

Size-dependent properties of small deposited chromium clusters by x-ray absorption spectroscopy

Matthias Reif, Leif Glaser, Michael Martins, and Wilfried Wurth*

Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

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Small, mass selected, deposited chromium clusters in the size range of 1–13 atoms per cluster have been investigated using x-ray absorption spectroscopy at the BESSY II storage ring at the chromium $L_{2,3}$ edges. The chromium clusters have been deposited on ultrathin iron films grown on a Cu(100) single crystal. A soft landing scheme and low temperatures have been used preventing the clusters from fragmenting and agglomerating, respectively. Spectroscopic parameters such as core level line shift, spin-orbit splitting, line shape, oscillator strength, and $L3/L2$ branching ratio have been determined and are discussed in detail.

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I. INTRODUCTION

Bringing atoms together and forming clusters provides tremendous insight in fundamental physics on the atomic length scale. In particular, the electronic structure of small clusters changes with cluster size, reflecting the transition from single atoms towards bulk properties.^{1–8}

With an increasing number of atoms in the cluster atomic or molecular like orbitals start forming the valence band of the cluster. Here, metallicity and electron delocalization are parameters in the evolution from atom to bulklike structures^{9,10} which are important for the properties of nano- and subnanoscale systems.

For future applications, clusters will have to be deposited on a substrate or in a matrix. An important parameter besides the intracluster coupling will then be the interaction with the environment. In the case of weak interaction between the cluster and the substrate, i.e., weak hybridization of cluster orbitals with substrate orbitals, characteristics of various cluster sizes are related to intrinsic cluster properties depending mostly on the average coordination of the cluster atoms.¹¹ For strongly interacting systems, i.e., strong hybridization between outer cluster and substrate orbitals, properties of the clusters change and their evolution with cluster size can differ fundamentally from that of free clusters.¹²

The strong influence of the cluster-substrate interaction on the measured properties of deposited clusters is for example seen in x-ray photoelectron spectroscopy (XPS) experiments for Pt clusters on metal [Ag(110) (Refs. 3 and 4)] and insulator (SiO_2) surfaces.² An increase of the Pt 4*f* binding energy with cluster size is found for the metal substrates, whereas in the case of the insulator surface a decrease of the Pt 4*f* binding energy with increasing cluster size is found. On substrates where no energy levels in the energy range of the cluster valence levels are present (e.g., insulators), the measured binding energy is mainly determined by the electronic structure of the cluster in the initial and final state of the photoemission process with the result of an increase of the level energy with decreasing coordination. In the case of strongly interacting cluster-substrate systems, cluster valence orbitals hybridize with substrate valence orbitals usually resulting in a lowering of the cluster energy levels.¹¹

To gain insight into electronic properties, spectroscopic investigation of the valence and core levels is a valuable tool.

Element specificity and the ability to investigate low target densities makes x-ray absorption spectroscopy (XAS) at third generation synchrotron sources an ideal tool for the exploration of low coverage cluster systems. It has been shown previously using XPS (Refs. 1–5) and XAS,^{7,11,13} that core level binding energies and line widths are sensitive to changes in the electronic structure of cluster systems. In the following, we present XAS results for chromium clusters deposited on an iron substrate. This system has been chosen because of its interesting magnetic properties, e.g., the system Cr/Fe was the first system where GMR was discovered.¹⁴ Furthermore, due to the antiferromagnetic coupling within the clusters and between cluster and substrate, a complex magnetic behavior is expected as a function of cluster size. For a detailed understanding of the magnetic properties, which will be reported in a separate publication, a profound knowledge about the electronic structure is a prerequisite. In this study we therefore focus on the electronic properties of these clusters. Our experiments show clear evidence for strong coupling of the clusters to the substrate. In addition, we see definite changes with cluster size which we attribute to the evolution of the valence electronic structure of the clusters.

II. EXPERIMENTAL SETUP

A detailed description of the experimental setup and the capability of the cluster source is given elsewhere.¹⁵ Clusters are generated by ion bombardment of a high purity chromium target (Goodfellow, 99.98%) with 30 keV xenon ions. The cluster formation process takes place in high vacuum at a base pressure of 1×10^{-8} mbar. The positively charged clusters are focused and accelerated by a lens system to a kinetic energy of 500 eV. Mass separation is performed using a dipole magnet deflecting the cluster beam depending on the mass of the clusters. A typical chromium mass spectrum is shown in Fig. 1. As a result of the sputtering process xenon ions are also present in the mass spectrum. The cluster current density for chromium clusters is sufficient to deposit an amount of clusters which is equivalent to a coverage of 0.04 monolayers (ML) of chromium atoms for clusters of a size up to at least 13 atoms per cluster in less than half an hour. The clusters are deposited onto a ~ 3 ML thick iron

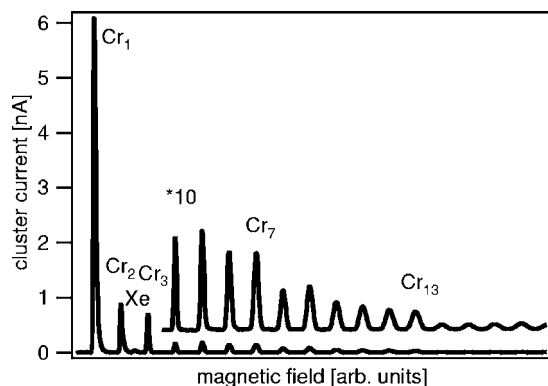


FIG. 1. Mass spectrum of free chromium clusters with zero kinetic energy.

film on a Cu(100) single crystal. The Cu(100) single crystal is cleaned by 1.5 keV argon sputtering and subsequent annealing up to 900 K. Surface cleanliness is checked using XAS and XPS. The ultrathin epitaxial iron film is produced by evaporating iron from a high purity (Goodfellow, 99.99%) iron sheet, heated by a direct current.

Before deposition onto the iron surface, the mass selected clusters are decelerated to a kinetic energy below 1 eV per atom, disregarding intrinsic energies from the sputter process. To avoid fragmentation, a soft landing scheme^{6,7} is used and the buffer layer thickness (argon) is controlled using XPS. Thin argon multilayers effectively suppress fragmentation during cluster deposition.^{16,17} To remove the remaining argon, the crystal is flash heated up to 80 K desorbing the argon and leaving the clusters on the bare iron surface. A ~ 0.04 ML coverage of the clusters (see above) and low temperatures in the range of 30–35 K are used to inhibit cluster-cluster interaction and cluster diffusion, respectively.

XAS measurements have been performed under UHV conditions at a base pressure below 3×10^{-10} mbar. The samples have been prepared *in situ* under UHV conditions and the absorption spectra have been recorded using the total electron yield (TEY), i.e., the sample current. Measurements have been performed at beamline UE56/1-PGM at the BESSY II storage ring in Berlin in a normal incidence geometry.

The resolution of the beamline has been set to 200 meV and the spectra have been taken with a step width of 200 meV and 276 data points per spectrum. For excitation, circular polarized light has been used. Each cluster sample has been measured twice for both photon helicities using 4s counting time per data point. White line spectra have been generated by taking the sum of the spectra measured with left and right circular polarized light, respectively.

The spectra have been normalized to the incident photon flux using the current of the refocussing mirror, i.e., the last optical element of the beamline. The mirror current contains a chromium oxide contamination which is too small to affect the normalization of the spectra, but can be used for energy calibration purposes. Three different ways of background treatment have been tested and compared for the cluster spectra to ensure reliable data evaluation. First, bare substrate spectra, i.e., spectra in the chromium energy range of

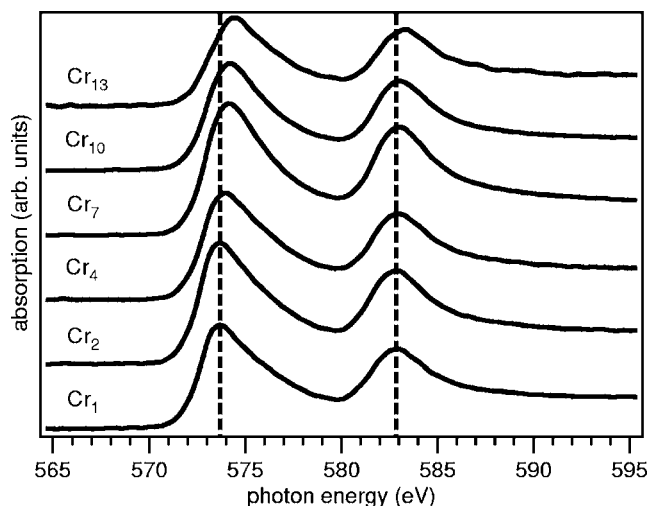


FIG. 2. X-ray absorption spectra of selected chromium clusters. Dashed vertical lines are a guideline for the eye.

the cluster free Fe/Cu(100) surface, have been subtracted from the cluster spectra to enhance the cluster related features. Secondly, the cluster spectra have been divided by these spectra to properly normalize the cluster spectra and eliminate variations of the photon flux with photon energy. Thirdly, the cluster spectra already divided by the bare substrate spectra have been corrected for an offset of the measuring system. As known from a detailed comparison of the normalization procedures used in XAS, the division by the bare substrate spectra usually gives more reliable results for spectra containing a structure in the normalization signal (mirror current).¹⁸ The third evaluation procedure using the offset correction was chosen to check the possible influence of small offsets in the electronics. It turns out that the differences in spectral shape, intensity, and peak position induced by the three procedures are small and trends discussed below are not influenced by the data treatment. Therefore, for all graphs presented in this paper the division of the spectra by the bare substrate spectra has been used for normalization.

The photon energies have been calibrated using the chromium oxide contamination arising from one of the beamline elements as a scale.¹⁹ According to Ito *et al.*,²⁰ the position of the chromium $2p_{3/2}$ absorption maximum can be found at 575.8 eV for Cr_2O_3 . Thus, all spectra have been calibrated, so that the maximum of the chromium $2p_{3/2}$ peak in the current from the mirror is at 575.8 eV. There is an uncertainty of the absolute energy calibration because of an unknown environment of the chromium oxide and an uncertainty of the values of Ito *et al.* However, the accuracy of the relative energy calibration is better than 80 meV.

III. RESULTS AND DISCUSSION

Figure 2 shows selected white line spectra of the chromium $2p \rightarrow 3d$ excitation which have been measured for monomers up to clusters with thirteen atoms per cluster. In a previous study,^{6,13} chromium clusters deposited on a Ru(001) surface have been shown to be very sensitive to oxidation. Chromium oxide can easily be recognized by a pronounced

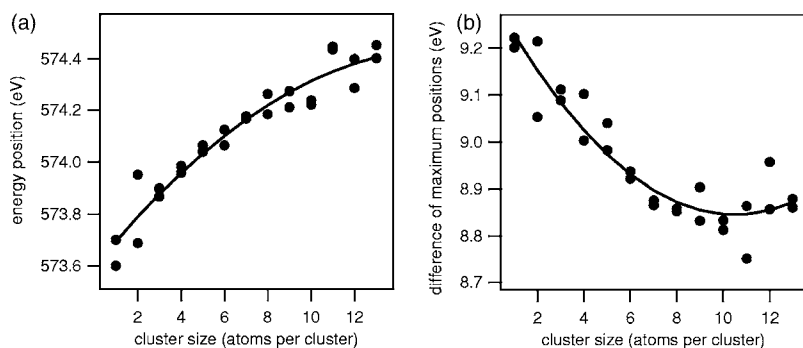


FIG. 3. (a) Position of the L_3 absorption peak maximum versus cluster size. (b) Difference of maximum positions of the L_3 and L_3 absorption peaks, i.e., spin-orbit splitting versus cluster size. Results of all preparations are shown. A guideline for the eye is appended to the graph.

structure at the low energy side of the $2p_{3/2}$ peak. The absence of this structure proves that the clusters discussed here are free from oxygen contamination. Free chromium atoms show a rich multiplet structure above the $2p$ absorption threshold.²¹ In contrast to the spectra of free chromium atoms, the shape of the cluster spectra presented here is comparable to chromium bulk spectra.²² We attribute the bulklike peak structure of the small deposited chromium clusters to dynamic effects related to the strong cluster-surface interaction. There are mainly three reasons for additional line broadening of the $2p$ absorption lines of the supported clusters. First, a strong phonon broadening can be observed for strongly coupled clusters.² Secondly, dynamic effects in the electron distribution, i.e., electron hole pair creation during the excitation process can enhance this effect¹ and will induce additionally a strong peak asymmetry. Thirdly, hybridization between the valence levels of the chromium clusters with the out of plane orbitals of the iron film will result in an enhanced width of the absorption resonances.^{3,4,23,24}

The positions of the $2p_{3/2}$ and $2p_{1/2}$ absorption resonances of the clusters have been determined very accurately by analyzing the smoothed first and second derivatives of the spectra. The results of this evaluation are displayed in Fig. 3. The resonance position shifts towards higher photon energies with increasing cluster size for both, the $2p_{3/2}$ and $2p_{1/2}$ absorption lines. As mentioned above the position of the peak maxima does not depend on background treatment and can be determined with high accuracy. The values obtained for different preparations of the same cluster, which are included in the figures differ by less than 100 meV. Compared to the energy position of the $2p$ absorption resonance for chromium bulk which is located at 576.5 eV (Ref. 22) for the $2p_{3/2}$ line, the values for the clusters are much smaller. The chromium monomer deposited onto the iron surface has a maximum position of the $2p_{3/2}$ line at an energy of 573.7 eV, taking the average value of the two cluster preparations. Interestingly, this is approximately the same resonance position as for the free chromium atom which is found at 573.5 eV.²¹

The origin of the observed energy shifts with cluster size can be discussed in terms of initial and final state effects. First, we will address possible initial state effects. The $2p \rightarrow 3d$ resonance positions are of course influenced by the energetic position of the $2p$ core levels as well as the $3d$ valence states. Therefore, size induced changes of both, the $2p$ and $3d$ orbitals, can contribute to a change in the peak position with cluster size. In the case of the $3d$ valence states a broadening of the valence states with increasing cluster

size due to intracluster hybridization is anticipated. In addition, a higher binding energy of the center of gravity of the d -states due to the bonding character of the interatomic chromium d - d overlap is expected. Hence, the binding energy of the lowest unoccupied molecular orbital (LUMO) of the clusters should increase with cluster size. For the $2p$ core levels, delocalization of the d -electrons due to intracluster coupling results in a lower d -electron density at atomic sites leading to a reduced electron-electron repulsion, and hence giving rise to a higher binding energy of the $2p$ core levels compared to the value for the free atoms as well. In general, however, the LUMO is affected much less than the core levels, resulting in a net increase of the resonance energy¹¹ for bulklike systems. This discussion takes only intracluster delocalization effects into account. Hybridization with the iron underlayer should enhance these effects. For two-dimensional clusters, this contribution however, is expected to be constant with cluster size and should therefore not contribute to a size dependent change of the energy position. Therefore we conclude, that the dominating initial state effect is the lowering of the energy position of the $2p$ core levels due to size dependent intracluster delocalization of the valence electrons.

Final state effects can of course also influence the resonance position. However, it is well known that these effects are less pronounced for excited states which are neutral as compared to ionic final states as in photoemission. For molecular systems experiments show that the position of absorption resonances are almost unchanged if the isolated molecules are coupled to different environments.²⁵

The XA final state is a highly excited neutral state with a $2p$ core hole and an extra d -valence electron. In the case of free atoms, the Coulomb interaction between the core hole and the excited localized $3d$ electron leads to a significant lowering of the resonance energy, relative to the difference in binding energies in a single particle model. However, in the case of more delocalized d -orbitals as for the bulk metal, the Coulomb interaction between the core hole and the excited electron is strongly reduced due to efficient extra-atomic screening of the core hole. Since the chromium clusters in our case are strongly coupled to the substrate we expect dynamic screening to be very efficient. Therefore, differences in Coulomb interaction between the core hole and the excited $3d$ electron due to size dependent changes in the intracluster screening should be less important. Hence, we consider final state correlation effects to be of minor importance for the observed trends in the resonance positions with cluster size.

Therefore we come to the conclusion that the shift of the resonance position is dominated by the intracluster delocalization, leading to a size dependent increase in $2p$ binding energy. A gradual increase of the absorption threshold with cluster size can be interpreted as the evolution of the delocalization of the chromium $3d$ -electrons starting from quasi-atomiclike properties towards more bulklike properties.

In previous experiments,^{6,13} XA spectra of chromium clusters of the size 1, 3, 4, 7, and 10 atoms per cluster deposited on a Ru(001) surface were investigated. In agreement with the results presented here, in these experiments a shift of the energy position of the chromium $2p_{3/2}$ absorption maximum towards higher photon energies with increasing cluster size was observed, with the exception of the Cr_{10} cluster. In this study, the energy position of Cr_{10} was found to be lower than the energy position of the Cr_7 cluster. This was attributed to a three-dimensional ground state geometry of the Cr_{10} cluster consisting of stacked two-dimensional Cr_7 and Cr_3 clusters.

In contrast to these findings, the shifts of the chromium clusters deposited onto the iron surface are monotonous with size, as depicted in Fig. 3(a). Comparing these findings with the results for chromium clusters on the Ru(001) surface we take this as a hint for two-dimensional cluster structures for the Cr_N/Fe clusters. Two-dimensional cluster structures are expected for strong coupling between cluster and substrate especially since both chromium and iron form bcc bulk structures with a lattice mismatch between the two elements of only 1.5%.²⁶ Therefore, pseudomorphic layer by layer growth of chromium on iron is predicted and found experimentally.²⁷

As explained above the cluster samples were prepared under soft landing conditions and at low temperatures. Because a monotonous shift of the chromium $2p$ levels towards higher photon energies is observed and the linewidths of the measured clusters do not change drastically with cluster size (see below), it can be inferred that the chromium clusters neither fragment nor agglomerate upon deposition.

In addition to the peak shift we find a small change of the line shape of the absorption peaks with cluster size (see Fig. 4). For better comparison the peak height of the spectra for the different cluster sizes in Fig. 4 are normalized to one and the corresponding energy position is aligned so that the rising $L3$ flanks of the spectra are at the same energy. Beside a gradual shift of the peak maximum we observe a tiny change in line shape at the low energy side of the maximum. We attribute this small change in the peak shape to a change in the local $3d$ density of unoccupied states when going from the monomer to larger cluster sizes. The absence of large changes indicate that dynamic effects (see above) dominate the line shape.

In order to compare the linewidths of the cluster spectra with the values for the bulk, chromium XA spectra of Fink *et al.*²² and Wende *et al.*²⁸ have been treated in the same way as the cluster spectra. The resulting values for the chromium bulk linewidths are 3.5 eV and 3.7 eV, respectively. The linewidth of the deposited chromium clusters of 4.3 eV is enhanced compared to the values for the bulk metal giving further evidence to strong cluster-substrate coupling.

In Fig. 3(b) the difference of the maximum positions of the $2p_{3/2}$ and $2p_{1/2}$ lines is plotted versus cluster size. A

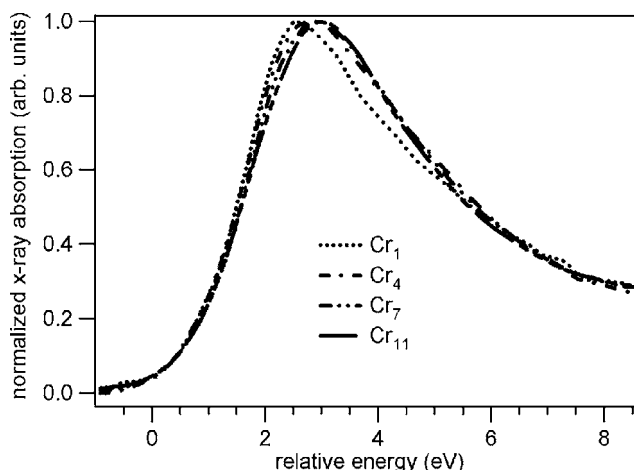


FIG. 4. X-ray absorption spectra of selected chromium cluster preparations. The $2p_{3/2}$ peak maximum was normalized to one and the spectra are shifted in energy, in order to visualize the change of the peak shape.

decreasing difference of the maximum positions with increasing cluster size is obtained. There are two possible contributions to a relative change of the energetic difference between the $L3$ and $L2$ maxima. First, the change in the shape of the unoccupied valence density of states results in a change of the peak shape and therefore the maximum position is shifted as discussed before. This could be different for the spin-orbit split core levels through symmetry induced coupling to different empty valence states. However, since we discuss white line spectra obtained by averaging left and right circular polarization this should be a minor effect. Secondly, the spin-orbit splitting can change with cluster size. A change in the spin-orbit splitting is reasonable, because the spin-orbit splitting Δ_{SO} is to first order proportional to a change in the potential $\Delta_{SO} \propto \partial V / \partial r$. The effective potential V seen by the core levels is expected to change with cluster size as discussed above. Therefore, the spin-orbit coupling should depend on the cluster size. Wernet and co-workers²⁹ report a change in the spin-orbit splitting in chromium systems, comparing linear dichroism spectra measured in photoemission and HF calculations of free chromium atoms with linear dichroism spectra of a 0.5 ML thick chromium film on an Fe(110) substrate. Here, the spin-orbit splitting of the free atoms turns out to be significantly larger than the spin-orbit splitting of the chromium film. In contrast, the cluster results show a reduced spin-orbit splitting compared to the bulk value which is found at 9.2 eV.³⁰ Hence, the trend from atom towards bulk appears to be nonmonotonous in this case.

In order to compare the oscillator strength of the absorption resonances for the different clusters, a step function with a step ratio of 2:1 for $L3$ and $L2$ -edge respectively, has been subtracted from the cluster spectra. The steps for each absorption line have been set to the corresponding point of inflection. This procedure is quite generally used in the literature to extract the absorption cross section for transitions to empty d -states. The oscillator strength is then taken as the integral of the white line spectrum (see Fig. 2) after normalizing the off resonance cross section to one. The values are plotted versus the cluster size in Fig. 5. Here, the average

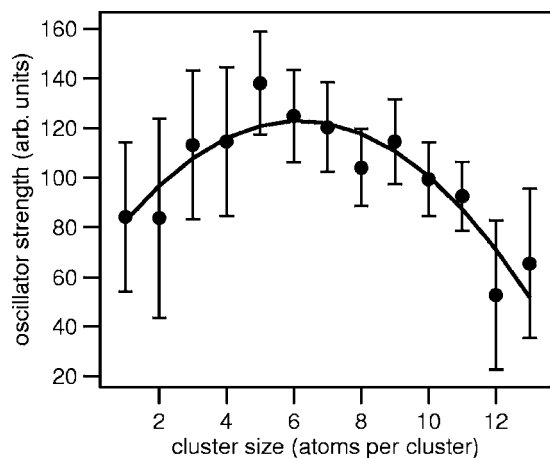


FIG. 5. Oscillator strength versus cluster size. A guideline for the eye is appended to the graph.

values of the different cluster preparations of the oscillator strengths are shown. For cluster sizes larger than four atoms per cluster, a trend towards decreasing values of the oscillator strength with increasing cluster size is observed. This decrease in the oscillator strength is present for all background treatments. Monomers and clusters up to size of four atoms per cluster deviate from this trend. However, it is very difficult to extract exact values for these very small clusters quantitatively as can be seen from the error bars.

In general, the oscillator strength is influenced by two contributions, which cannot be separated using XAS. A change of the oscillator strength can either be assigned to a change in the integral LDOS or to a change of the dipole matrix element, according to Fermi's Golden Rule. Since the dipole matrix element contains the overlap of the $2p$ core and $3d$ valence orbitals, an increasing delocalization of the $3d$ -electrons will result in a reduced oscillator strength. A change in the shape of the cluster LDOS will not result in a change of the oscillator strength, because the oscillator strength is determined by integration over all LDOS contributions. Therefore only a change in the d -band-filling would have an impact on the oscillator strength. However, the d -band-filling is expected to be fairly constant with cluster size.^{31,32} Hence the decrease of the oscillator strength for clusters with more than four atoms per cluster can again be explained in terms of delocalization of d -electrons. A size dependence is again expected for intracuster delocalization only.

For very small clusters it appears to be obvious that hybridization of the chromium $3d$ orbitals with iron $3d$ orbitals is more important than intracuster delocalization so that a different behavior is found.

By separately integrating the $L3$ and $L2$ areas, the ratio of the $L3$ to $L2$ contributions can be quantified. A deviation from the statistical ratio of 2:1 for the early $3d$ transition metals is well established and has been observed by Leapman *et al.*^{33,34} and Fink *et al.*²² The discrepancy between the

measured values and the statistical ratio is explained by the interaction of the core hole with the excited electron. This deviation from the single particle model shows the importance of correlation effects which is confirmed by calculations.^{35,36} Schwitalla *et al.*³⁷ report values for the $L3/L2$ ratio from calculations of 1.50 for chromium bulk in good agreement with the experiments by Leapman *et al.*³⁴ and by Fink *et al.*²² The chromium clusters on the iron surface show within the error bars a constant $L3/L2$ ratio with cluster size; the mean value for all preparations and background treatments indicates a reduced ratio of 1.4 ± 0.2 which is in good agreement with the calculations of Schwitalla *et al.*

In contrast, for chromium clusters on a graphite surface a deviation from the bulklike ratio of 1.5 is reported by Lozzi *et al.*¹² from electron energy loss spectroscopy. Here, the $L3/L2$ ratio decreases down to 1 for small clusters. Since the major difference between chromium clusters supported on graphite and on an iron surface is the hybridization of the outer cluster orbitals with the substrate this appears to be an effect of cluster-substrate interaction.

IV. SUMMARY AND CONCLUSION

Mass selected chromium cluster supported on iron in the size range of one to thirteen atoms per cluster have been prepared and XA spectra have been measured. A monotonous energy shift of the $2p_{1/2}$ and $2p_{3/2}$ absorption resonances towards higher photon energies with increasing cluster size has been observed and is interpreted in terms of delocalization of chromium d -electrons with increasing cluster size. Since XA spectra include the properties of the empty parts of the cluster valence band, a change of the spectral shape with cluster size is interpreted as a size dependent change in the $3d$ valence density of states. Due to the change in the potential which is induced by these changes in the d -electron density, the $2p_{1/2}^{-1}$ to $2p_{3/2}^{-1}$ spin-orbit splitting is found to depend on the cluster size. In addition, a size dependence of the oscillator strength has been found and is explained in terms of a change of the dipole matrix element again due to delocalization of the cluster d electrons. The $L3/L2$ branching ratio is found to be constant and close to bulk values.

In conclusion our XAS experiments clearly show that we are able to deposit size-selected clusters. In addition they provide evidence for size dependent changes in the localization of the d -electrons of the clusters.

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*Electronic address: Wilfried.Wurth@desy.de

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