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Photoelectron spectra of Na_n^- and Cu_n^- with $n = 20$–40: observation of surprising similarities

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Abstract. Cold, size selected sodium and copper cluster anions have been studied by photoelectron spectroscopy. The structure of the uppermost part of the *s*-band of the copper clusters turns out to be close to identical to the one observed in the density of states of sodium clusters of the same size. This result indicates that in the studied size range sodium and copper clusters adopt the same geometries, and that electron-lattice interaction is of comparable strength in both systems. The observed *s*-band level density scales almost perfectly with the bulk Fermi energies of the materials, which demonstrates that close to the threshold both systems follow the same electron dispersion relation.

PACS. 33.60.Cv Ultraviolet and vacuum ultraviolet photoelectron spectra – 36.40.Cg Electronic and magnetic properties of clusters – 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals

1 Introduction

The free electron model is the simplest description of the electronic structure of metals [1]. It assumes the electrons to move freely through the crystal, without any interaction with the atomic lattice. In quantum mechanical calculations this can be achieved by using the so-called jellium model, which assumes the positive charge of the atomic cores to be smeared out into a homogeneous positive background charge. Application of the jellium model to metal clusters predicts a very simple density of states (DOS), the electron shell structure. In the case of spherical clusters the electrons occupy the highly degenerate angular momentum eigenstates, thus producing a very simple, strongly discretized DOS. But already for ideal free electron clusters the DOS will be more complicated than that due to Jahn-Teller deformations of open shell clusters, which partially lift the high degeneracy and lead to characteristic splittings of the spherical shells. These effects have been studied in detail by ab initio calculations [2,3], but already simple models like the Clemenger-Nilsson model can provide fairly accurate estimates [4]. Evidence for the existence of an electron shell structure as predicted by these models has been found in a wealth of experiments [5]; for alkaline and noble metal clusters shell structure effects have been observed for example in the size dependence of the ionization potentials [6,7]. Photoelectron spectroscopy in principle allows one a direct observation of the electronic DOS; here shell-like patterns have been observed, e.g., for sodium [8–10], potassium [11], copper [12,13] and silver clusters [14,15].

So undoubtedly the free electron model provides a good estimate for the electronic structure of simple metal clusters. The question remains whether it is capable to reproduce even fine details of it. One can expect that if it works well at all, it will do so for sodium clusters. Bulk sodium is the model case of an ideal free electron metal. Its electron density ($r_s = 3.99\ a_0$) is very close to the value of an ideal jellium metal, that is the density at which the pressure of the free electron gas balances the Coulombic contraction of the metal [16]. Furthermore its bulk modulus (0.064 Mbar) is close to the ideal electron gas value (0.086 Mbar) [1]. Copper, on the other hand, appears to be not as ideal. Its valence s-electron density ($r_s = 2.67\ a_0$) is more than three times higher than that of an ideal free electron metal, indicating a strong additional compression of the material. The same is indicated by its modulus (1.34 Mbar) [1], which is more than two times larger than that of a free electron gas of the same density (0.64 Mbar), as well as by its binding energy, which is three times higher than that of (apart from the filled atomic 3*d*-shell) isoelectronic potassium. As is well-known, all these effects are caused by the "*d*-band", a band of states derived from the atomic 3*d*-orbitals situated 2–5 eV below the Fermi energy. Obviously these states strongly enhance the bonding between the atoms, thus leading to shorter bond lengths and an enhanced modulus. As a completely filled band should have a nonbonding character, this fact directly indicates an appreciable hybridization of the *s*- and the *d*-band. This hybridization, on the other hand, adds some localized *d*-character to the *s*-band states, leading to a

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stronger electron lattice interaction. Indeed very recently a study of Cu, Ag, and Au clusters demonstrated a rather strong perturbation of free electron states in these clusters [17].

In this report we are comparing the results for copper and sodium clusters, in order to observe possible similarities or differences. Both systems have been investigated a couple of times by photoelectron spectroscopy [8–10,13,18,19], but only for smaller sizes or with lower resolution. The photoelectron spectra of sodium clusters presented here are the first ones measured at low temperatures. The sodium cluster spectra previously published [9,10] were measured on clusters with close to room temperature, which were probably liquid or at least strongly vibrationally excited and thus prone to isomerization.

2 Experiment

The clusters are produced by a gas aggregation source. Sodium is evaporated from a small crucible inside a liquid nitrogen cooled aggregation tube, through which helium flows at a pressure of about 0.5 mbar. A weak discharge burning at the crucible serves to produce charged clusters. In the case of the copper clusters a magnetron sputter source is used to produce the metal vapor; here the aggregation gas consists of a mixture of helium and argon (typical composition 4:1). After expansion into the vacuum the clusters enter a rf octupole ion guide. The octupole has a pulsed exit aperture and can therefore be used as a temporal trap for the cluster ions in order to bunch the continuous output of the cluster source. This enhances the cluster intensity in a bunch by a factor of 10–100. Cooling a copper shield around the octupole by liquid nitrogen allows to cool the clusters to about 100 K. The cluster ion bunches are inserted into a high resolution double-reflectron time-of-flight mass spectrometer, where a multiwire mass gate positioned at the focus point of the first reflector can be used to select single cluster sizes with a selectivity of up to $m/dm = 2000$. After passing the second reflector the size selected clusters are decelerated and inserted into a magnetic bottle photoelectron spectrometer, where they are irradiated by a XeCl or ArF excimer laser ($h\nu = 4.02$ eV and 6.42 eV, respectively). The flight time distribution of the emitted electrons is measured and converted into a binding energy distribution. The spectrometer has an energy resolution of about $E/dE = 40$. It has been calibrated by measuring the known spectrum of Pt^-, which for the highest energy electrons leads to an error of the energy axis of less than 50 meV, and for the lowest energy ones of less than 10 meV. In most cases the photoelectron spectra have been averaged over 30 000 laser shots at a repetition rate of 100 Hz.

3 Results

Figure 1 shows the spectra obtained for Na_{20}^- at two different temperatures (100 K and 300 K), compared to the

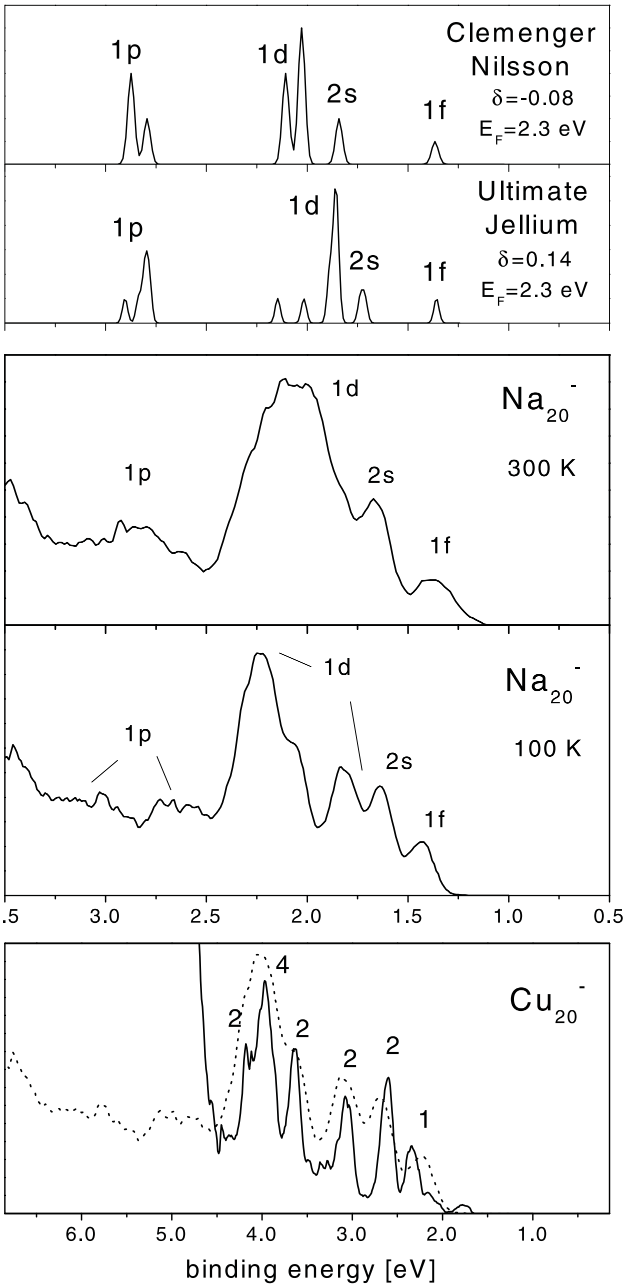

Fig. 1. Photoelectron spectra of hot and cold Na_{20}^- (with temperatures of 300 K and 100 K), measured at a photon energy of 4.02 eV, and of room temperature Cu_{20}^-, measured at a photon energy of 6.42 eV. The energy axes have been scaled according to the ratio of the bulk Fermi energies ($E_F(\mathrm{Cu})/E_F(\mathrm{Na}) = 2.23$). In the sodium spectra the visible electron shells are identified by their quantum numbers; in the copper spectrum the numbers of electrons probably occupying each state have been indicated. Additionally the DOS as obtained from the Clemenger/Nilsson model [4] and from the "ultimate jellium" model [20] are shown. In both cases the total bandwidth (the energy interval between the shells 1*s* and 1*f*) has been chosen as 2.3 eV, which gave the best fit to the observed peak structure. Note that the Clemenger model predicts an oblate deformation of the cluster, while the ultimate jellium predicts a dominantly prolate one. Nevertheless both models fail to reproduce the observed spectrum.

density of states of a 21 electron cluster as predicted by two different theoretical models. Additionally the spectrum of a room temperature Cu_{20}^- is shown.

In the room temperature spectrum of Na_{20}^- one can observe a couple of broad peaks, which can be identified as the electronic shells $1p$, $1d$, $2s$ and $1f$ (the development of these shells in the size range $n = 4-19$ has been published earlier [10]). Obviously this cluster has a shell-like electronic DOS. Nevertheless the observed pattern demonstrates that simple free electron models are not sufficient to describe details of the electronic structure. Both the simple Clemenger Nilsson model [4] as well as the ultimate jellium model [20] obtain a much smaller broadening of the electron shells as the one observed. Furthermore in the measured spectrum the $2s$ shell lies closer to the $1f$ shell than to the center of the $1d$ shell; both calculations fail to predict this. The discrepancy between the simple models and the measured DOS is even more evident in the spectrum of the cold Na_{20}^-. At this temperature the cluster should be solid and have a well defined geometric structure. Indeed the spectrum is much better resolved than the room temperature one. The $1d$-shell splits up into several levels (probably into three singly and one doubly degenerate state as in the case of Cu_{20}^-). Such a splitting cannot be obtained in a spheroidal jellium model; one has to allow for triaxial deformation to lift the angular momentum eigenstate degeneracy in this manner. But even the ultimate jellium model [20], which allows any deformation, fails to reproduce this spectrum. Obviously a simple deformation cannot explain the results; it therefore seems to be the electron-lattice interaction which leads to this strong perturbation of the electron shell structure.

The same applies to the case of Cu_{20}^-. As has been discussed in detail in [21], the photoelectron spectra of copper clusters exhibit a sharp onset of the $3d$-band roughly 2.5 eV below the threshold. Between this onset and the threshold the highly structured upper part of the $4s$-band can be observed. If one normalizes the energy axes of the spectra according to the Fermi energies of the bulk materials ($E_F(\mathrm{Na})/E_F(\mathrm{Cu}) = 2.23$ [1]), this part of the DOS should therefore have some similarity with the DOS of sodium clusters. Indeed Cu_{20}^- in this energy region exhibits almost exactly the same spectrum as Na_{20}^-. The only difference is a better resolution, the reason for which is the stiffer lattice of the copper cluster (for the same reason copper clusters exhibit practically identical spectra at 100 K and 300 K). As here the electronic structure is clearly visible, the probable occupation of the observed levels has been indicated by electron numbers. The two very small peaks at the onset are too small to be part of this pattern; they probably indicate the presence of another isomer with a smaller electron affinity.

These observations have a couple of consequences: in contrast to naive expectations as described in the introduction the electron-lattice interaction seems to be very similar in sodium and copper clusters of this size (taking the splitting of the electron shells as a measure for its strength). Secondly both clusters seem to adopt exactly the same geometry, as the details of photoelectron spectra in general depend very sensitively on the atomic arrangement. And, thirdly, is is surprising that the observed s-band bandwidth scales so perfectly with the bulk Fermi energy (as calculated from the idealized bulk electron density). As has been shown by calculations [22,23], the d-band crossing the s-band tends to push the s-band states to lower or higher energies; furthermore strong hybridization takes place, giving even the s-band states at the Fermi energy some d-character. Nevertheless the level density in the copper cluster is exactly the same as in the sodium case when scaled according to the different bulk electron densities, indicating a very similar electron dispersion relation in this region of the bandstructures of the two systems.

Note that the comparison with the theoretical results allows one to estimate the total valence band width of the clusters; for sodium a value of 2.3 eV is obtained, which shows that the Fermi energy in this size range still is appreciably smaller than for the bulk.

In Figure 2 a series of spectra of sodium and copper clusters with sizes between 21 and 40 atoms is shown. As in Figure 1 the energy axes have been scaled according to the ratio of the bulk Fermi energies. A couple of observations can be made immediately. For almost all sizes (especially for sizes larger than 28) the spectra of sodium and copper clusters are close to identical. Here the geometrical structure of the clusters should be exactly the same. For some sizes (21, 22, 23, and 31) the spectra have very similar overall shapes, but not the one-to-one correspondence of all visible peaks as observed for the other sizes; these clusters might differ slightly in their geometrical structure.

Actually the form of the spectra allows one direct statements about the structure in some cases. Na_{39}^- and Cu_{39}^- contain 40 s-band valence electrons and should have a closed shell electronic structure within the free electron model. Deformable jellium models therefore predict a spherical shape for these clusters. Inspection of the spectrum immediately shows that this is not the case. In both spectra one observes two bands of peaks, which can be identified as the $1f$ and the $2p$ shell. In a spherical cluster both shells should be completely degenerate; here one observes a clear splitting of both of them. The splitting of the $2p$ shell into a lower lying larger peak and a higher lying small peak allows to identify the deformation of the clusters as dominantly oblate; maybe they adopt the oblate "Mackay-type" geometry as described in [26].

Also in the case of Cu_{38}^- one can immediately falsify an earlier prediction: calculations performed on noble metal clusters often find a highly symmetric cuboctahedral structure for 38 atom clusters [24,25]. In such a symmetry the $2p$ shell would be degenerate, independent of the strength of the electron-lattice interaction. Instead in the measured spectrum one observes a clear splitting of the $2p$ shell in the case of Cu_{38}^-, indicating again an oblate structure.

Finally we will now comment on the gap at the threshold visible in the spectra. This gap indicates the size of the HOMO-LUMO-gap of the neutral cluster (in the ground

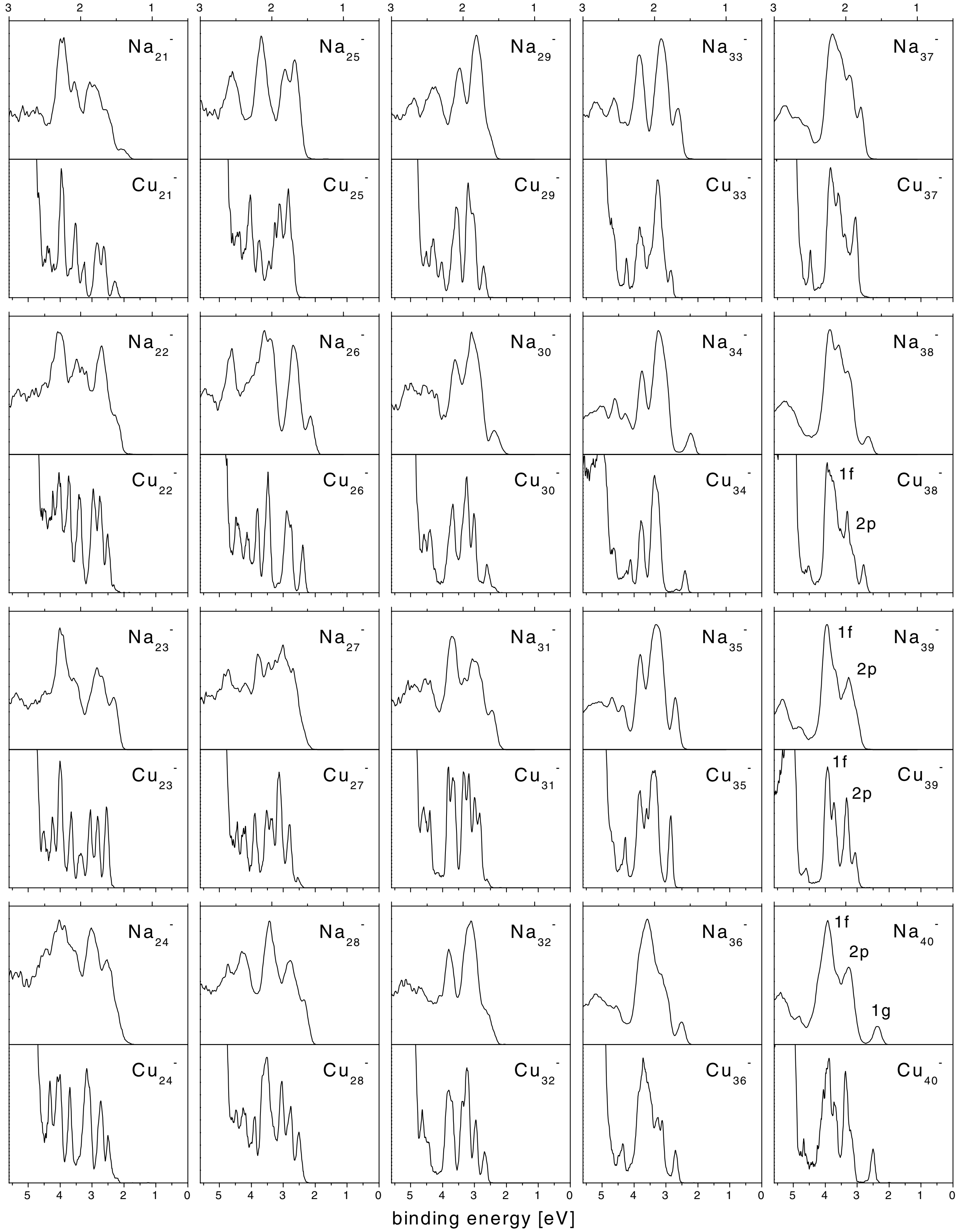

Fig. 2. Photoelectron spectra of cold Na_n^- and of room temperature Cu_n^-, measured at photon energies of 4.02 eV and 6.42 eV, respectively. As in Figure 1 the energy axes have been scaled according to the bulk Fermi energies. Note the close resemblance between the spectra for most sizes.

state geometry of the anion). For the case of the copper clusters its size dependence has already been determined by Petiette et al. [13]. The higher resolution spectra presented here confirm their results for most sizes. As the authors have discussed, the size dependence of the gap follows quite well the predictions of deformable jellium model predictions. One could, however, already observe in their results that the gap observed for the magic sizes was consistently smaller than predicted, while the gaps in the intermediate cases always were larger. As the sodium clusters exhibit identical spectra, the same conclusion applies for them: both systems roughly follow simple jellium model predictions, but the influence of the lattice is in no way negligible, which means that details of the electronic structure can only be understood if the geometric structure is taken into account.

4 Summary

Photoelectron spectra of cold sodium and copper cluster anions with 20 to 40 atoms have been measured. The observed density of states exhibit identical patterns for most sizes, which demonstrates that in this size range sodium and copper clusters adopt the same geometrical structures. The energy differences between the observed electron shells turn out to scale perfectly with the Fermi energies of the bulk materials, which indicates that both materials follow the same electron dispersion relation in the part of the bandstructure studied here. This is surprising, as an appreciable *s*-*d*-hybridization can be expected for the copper case. The results show that the electronic structure of both copper and sodium clusters exhibit an overall good agreement with simple jellium model predictions, but that electron-lattice interaction has quite a strong perturbing effect. In cases where details of the electronic structure play a role (e.g. reactivity, magnetism, fine structure of absorption spectra) full treatment of the geometrical structure is therefore indispensable.

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