1S_0 \rightarrow {}^3P_0$ excitation energies[15] in Fig. 2(b); indeed one can see that the band-gap curves qualitatively extrapolate to these atomic energies, which again demonstrates the success of this simple model.

Summarizing, we have shown that zinc clusters exhibit a strong transition in their electronic structure as a function of size with a significant band gap for small sizes and close to ideal free-electron behavior for large sizes. This distinct change of properties makes zinc an ideal candidate for the study of MIT in clusters.

[1] B. v. Issendorff and O. Cheshnovsky, Annu. Rev. Phys. Chem. **56**, 549 (2005).

[2] C. Brechignac, M. Broyer, Ph. Cahuzac, G. Delacretaz, P. Labastie, J. P. Wolf, and L. Wöste, Phys. Rev. Lett. **60**, 275 (1988); C. Brechignac, M. Broyer, Ph. Cahuzac, G. Delacretaz, P. Labastie, and L. Wöste, Chem. Phys. Lett. **120**, 559 (1985); H. Haberland and H. Langosch, Z. Phys. D: At., Mol. Clusters **19**, 223 (1991); H. Haberland, B. v. Issendorff, J. Yufeng, and T. Kolar, Phys. Rev. Lett. **69**, 3212 (1992); H. Haberland and H. Langosch, Z. Phys. D: At., Mol. Clusters **19**, 223 (1991); H. Haberland, B. v. Issendorff, J. Yufeng, T. Kolar, and G. Thanner, *ibid.* **26**, 8 (1993); K. Rademann, O. Dimopoulou-Rademann, M. Schlauf, U. Even, and F. Hensel, Phys. Rev. Lett. **69**, 3208 (1992); K. Rademann, B. Kaiser, U. Even, and F. Hensel, *ibid.* **59**, 2319 (1987); K. Rademann, B. Kaiser, T. Rech, and F. Hensel, Z. Phys. D: At., Mol. Clusters **12**, 431 (1989); K. Rademann, Ber. Bunsenges. Phys. Chem. **93**, 653 (1989).

[3] G. M. Pastor and K. H. Bennemann, in *Clusters of Atoms and Molecules I*, edited by H. Haberland (Springer, Berlin, 1995), p. 86; G. M. Pastor, P. Stampli, and K. H. Bennemann, Z. Phys. D: At., Mol. Clusters **12**, 365 (1989); Y. X. Wang, H. J. Flad, and M. Dolg, Phys. Rev. B **61**, 2362 (2000); B. Hartke, H. J. Flad, and M. Dolg, Phys. Chem. Chem. Phys. **23**, 5121 (2001); G. E. Moyano, R. Wesendrup, T. Sohnel, and P. Schwerdtfeger, Phys. Rev. Lett. **89**, 103401 (2002).

[4] R. Busani, M. Folkers, and O. Cheshnovsky, Phys. Rev. Lett. **81**, 3836 (1998).

[5] R. Busani, M. Folkers, and O. Cheshnovsky, Philos. Mag. B **79**, 1427 (1999).

[6] Throughout this report we use the simplifying terms "*s* band" and "*p* band" for the fully occupied and the empty band present in smaller bivalent metal clusters, although appreciable hybridization between both bands can be expected to occur much earlier than the actual band gap closure.

[7] O. C. Thomas, W. Zheng, S. Xu, and K. H. Bowen, Phys. Rev. Lett. **89**, 213403 (2002).

[8] Th. Diederich, T. Döppner, J. Braune, J. Tiggesbäumker, and K.-H. Meiwes-Broer, Phys. Rev. Lett. **86**, 4807 (2001).

[9] I. Katakuse, T. Ichihara, M. Morris, T. Matsuo, T. Sakurai, and H. Matsuda, Int. J. Mass Spectrom. Ion Process. **91**, 85 (1989).

[10] H. Häkkinen, M. Moseler, O. Kostko, N. Morgner, M. Astruc Hoffmann, and B. v. Issendorff, Phys. Rev. Lett. **93**, 093401 (2004).

[11] G. Wrigge, M. Astruc Hoffmann, and B. v. Issendorff, Phys. Rev. A **65**, 063201 (2002).

[12] The electron affinity of a classical metallic sphere is the work function minus the charging energy; quantum treatment leads to corrections, but a roughly linear dependence on the inverse radius is conserved (Refs. 16 and 17).

[13] W. deHeer, Rev. Mod. Phys. **65**, 611 (1993); M. Brack, *ibid.* **65**, 677 (1993).

[14] C. L. Pettiette, S. H. Yang, M. J. Craycraft, J. Conceicao, R. T. Laaksonen, O. Cheshnovsky, and R. E. Smalley, J. Chem. Phys. **88**, 5377 (1988).

[15] We chose the lowest possible energy, but qualitatively the same effect is observed when using the singlet-triplet average values of the *s* to *p* excitation.

[16] M. Seidl, J. P. Perdew, M. Brajczewska, and C. Fiolhais, J. Chem. Phys. **108**, 8182 (1998).

[17] K.-H. Meiwes-Broer, Hyperfine Interact. **89**, 263 (1994).