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Ioniclike energy structure of neutral core-excited states in free Kr clusters

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The development of electronic states in krypton clusters is investigated by high-resolution core-level electron spectroscopy. The energy ordering of bulk versus surface $3d^{-1}np(n>5)$ core-excited states in neutral clusters is demonstrated to be reversed to the $3d^{-1}5p$ level situation. The cluster $3d^{-1}6p,7p$ states are proven to be at a lower energy than the corresponding atomic levels. These findings reveal the ioniclike energy structure of the *neutral* cluster core-excited levels. The phenomenon is explained by a spatial spread of the excited orbitals over the cluster lattice.

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The electronic structure of clusters, gradually changing with the size from atomic to the solid, is a subject of wide interest [1]. Free rare-gas clusters have been extensively investigated by various techniques. Modern high-resolution x-ray absorption (XA) spectroscopy, which probes the unoccupied levels, is able to separate the signal from the inner cluster atoms ("bulk") from that of the surface atoms. Argon clusters were the first studied with this technique [2,3]. In krypton clusters the *lowest* core-excited state close to the $3d$ ionization threshold was also investigated and assigned as the $3d^{-1}5p$ state [4]. Cluster features were found *higher* in excitation energy (blueshifted) than the corresponding atomic level, the bulk state being further away than the surface one. However, the origin of cluster features and the energy ordering of bulk versus surface cannot always be understood from just x-ray absorption spectra alone. The origin of the Kr cluster features, above the $3d^{-1}5p$ state, and their relation to the absorption structure of atomic and solid Kr has remained unclear. These cluster states were instead assumed to be lower in energy (redshifted) relative to the parent atomic states [4]. To identify their nature knowledge of the final singly ionized cluster states reached after Auger decay of the resonantly excited core states is helpful as recently demonstrated for free Ar clusters [5,6]. In the present work on free Kr clusters resonant Auger (RA) spectroscopy revealed the ioniclike energy structure of the *neutral* $3d^{-1}np$, $n>5$, core-excited levels. We confirm that these cluster levels are redshifted relative to the corresponding atomic states, and we explain the nature of the shifts. Moreover, we show that the bulk-to-surface energy ordering is reversed in comparison to the $3d^{-1}5p$ case.

The experiments were performed at MAX-Lab, the national Swedish synchrotron radiation facility, at beamline I411 [7], equipped with a Zeiss SX-700 monochromator and a Scienta SES-200 electron energy analyzer fixed at 54.7° with respect to the polarization plane of the radiation. The cluster source [6] based on an adiabatic expansion was mounted at 90° to the spectrometer acceptance axis and to the light propagation direction. The mean cluster size $\langle N\rangle$ was varied by changing the Kr gas pressure and was estimated using the scaling parameter Γ^* formalism [8]. The monochromator contribution to the total instrumental spectral broadening has constituted ≈ 10 meV in the x-ray absorption and ≈ 40 meV in the resonant Auger measurements. The photon and kinetic-energy calibration was made using atomic Kr lines [9,10] appearing in spectra due to the presence of uncondensed atoms in the cluster jet.

An approximate x-ray absorption spectrum can be obtained by different methods [4,6]. The method used in the present work on Kr clusters is based on collecting Auger electrons ejected after core-level excitation. The chosen 40–75 eV kinetic-energy interval contains the main resonant Auger lines for free Kr atoms [10] and for cluster atoms. In free Kr atoms the excitation of $3d$ core electrons populates two spin-orbit split series of Rydberg levels which converge to the $3d_{5/2}{}^{-1}$ and $3d_{3/2}{}^{-1}$ core-ionized states at 93.83 and 95.04 eV [11] [Fig. 1, spectrum (a)]. The core excitation to the first dipole-allowed level creates the $3d_{5/2}{}^{-1}5p$ state ($\mathbf{A}_1$, Fig. 1) and its spin-orbit twin $3d_{3/2}{}^{-1}5p$ ($\mathbf{A}_2$). The next dipole-allowed atomic transitions produce the $3d_{5/2}{}^{-1}6p$ and $3d_{5/2}{}^{-1}7p$ states ($\mathbf{A}_3,\mathbf{A}_4$). Transitions to nf orbitals are optically allowed for $3d$ electrons, but have negligible cross sec-

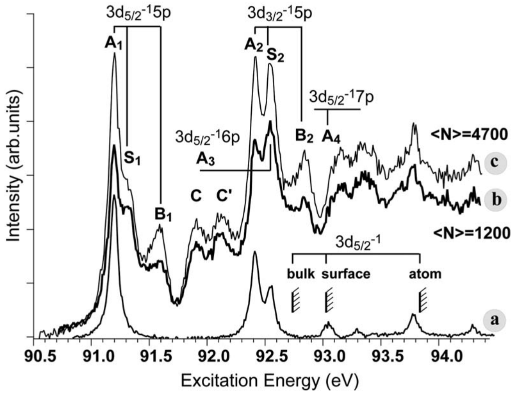

FIG. 1. Krypton x-ray absorption spectra normalized to the photon flux: (a) atoms; (b, c) clusters of average sizes $\langle N\rangle \approx 1200$ and $\langle N\rangle \approx 4700$, respectively. ($\mathbf{A_1},\mathbf{A_2},\mathbf{A_3},\mathbf{A_4}$) $3d_{5/2}{}^{-1}5p$, ${}_{3/2}{}^{-1}5p$, $3d_{5/2}{}^{-1}6p$, $3d_{5/2}{}^{-1}7p$ atomic lines. ($\mathbf{S_1}$, $\mathbf{S_2}$ and $\mathbf{B_1}$, $\mathbf{B_2}$) established $3d_{5/2,3/2}{}^{-1}5p$ surface and bulk features.

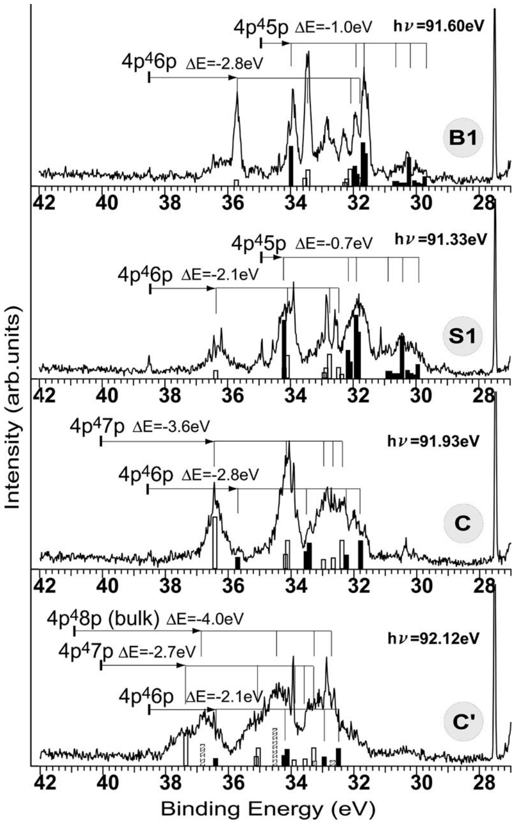

FIG. 2. Resonant Auger spectra measured at the states indicated in Fig. 1 for clusters of size $\langle N\rangle \approx 4700$. The photon energies are: $\mathbf{B_1}$, $h\nu=91.60$ eV; $\mathbf{S_1}$, $h\nu=91.33$ eV; **C**, $h\nu=91.93$ eV; and **C′**, $h\nu=92.12$ eV. The $4p^45p$, $6p$, $7p$, and $8p$ states are shown with vertical bars proportional to the experimental intensities [10]. The energies are shifted from the atomic values by an amount indicated in the figure.

tion due to the high centrifugal potential barrier for *f* electrons [12]. The cluster $3d_{5/2}^{-1}5p$ features, being *blueshifted*, are still well separated from the rest of the cluster absorption spectrum. From its size dependence [spectra (b) and (c) in Fig. 1] the $\mathbf{B_1}$ feature has been assigned to the cluster signal from the bulk, and $\mathbf{S_1}$ as due to the cluster surface [4]. As the cluster size grows, the fraction of the atoms located at the cluster surface decreases. For inert gas clusters the blueshift for the lowest observed cluster state ($3d_{5/2}^{-1}5p$ in Kr) has been explained by compression of the spatially extended Rydberg orbitals by neighboring atoms [3,4]. Indeed, in free Kr atoms the maximum in the radial charge distribution (orbital radius) of the $3d_{5/2}^{-1}5p$ state is ≈3.4 Å [13], while the interatomic distance in Kr clusters is ≈3.3 Å [14]. The compression is stronger for the bulk than for the surface, so the bulk peak is higher in energy.

The x-ray absorption features next to the $\mathbf{B_1}$ peak, the **C** and **C′** peaks in the 91.8–92.3 eV region (Fig. 1), are lower in energy than any allowed atomic state except for the $3d_{5/2}^{-1}5p$. The most obvious speculation concerning the nature of **C** and **C′** is that these features are due to the $3d \rightarrow np$ ($n>5$) surface and bulk excitations [4] with the $3d_{5/2}^{-1}6p$ level ($\mathbf{A_3}$) at 92.55 eV as the closest candidate for the "parent" atomic state. However, there is no clear explanation of the apparently redshifted positions of these peaks. Comparing the cluster absorption spectrum for $\langle N\rangle \approx 4700$ with that of solid Kr [15], where peaks were observed at ≈92.0 and 92.2 eV, it may be surmised that **C** at 91.92 eV and **C′** at 92.10 eV are the corresponding cluster bulk peaks. But some questions remain. Which atomic states correspond to the bulk cluster features? If both **C** and C′ are due to the bulk, where are the cluster features due to the surface atoms in the same excited states?

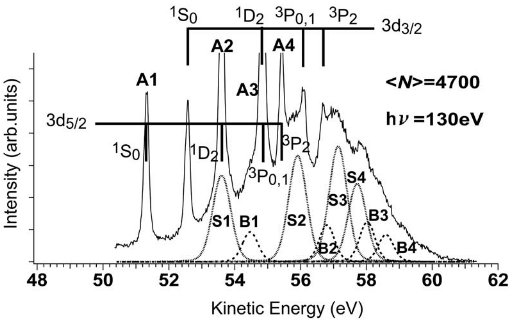

FIG. 3. $M_{4,5}N_{2,3}N_{2,3}$ normal Auger spectrum of Kr atoms and clusters with $\langle N\rangle \approx 4700$. In atoms, each of two $3d_{5/2,3/2}^{-1}$ core-ionized states decays into five, final, doubly ionized $4p^4$ states: $^1S_0$, $^1D_2$, and $^3P_{0,1,2}$. In clusters the final states are split into bulk (dashed curves) and surface (solid curves) components. Only the peaks for the $3d_{5/2}^{-1}$ core-ionized initial states are shown.

We search for the origin of the red x-ray absorption energy shifts in the similarity of the core-excited and core-ionized states in Kr clusters. For $N \geqslant 4000$ the core-ionized $3d_{5/2}^{-1}$ bulk state at 92.7 eV is ≈1.1 eV lower in energy than the $3d_{5/2}^{-1}$ atomic level [14]. The surface $3d_{5/2}^{-1}$ level is ≈0.8 eV below the free-atom value. Similarly, the **C** and **C′** features are ≈0.6–0.4 eV lower than the closest related atomic level $\mathbf{A_3}$ (Fig. 1). These negative cluster-to-atom energy shifts for the *core-ionized* and for the *higher core-excited* states can indicate that the origin of the redshift in both types of states is the same. In ionic states of rare-gas clusters the mechanism for the energy-level shifts is the electron charge polarization induced in the surrounding atoms by the positive ion [3]. It leads to a lowering of the electron binding energy relative to the free atom. The bulk state is influenced by more neighbors than the surface state, resulting in a lower binding energy. For the higher core-excited states the spatial size of the orbital may exceed the closest coordination shell of 3.3 Å radius: in free Kr atoms the orbital radii are ≈8 and 16 Å for the $3d_{5/2}^{-1}6p$ and $3d_{5/2}^{-1}7p$ states [13]. Hence, in Kr clusters a large part of the excited-state electron density can extend beyond the nearest coordination shell. A similar situation was recently predicted for the bulk Ar $2p_{3/2}^{-1}5s$ core-excited state [16], in which the main part of the $5s$ electron density is spread over a large area of the crystal. The positive charge remaining inside the closest shell induces a polarization of the electrons in the surrounding atoms. In the neutral clusters the resulting screening field leads to a lowering of the final-state energy (redshift), as in the case of core ionization.

Recently, it has been shown that a cluster resonant Auger spectrum can be assigned by shifting the corresponding

TABLE I. Energy levels for excited and ionized states for free Kr atoms [8] and clusters (present work). In the last column the free-atom radii of excited orbitals are given [12]. The cluster interatomic distance is 3.3 Å. The energy of the surface $3d_{5/2}{}^{-1}7p$ state is obtained by assuming that the bulk-to-surface shift ratio is the same as in the core-ionized case. Notations $\Delta(b-a)$ and $\Delta(s-a)$ stay for separations between the atomic line and corresponding cluster surface and bulk features.

	State energy (eV)			Energy shift (eV)		
state	atom	bulk	surface	$\Delta(b-a)$	$\Delta(s-a)$	r, Å
$3d_{5/2}{}^{-1}5p$	91.20	91.60	91.33	0.40	0.13	3.4
$3d_{5/2}{}^{-1}6p$	92.55	91.92	92.12	−0.63	−0.43	8
$3d_{5/2}{}^{-1}7p$	93.06	92.12	≈92.4	−0.94	≈−0.6	16
$3d_{5/2}{}^{-1}$	93.83	92.73	93.03	−1.10	−0.8	

TABLE II. Experimental energy shifts for the final, singly ionized $4p^4np$ and doubly ionized $4p^4$ states in Kr clusters relative to the corresponding free Kr atom states [9,20].

State	$\Delta(b-a)$ (eV)	$\Delta(s-a)$ (eV)
$4p^45p$	−1.0	−0.7
$4p^46p$	−2.8	−2.1
$4p^47p$	−3.6	−2.7
$4p^48p$	−4.0	
$4p^4$	−4.3	−3.2

atomic final states (obtained for the same-orbital excitation) to lower binding energy [6,17]. The energy of the cluster valence-ionized final states reached via resonant Auger decay decreases due to the polarization screening effect—analogous to the core-ionized states. The *atomic* Kr resonant Auger spectra have been recorded and identified in Ref. [10]. The Kr cluster spectra measured at photon energies corresponding to the maxima of the $\mathbf{B}_1$, $\mathbf{S}_1$, **C**, and **C**′ features (Fig. 1) are shown in Fig. 2. To our advantage the necessary information on the $4p^46p$ final states in clusters is contained in the spectra produced as a result of the $3d_{5/2}{}^{-1}5p$ excitations at the known surface $\mathbf{S}_1$ and bulk $\mathbf{B}_1$ absorption peaks. In the case of the $3d\rightarrow5p$ excitation $4p^46p$ states are efficiently populated by the shakeup process [10], and are expected in the cluster spectra resulting from the excitations at **C** and **C**′.

In the RA spectrum (Fig. 2, $\mathbf{B}_1$) excited at the bulk $\mathbf{B}_1$ absorption peak, the features between 30.9 and 29.4 eV, as well as the peaks at 31.6, 31.9, and 33.9 eV, are well explained by atomic $4p^4({}^3P,{}^1D,{}^1S)5p$ states shifted for −1.0 eV. The rest of the peaks can be successfully accounted for by shifting the atomic $4p^46p$ features by ≈−2.8 eV. This leads to the corresponding cluster bulk features at 32.2, 33.5, and at 35.7 eV. The intensities of the transitions to the $4p^45p$ final states and to the shakeup $4p^46p$ final states are of similar magnitude, indicating an enhanced shakeup probability compared to the atomic case (20%, [10]).

For the RA spectrum (Fig. 2, $\mathbf{S}_1$) excited at the surface $\mathbf{S}_1$ absorption feature, a similar picture holds supposing a −0.6 eV binding-energy shift for the $4p^45p$ states, and a −2.1 eV binding-energy shift for the $4p^46p$ state. The shifts of the $4p^46p$ states for both bulk and surface atoms are much larger than those of the $4p^45p$ states.

In analogy to the bulk-to-surface relative position in the $3d^{-1}5p$ cluster state, it is tempting to fit the RA spectrum, excited at the **C** absorption peak (which is ≈0.2 eV lower than the closest neighbor **C**′), with the $4p^46p$ *surface* states using −2.1 eV shift (Fig. 2, **C**). However, in this case there would be no spectral features left to be explained by the $4p^47p$ states, for which a contribution of at least 50% due to shakeup is expected [10]. Therefore, the **C** peak (Fig. 1) cannot be attributed to surface-atom excitations. The alternative is to account for the RA spectrum (Fig. 2, **C**) excited at the absorption feature **C** with the $4p^46p$ *bulk* states, whose positions are already known from the spectrum excited at the absorption feature $\mathbf{B}_1$. The remaining peaks can be explained by $4p^47p$ bulk states, which are broadened and shifted by −3.6 eV (Fig. 2) to 32.8, 34.2, and 36.4 eV. (The shakeup probability to the $4p^47p$ states is again enhanced when going from free atoms to clusters). *Conclusion 1:* The **C** peak in the absorption spectrum is due to the $3d_{5/2}{}^{-1}6p$ *bulk* state, redshifted by −0.63 eV from the atomic level.

An attempt to fit the RA spectrum excited at the **C**′ absorption peak with the $4p^46p$ surface states and the accompanying $4p^47p$ shakeup states works well (Fig. 2, **C**′). For the latter, a −2.7 eV shift was found, which is 0.6-eV larger than for the $4p^46p$ surface states. An alternative explanation of the **C**′ spectrum with *bulk* final states fails in the higher-energy part: the intensity around 37.3 eV cannot be due to either $4p^46p$ or $4p^47p$ bulk states, since its separation from the only possible parent candidate atomic $4p^4$ $({}^1S)6p,7p$ states would be too small. *Conclusion 2:* The **C**′ x-ray absorption peak is to a great extent due to the $3d_{5/2}{}^{-1}6p$ states in the *surface* atoms. There are, however, two intense features in the **C**′ spectrum (Fig. 2), at ≈36.8 and ≈34.5 eV, that remain unexplained by the surface hypothesis. A plausible explanation is that the $3d_{5/2}{}^{-1}6p$ *surface* excitation overlaps with the $3d_{5/2}{}^{-1}7p$ *bulk* excitation. Indeed, both **C** and **C**′ maxima in the absorption spectrum change in the same way as the cluster size increases. That should not be the case if the **C**′ peak were a pure surface feature. The observed behavior can be explained consistently if one recollects that the $7p\rightarrow8p$ shakeup process contributes 75% of the intensity to the atomic $3d_{5/2}{}^{-1}7p$ Auger spectrum [10], the most intense lines being at 40.48 and 38.56 eV. The two unidentified cluster peaks are about 4.0 eV lower in binding energy than these atomic states. Such a large shift can only occur for the *bulk* final states.

The reasons for $4p^4np$ $(n\geqslant6)$ cluster shifts increasing with n lies in the fact that the electronic configurations of the higher, singly ionized final states approach that of doubly ionized $4p^4$ states. The latter states are reached after the core *ionization* by $M_{4,5}N_{2,3}N_{2,3}$ normal Auger decay $(3d^{-1}\rightarrow4p^4$ transition). In the resonant Auger decay of krypton clusters the electron remains on a remote orbital, and similarly to the core-excited states should be partly screened by neighboring atoms and weakly influencing the final $4p^4np$ $(n\geqslant6)$ state.

Thus the cluster shifts are expected to be comparable for both types of the final states—for $4p^4np$ and for $4p^4$. The shifts for the latter can be obtained from the normal Auger spectrum of Kr clusters (Fig. 3). For the analysis it has been assumed that in clusters the final, doubly charged valence-ionized states are shifted four times the initial core-ionization shift. This leads to kinetic-energy shifts relative to the atomic normal Auger lines of about three times the cluster core-ionization shift [18,19]. In the present work kinetic-energy shifts of ≈ 3.2 eV for the bulk, and ≈ 2.3 eV for the surface have been obtained from the fit of the cluster normal Auger spectrum (Fig. 3). These values are indeed about three times that of the core-ionized state. Binding-energy shifts of ≈ -4.3 eV for the bulk and ≈ -3.2 eV for the surface relative to the known atomic case [20] were extracted for the $4p^4$ doubly ionized states. These values are the upper limits for the $4p^4np$ ($n \geqslant 6$) excited, singly ionized states, and can be closely approached. A similar evolution of the RA spectra towards the normal Auger spectra has been observed for atoms and molecules [21,22].

As explained above, the **C**′ x-ray absorption peak at 92.12 eV is also due to a bulk level, separated from the related atomic $3d_{5/2}{}^{-1}7p$ core-excited state by -0.94 eV, which is almost as large as the 1.1 eV shift for the core-ionized states. Recalling the two peaks close to 92 eV in the x-ray absorption spectrum of solid Kr [15], one concludes that they correspond to **C** and **C**′ and are of $6p$ and $7p$ nature.

Finally, it is necessary to rule out possible explanations for **C** and **C**′ x-ray absorption peaks as dipole-forbidden transitions. Such transitions were observed in Ar clusters [5,17]. In Ref. [9] an atomic $3d \to 4d$ transition was identified at 92.0 eV, i.e., between the **C** and C′ peaks. However, for Kr clusters most of the final states populated after the resonant excitations at **C** and **C**′ are at higher binding energies than the $3d_{5/2}{}^{-1}4d$ atomic states. Thus, the basic principle would be violated: the energy levels of ionized clusters should be lower in binding energy than the parent atomic levels. Hence, the possibility of **C** and **C**′ being due to the dipole-forbidden transitions in clusters can be rejected. Experimental results and assignments are summarized in Tables I and II.

We conclude that the positions of the related cluster and atomic states, and the energy order of the $3d^{-1}6p, 3d^{-1}7p$ excited states in bulk and surface atoms, are reversed compared to the $3d^{-1}5p$ state. The energy shifts of the higher core-excited states in cluster atoms grow towards the limiting values of the core-ionized states. We explain these experimental findings by a spatial spread of the excited orbitals over the cluster lattice. We demonstrate that, according to the theoretical results [16], the interplay of the two main effects—confinement and polarization—leads to qualitatively different situations. When the excited orbital radius is less than the interatomic distance in clusters ($3d^{-1}5p$ state in Kr), the confinement dominates. If the excited orbital radius exceeds the nearest-neighbor distance ($3d^{-1}np$, $n > 5$ states in Kr), the polarization takes over and the energy-level structure becomes ioniclike.

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