

Size Dependence of $L_{2,3}$ Branching Ratio and $2p$ Core-Hole Screening in X-Ray Absorption of Metal Clusters

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Resonant $2p$ x-ray absorption spectra of size-selected transition metal ions and clusters consisting of $1 \leq n \leq 200$ atoms are reported. Remnants of atomic multiplet splitting in $L_{2,3}$ -edge x-ray absorption can be resolved up to the trimer, above which the overall line shape is already bulklike. A strong cluster size dependence of the $L_{2,3}$ branching ratio was found for titanium, vanadium, and cobalt clusters. While $3d$ electron delocalization increases with cluster size, the apparent $2p$ spin-orbit splitting remains constant within the error bars. The size dependence of the $L_{2,3}$ branching ratio can be attributed to cluster size specific screening of the $2p$ - $3d$ Coulomb interaction by $3d/4s$ valence electrons.

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X-ray absorption spectroscopy (XAS) is a standard technique to investigate the local electronic properties of pure and compound systems. $L_{2,3}$ -edge absorption is especially interesting since also magnetic properties can be studied by x-ray magnetic circular dichroism (XMCD) spectroscopy. By exciting $2p \rightarrow 3d$ transitions at the $L_{2,3}$ edges of $3d$ transition metals, the unoccupied $3d$ density of states, modified by the core-hole interaction [1–5], can in principle be probed. Since XAS and XMCD are widely used as fingerprint techniques as well as to extract quantitative information, a detailed understanding of the processes involved in L-shell X-ray absorption is of fundamental importance for many analytical applications. This is especially true for XMCD, where the separation of $L_{2,3}$ -edge x-ray absorption into $j = 3/2$ and $j = 1/2$ components is a prerequisite for the application of sum rules [2,6–9] to obtain absolute values of the spin and orbit contributions to the total magnetic moment. The precise separation of the different j contributions is one of the main difficulties in analyzing XMCD spectra, in particular, for the early $3d$ elements. Although $3d$ transition metals have to be described in intermediate coupling where j is not a good quantum number, the $L_{2,3}$ edge spectra of bulk $3d$ transition metals are still dominated by two broad lines which are generally attributed to resonant excitation at spin-orbit split $j = 3/2$ (L_3) and $j = 1/2$ (L_2) levels. For small $2p$ spin-orbit splitting in early $3d$ metals these lines overlap strongly. In addition, core-hole interaction causes intermixing of these two lines, transferring spectral weight from one transition to the other [1–5]. Both effects lead to a so-called “anomalous” branching ratio [10,11], i.e., a strong deviation from the statistical 2:1 ratio [12] of L_3 to L_2 x-ray absorption lines, which has been a matter of intense discussion over the last 20 years [1–5]. Several approaches have been made to explain the evolution of

the anomalous branching ratio along the $3d$ series by the failure of the independent particle approximation, stressing different aspects of atomic multiplet splitting, $2p$ spin-orbit coupling, or Coulomb and exchange-correlation effects of core-hole interaction [1–5].

So far, however, the evolution of $2p$ spin-orbit splitting and $L_{2,3}$ branching ratio in $2p$ x-ray absorption of $3d$ transition metals has only been investigated *along* the $3d$ series, both for isolated gas phase atoms [13] and bulk metals [11]. Here, we present the first experimental investigation of $L_{2,3}$ x-ray absorption of size-selected free metal clusters. So far, with the exception of stable clusters like C_{60} [14] that can be generated in macroscopic quantities, only deposited size-selected clusters [15,16] as well as free clusters with a broad size distribution [17–19] have been investigated with XAS. By exploring the cluster size dependence of resonant $2p \rightarrow 3d$ x-ray absorption for a given $3d$ element, we can extend the investigation on bulk metals into a third dimension *perpendicular* to the periodic table. Now, the amount of core-hole screening for a given $3d$ element can be altered by changing the metallic character, i.e., valence electron delocalization, with cluster size. The experiments show a pronounced cluster size dependence in the $L_{2,3}$ branching ratio and the L_3 absorption onset, which is a measure of core-hole screening. In contrast, the apparent $2p$ spin-orbit splitting is constant within the error bars. Even for cobalt with a large apparent spin-orbit splitting of about 15.3 eV and very little overlap of the $L_{2,3}$ lines, intermixing of the transitions occurs via core-hole interaction. This emphasizes the importance of core-hole screening effects on the $L_{2,3}$ branching ratio [3,4].

The size dependence of the x-ray absorption at the $L_{2,3}$ edges of vanadium, titanium, and cobalt clusters has been investigated in the size range of $1 \leq n \leq 200$ atoms using two different experimental setups, both of which will be

described in detail in a forthcoming publication. In brief, transition metal clusters were produced in a magnetron cluster source in both cases. In the first setup, small cluster cations were mass selected in a quadrupole mass filter and stored in a linear ion trap, where they were irradiated by a collinear synchrotron beam. Ion bunches were extracted from the trap and analyzed in a time-of-flight mass spectrometer. X-ray absorption spectra were obtained by monitoring the generated daughter ion intensities as a function of incident photon energy. This approach allowed to record x-ray absorption spectra of size-selected free clusters for the first time. In the second setup, larger neutral clusters (with up to a few hundred atoms) were produced by the cluster source and ionized by synchrotron radiation directly in the extraction region of the time-of-flight mass spectrometer. Careful analysis of the high resolution mass spectra obtained allowed to determine the cluster ion charge states (as well as the amount of fragmentation taking place) and thereby the true sizes of the original clusters. Measuring the ion intensity in a certain size range (with a typical width of five atoms) as a function of photon energy yielded the size dependent x-ray absorption spectra for larger cluster sizes ($40 \leq n \leq 200$). Although this

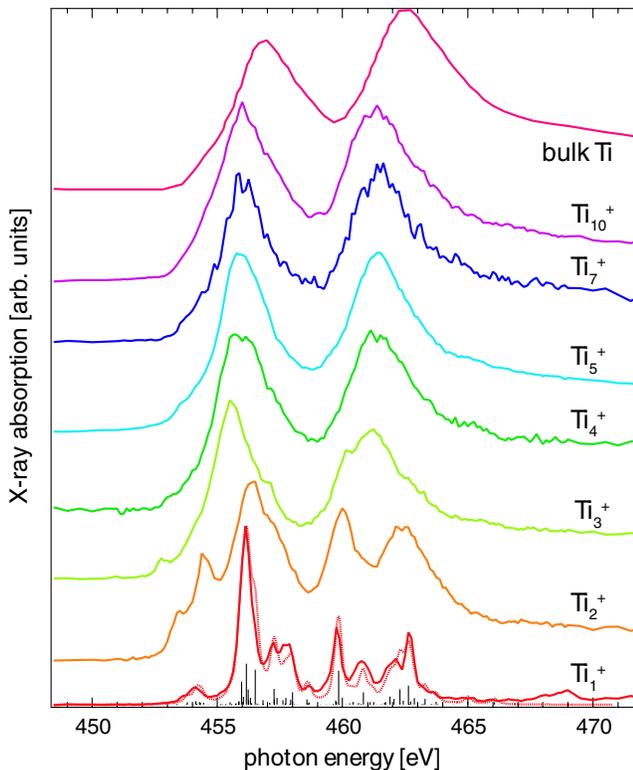


FIG. 1 (color online). $L_{2,3}$ x-ray absorption spectra of size-selected titanium clusters, measured at a photon energy resolution of 125 meV, compared to bulk titanium [5]. Already for the tetramer, the line shape is bulklike. There is good agreement of the monomer spectrum with the neutral atom [13] and calculations using the COWAN code [20] (stick spectrum and dotted line).

method works well for cobalt and vanadium clusters, data analysis for titanium clusters is complicated by the isotope distribution. Therefore, mass-integrated data for titanium clusters larger than 10 atoms are shown here. All spectra were taken at the Berlin synchrotron radiation facility BESSY II beam lines U49/2-PGM-1 and UE56/2-PGM-1. From these x-ray absorption spectra, the apparent $2p$ spin-orbit splitting was measured as the peak-to-peak distance of the $L_{2,3}$ absorption lines, while the $L_{2,3}$ branching ratio was deduced from the relative height of the resonance lines [3,4]. This procedure was used for simplicity as well as to facilitate the comparison with existing bulk $3d$ metal data [11] and theoretical branching ratios [3,4], although the area of the L_3 and L_2 lines would be the correct measure of their intensity [5]. In determining the area, however, assumptions would have to be made on the continuum contribution $2p \rightarrow \epsilon d$, ϵs and on the *a priori* unknown overlap of the $L_{2,3}$ lines, both of which would introduce additional uncertainties.

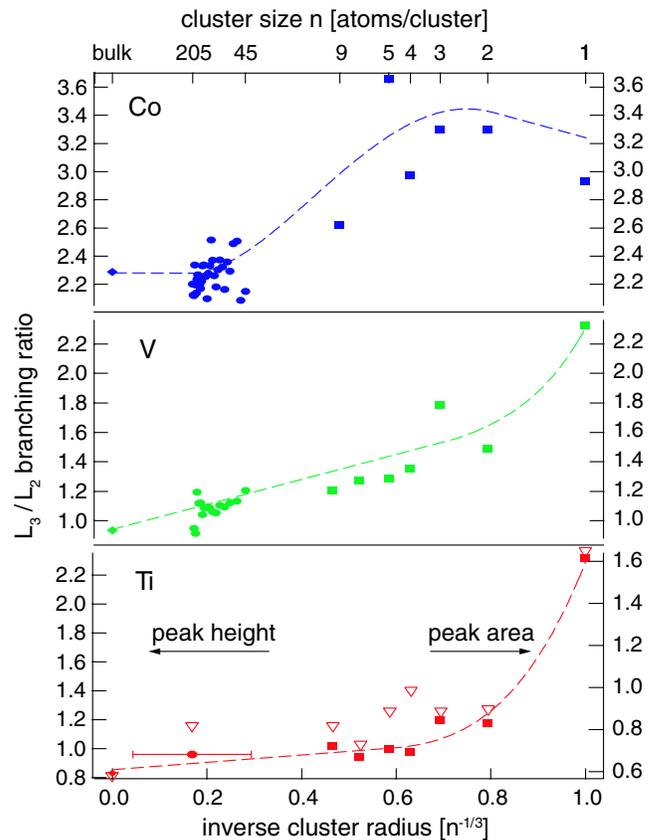


FIG. 2 (color online). $L_{2,3}$ branching ratio of size-selected cobalt, vanadium, and titanium cluster ions (squares) and neutral clusters with a typical mass-resolution of five atoms (circles). For all clusters, intensity is transferred from the L_3 to the L_2 line with increasing cluster size. Bulk values are taken from [5,22]. The dashed line is a guide to the eye. For titanium, data evaluated from the peak areas (triangles) are given for comparison.

X-ray absorption spectra of small titanium clusters are shown in Fig. 1. The spectra of the neutral atom [13] and the monomer cation are almost identical and well structured, although individual lines cannot be resolved because of lifetime broadening. The monomer cation spectrum is in good agreement with calculation [20], assuming an initial $2p^6 3d^2 4s^1$ configuration (stick spectrum and dotted line). The dimer cation still shows several well-separated peaks at the L_3 and L_2 edges, but already for the trimer cation the increasing number of $2p \rightarrow 3d$ transitions leads to broader, less structured peaks, which for the tetramer cation already are almost bulklike in line shape. From these spectra, the cluster size evolution of $L_{2,3}$ branching ratio, L_3 absorption onset, and apparent $2p$ spin-orbit splitting can be followed, as shown in Figs. 2–4. Qualitatively, the behavior of small titanium, vanadium, and cobalt clusters is very similar. Although the transition to bulklike behavior proceeds very rapidly in x-ray absorption spectroscopy, the spectra in Fig. 1 show for the first time that atomiclike multiplet splitting is still present in $2p$ x-ray absorption of transition metals at the molecular limit of very small clusters.

The size evolution of the $L_{2,3}$ branching ratio is shown in Fig. 2. For all clusters investigated, there is a clear decrease

in branching ratio as the cluster size increases from monomer to bulk. This is not limited to the early $3d$ transition metals titanium and vanadium which as bulk metals show strong deviations from the statistical 2:1 ratio, but is evident even for cobalt, where a large apparent $2p$ spin-orbit splitting of L_3 and L_2 lines. Still, the transitions are coupled by Coulomb and exchange-correlation terms of the core-hole interaction [1–5], and there is transfer of spectral weight from the L_3 to the L_2 line with increasing cluster size. This transfer can be understood by analyzing the size dependence of core-hole screening and $2p$ spin-orbit splitting, shown in Figs. 3 and 4.

The amount of core-hole screening by delocalized valence electrons in size-selected clusters can be inferred from a shift in L_3 x-ray absorption onset. Screening of the core hole in the final state weakens the $2p$ – $3d$ Coulomb interaction, leading to a shift of resonance position to higher photon energy. This can be seen in Fig. 3, where the L_3 x-ray absorption onset is plotted against inverse cluster radius. For vanadium and cobalt clusters with their nearly empty and nearly filled $3d$ band, respectively, the absorption onset shifts to higher energy with increasing cluster size, by about 3 eV from monomer to bulk, reflect-

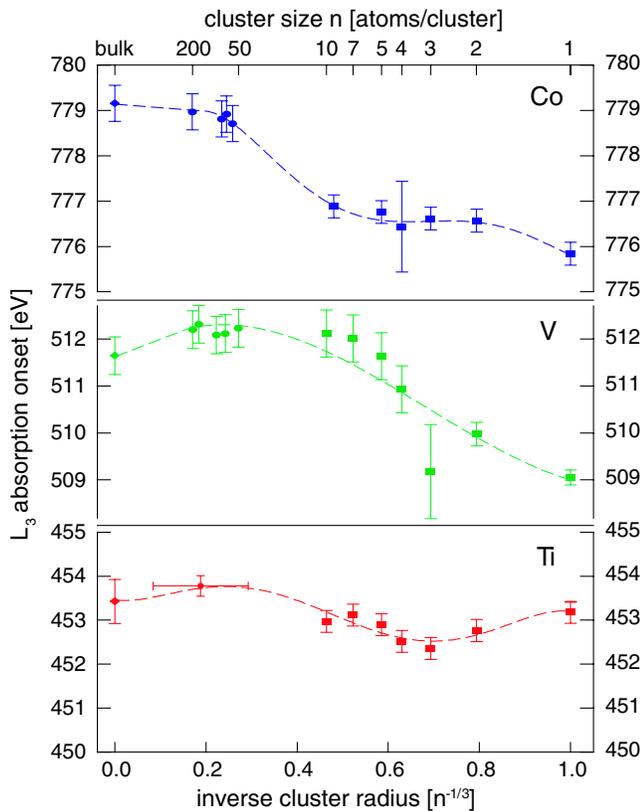


FIG. 3 (color online). L_3 x-ray absorption onset of free cobalt, vanadium, and titanium clusters (circles and squares as in Fig. 2). For vanadium and cobalt, the onsets shifts by ≈ 3 eV from monomer to bulk [5,22]; this shift is smaller for titanium. The dashed line is a guide to the eye.

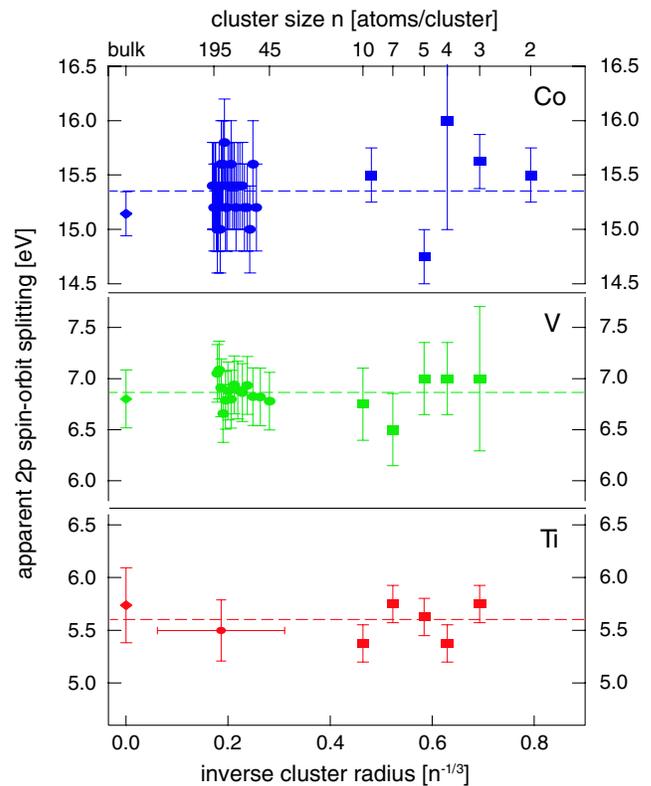


FIG. 4 (color online). Apparent $2p$ spin-orbit splitting of free cobalt, vanadium, and titanium clusters (circles and squares as in Fig. 2). For all clusters up to the bulk [5,22], the apparent $2p$ spin-orbit splitting is constant within the error bars. The dashed line gives the average value.

ing the increasing metallicity and electron delocalization in these clusters. Interestingly, for titanium there is hardly any shift in the L_3 x-ray absorption *onset* when going from monomer to bulk, although the L_3 *maximum* is clearly shifted by ≈ 1 eV, also indicating an increased $3d/4s$ electron delocalization.

As shown in Fig. 4, the $2p$ spin-orbit splitting is constant within the error bars for all clusters investigated. To some extent, this can be expected since the spin-orbit coupling parameter ζ_{2p} is an atomic property and should not change with cluster size, although x-ray absorption spectroscopy only measures an *apparent* $2p$ spin-orbit splitting which is smaller than the splitting derived from x-ray photoemission spectroscopy [1,21].

These findings clearly show that for vanadium and cobalt clusters, the observed cluster size dependent variation of the $L_{2,3}$ branching ratio is rather caused by core-hole screening than by spin-orbit splitting. Mixing of the $L_{2,3}$ lines is determined by the interplay of the $2p$ - $3d$ core-hole Coulomb interaction, which shifts intensity *towards* threshold, on the one hand, with higher multipole and exchange-correlation interactions on the other hand, which shift intensity *away* from threshold and *decrease* the branching ratio [1]. Since the $2p$ - $3d$ Coulomb interaction is more efficiently screened by delocalized valence electrons than higher multipole and exchange-correlation terms [1], its counterbalancing effect decreases with increasing cluster size and leads to the observed size dependence of the $L_{2,3}$ branching ratio in vanadium and cobalt clusters. For titanium clusters, no clear correlation can be made between the branching ratio and $2p$ spin-orbit coupling or core-hole screening from the existing data. However, a similar trend in $L_{2,3}$ branching ratio suggests that electron delocalization and screening might also be important for titanium clusters.

To summarize, x-ray absorption spectra of size-selected free transition metal clusters have been presented. The transition from atomic to bulklike line shape in $2p$ x-ray absorption spectra was found to proceed rapidly in pure transition metal clusters and is already completed at the tetramer. In spite of the overall bulklike line shape, even for larger clusters there is a clear size evolution in the $L_{2,3}$ branching ratio towards the bulk value, with transfer of spectral weight from the L_3 to the L_2 line as the cluster size increases. Core-hole screening, measured via the L_3 x-ray absorption onset, increases with cluster size for cobalt, vanadium, and to a lesser extent for titanium, while the apparent $2p$ spin-orbit coupling is constant. The size dependent variation of the branching ratio in vanadium and cobalt can be explained by screening of the $2p$ - $3d$ Coulomb interaction with increased electron delocalization in larger clusters.

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