Production of Hollow Atoms by the Excitation of Highly Charged Ions in Interaction with a Metallic Surface

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The capture of many electrons by Ar^{17+} ions, at low velocity, near a metallic surface, has been studied. Multiexcited bound states with many electrons in the outermost shells (hollow atoms) have been observed. The surrounding of an ionic excited core by many outermost electrons greatly decreases the lifetimes of the states. This characteristic decrease explains the main striking features of the relaxation of the ions.

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The behavior of slow, very highly charged ions traveling near a metallic surface has been studied only in the last few years.[1-6] We present in this paper some results obtained with the Ar^{17+} ions delivered, at low velocity, by the 16-GHz electron-cyclotron-resonance source of Grenoble (designed by R. Geller). As shown below, these very highly charged ions capture, in a very short time, a large number of electrons from the target, leading to unusual situations where most of the electrons of the ion are excited into outermost shells (hollow atoms). It is the purpose of this Letter to study the original properties of these multiexcited (hollow) atoms, and the period of time they can survive.

Most of the experiments to date have dealt with the study of the electrons ejected at the time of the interaction of the ions with the surface. In 1985 Donets[3] first studied, at low resolution, the x rays emitted by Ar^{17+} ions impinging on various metallic surfaces. More recently, we repeated this experiment under different conditions.[6,7] We present in Fig. 1 the typical x-ray spectrum observed with a Si(Li) detector when Ar^{17+} ions hit a metallic surface. The large broadening of the lines observed in this spectrum clearly shows that these Ly-α and Ly-β rays come from a very complex array of unresolved lines. We present here a more detailed study of this spectrum with a crystal spectrometer.

With a 20-kV extraction potential, the argon-ion beam is mass and charge analyzed, and Ar^{17+} is selected. The typical available current on the solid silver target is of the order of 10–20 nA (e). The beam reaches the target under normal incidence. The x rays ($2p \rightarrow 1s$ transitions) emitted in flight are observed at 90° to the beam direction with a specially designed crystal spectrometer made of a mosaic graphite flat crystal ($\Delta\alpha = 0.4°$) and located at 150 mm from the target. It focuses the emitted x-ray beam to a point, symmetric to the perpendicular of the crystal surface, on a "backgammon type" position-sensitive detector. The focusing properties of this spectrometer, together with the narrow size of the emitting zone (few tenths of a millimeter depending on the takeoff angle, typically 1°), allow a large solid angle ($\Omega/4\pi = 5\times10^{-6}$) and a good resolution $R \sim 5$ eV. The energy calibration uses the L x rays emitted by the silver target irradiated by a 5-keV auxiliary electron beam.

We present in Fig. 2 the $(1s)(2p) \rightarrow (1s)^2$ spectrum observed with the crystal spectrometer. This spectrum exhibits eight well separated lines, of comparable intensities, whose energies correspond to the well-known $2p \rightarrow 1s$ transitions in ions having n L spectator electrons, $1 \leq n \leq 8$ (labeled KL^n). The exact energies of these lines, which were measured with an accuracy of ~ 2 eV, are compared with Bhalla's calculations,[8] our detailed Dirac-Fock calculations,[9] and previously known

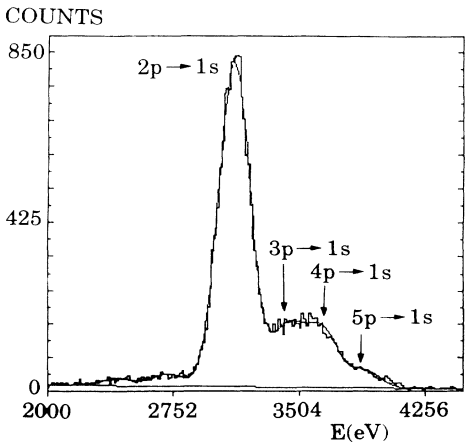

FIG. 1. Overall spectrum observed with a Si(Li) detector (arrows refer to $np \rightarrow 1s$ in heliumlike ions).

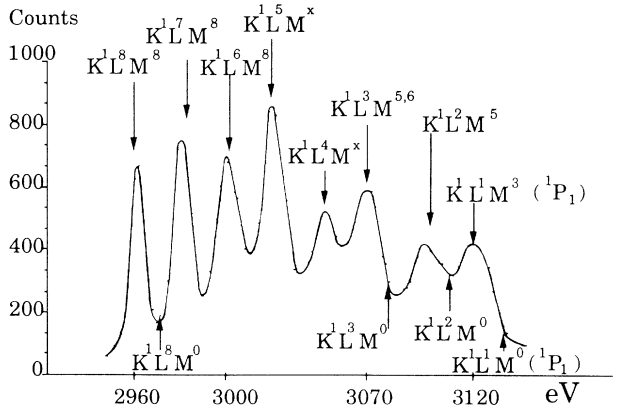

FIG. 2. $(1s)(2p) \rightarrow (1s)^2$ spectrum observed with Ar^{17+} ions impinging on a Ag target. The energy axis has no linear dependence (Bragg law).

values[10] (Table I), in order to determine the number of M spectator electrons present at the time of the radiative decay [the energy of a KL^n line increases with the number of M electrons, from 5.5 eV per M electron for heliumlike ions ($n=1$) to ~ 2 eV for atoms with a closed M shell ($n=8$)].[7,8]

The energies of the four KL^n lines with $1 \leq n \leq 4$ correspond to ions whose M shell is incompletely filled. Their widths are roughly twice the instrumental width which implies some fluctuation in the number of M electrons. This series of lines, of known energies, beginning with that of the ions having only one L electron [heliumlike $(1s)(2p)\,^1P_1$ core] and few M electrons, ends with ions having four L electrons and many M electrons (the $^3P_1$ core of the KL^1 state, which has a much longer lifetime than that of $^1P_1$, cannot be observed). The four KL^n lines with $5 \leq n \leq 8$ exhibit similar shapes. The energies and the widths of the last three lines ($5 < n \leq 8$) fit exactly with those of ions having a closed M shell ($K^1L^nM^8$). By extrapolating known values from other elements, it is very likely that the other one, KL^5, also belongs to ions with a closed M shell.[7,8]

The overall Lyman-α,β,γ spectrum observed with a Si(Li) detector (see Fig. 1) provides additional information on the outermost-shell population. As pointed out in Ref. 7, the Lyman-β,γ lines are roughly 4 times larger than in a neutral atom, which means that a larger number of surrounding outermost electrons are present, in addition to the M electrons, at the time of the decay. (A detailed analysis of this spectrum will be presented in a more extended paper.[9]) These considered atomic species thus have many electrons in the outermost shells and a large number of inner-shell vacancies.

The description of the interaction of Ar^{17+} ions with metallic surfaces, proposed by Donets,[3] is based on the extrapolation of the model used for very slow, singly ionized ions with surfaces. The electrons are supposed to be extracted from the metal, via charge-exchange processes, to be captured by the ion. A straightforward extension of the resonant-neutralization model[11] leads to the hypothesis that many electrons, from the metal conduction band, are captured into the high Rydberg states of the ion ($n \sim 20$–30), at relatively large distances from the surface ($25 < s < 50$ Å).[12,13] These very excited states are then supposed to decay, via a cascade of Auger transitions, by steps of $\Delta n \sim 3$–5 (energy conservation law), to fill up the innermost shells of the ion. At the end of the cascade the filling of the K shell may proceed via the emission of the observed K x rays.

In order to check the validity of this model and to explain the results presented above, we have calculated the Auger rates for some specific decay channels of these multiexcited states (Table II), assuming that these electrons are really captured and that these states are really stationary states. As shown in Table II, the shortest lifetimes for the *first* step of the Auger cascade (i.e., those corresponding to initial s configurations) are always longer than $\sim 10^{-15}$ s when all allowed decay channel rates are summed up. These lifetimes, for the first step of the cascade, are then longer or comparable to the time the ions need to reach the surface from the point where they begin to extract the electrons ($4\times10^{-15} < t < 2\times10^{-14}$ s in Donets and the present experiments). It is then very unlikely that the x rays are emitted by the ions prior to reaching the surface and that these weak (stationary?) states may actually survive when the ions

TABLE I. Energy of the measured $2p \rightarrow 1s$ lines (in eV) presented in Fig. 2 [heliumlike: one more M electron (e_M) $\rightarrow$ 5.5 eV; closed M shell: one less $e_M \rightarrow$ 2–3 eV].

Incompletely filled M shell				Closed-M-shell configuration ($8e_M$)		
Line	Energy (eV)	Number of M electrons		Line	Energy (eV)	
KL^1 ($^1P_1$)	3122	3	$E=3122$ [a,b]	KL^5	3020	[$Ka_{6,7}$ (interpol.: 3018)[a,c]]
KL^2	3098	5	$E=3096$ [a,b]	KL^6	2998	[$Ka_{4,5}$ sat. (interpol.: 2997)[c]]
KL^3	3066	5–6	$E=3066$ [b]	KL^7	2977	[$Ka_{3,4}$ sat.: 2976[c]]
KL^4	3046	...		KL^8	2957	[Ka_1 (neutral: 2957)[c]]

[a]Reference 8.
[b]Reference 9.
[c]Reference 10.

TABLE II. Some typical Auger rates A, in 10^{12} s^{-1}, for three-electron ions (first two) and thirteen-electron ions (last two). Calculations for many other configurations always lead to Auger rates $< 10^{13}$ s^{-1}.

Decay channel	A
$(1s)^1(23s)^2\,{}^1S_0 \rightarrow (1s)^1(16s)^1\,{}^3S_1$	0.13
$(1s)^1(10s)^2\,{}^1S_0 \rightarrow (1s)^1(7s)^1\,{}^3S_1$	3.0
$(1s)^1\cdots(20s)^2(21s)^2\cdots(25s)^2\,{}^1S_0$ $\rightarrow (1s)^1\cdots(17s)^2(21s)^2\cdots(25s)^2\,{}^3S_1$	1.9
$(1s)^1\cdots(10s)^2(11s)^2\cdots(15s)^2\,{}^1S_0$ $\rightarrow (1s)^1\cdots(8s)^1(11s)^2\cdots(15s)^2\,{}^3S_1$	13.9

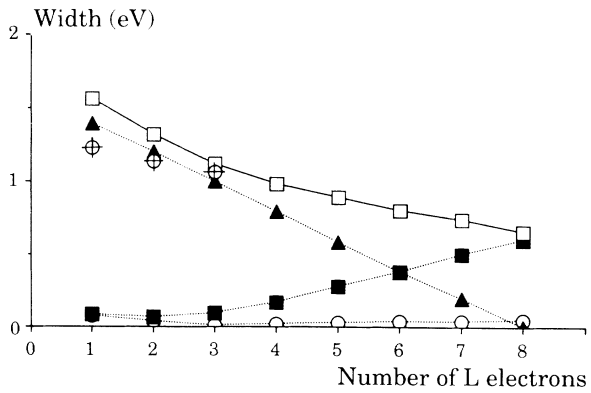

FIG. 3. (■) $\Gamma_{L\rightarrow K}$: ($K\alpha$+Auger KLL) from Bhalla (Ref. 8). (▲) Γ_{LMM}: statistical scaling law (Ref. 16) for 8 M electrons (the value for $n_L=7$ is 0.2 eV) (Ref. 17). The KL^1, KL^2, and KL^3 states have, respectively (see Fig. 2), 3, 5, and 6 M electrons instead of 8. The corresponding points deduced from the statistical model are shown as ⊕. (○) Γ_K: partial width of $K\alpha$ decay. (□) $\Gamma_{\rm tot}$: $\Gamma_{LMM}+\Gamma_{L\rightarrow K}$. The lines are drawn to guide the eye.

touch the surface. Moreover, at the considered velocities the adiabatic model cannot apply to the *electrons of the conduction band* whose velocity is comparable to that of the ion (e.g., for a typical kinetic energy of the conduction-band electron of 5 eV).

Much closer to the surface, electron capture may occur with *bound* electrons of the target, e.g., in the N ($56 < B_N < 95$ eV) or M ($367 < B_M < 712$ eV) shells of silver. In such cases, according to the resonant-neutralization model, the electrons of the target whose energies fit with those of the M and N shells of Ag are captured in the $3 \leq n < 7$ shells of the argon ions at distances of the order of 0.5 to 3 a.u. While entering the first atomic layer the largest realistic distance of interaction must be smaller than half that of the interatomic distance, i.e., ~2.5 a.u. The capture cross sections with such ions are so large ($\sigma \sim 10^{-14}$ cm^{-2}) that many electrons must be captured at the same time in the M, N, and O shells of the ions, in the first atomic layers of the target (i.e., an atomic superficial density of few 3×10^{15} cm^{-2}), leading to the formation of these hollow stems. This is what is observed in Fig. 2: The M shell is very rapidly filled up, lines KL^1M^3, KL^2M^5,... (not taking into account the outermost electrons), while the transitions filling the L (and K) shells are much slower.

In these ions, the simultaneous presence of K and L holes opens up two decay channels whose transition probabilities vary dramatically in a very short time:

(i) The filling of the K hole mainly proceeds through the emission of KLL Auger electrons, or, with a lower probability (~12%), through the emission of $K\alpha$ lines. While the fluorescence yield is roughly independent of the number of L electrons, as demonstrated by Bhalla[8] (except in the case of the first two states with $n_L=1$ and $n_L=2$), the total $L\rightarrow K$ transition rate strongly depends on the L shell population. This leads to a $L\rightarrow K$ transition rate increasing with the number of L electrons, from 0.07 eV/$\hbar$, when only one $2p$ electron is present,[14] to 0.68 eV/$\hbar$ for closed L and M shells (see Fig. 3).[15]

(ii) The filling of the L holes mainly proceeds through Auger transitions involving M or N electrons. According to the Larkins statistical model,[16] the LMM Auger transition rate is a linearly decreasing function of the L electron number and increases with the number of M electrons. This transition rate, which is of the order of 0.2 eV/$\hbar$ (Ref. 17) in the case of singly ionized argon ions, may reach values larger than 1 eV/$\hbar$ with one or two L electrons (see Fig. 3).

The total decay rate of any $K^1L^xM^y(N,O,\ldots)^z$ stationary state of the ion, which is equal to the sum of the $L\rightarrow K$ and $M,N,\ldots\rightarrow L$ decay rates, ranges, as shown in Fig. 3, between 1.2 and 0.7 eV/$\hbar$. This leads to the three following conclusions.

(i) The lifetimes of the ions at the very first steps of the cascade, e.g., $K^1L^1M^yN^z$ states, are strongly reduced with respect to those of heliumlike ions (K^1L^1). When a heliumlike ion is surrounded by a large number of M ($N,\ldots$) electrons, a new deexcitation channel is opened: the filling of the L shell via LMM Auger transitions (not taken into account in Bhalla's calculations). There is then a competition in the filling of the K shell (via $K\alpha$ or KLL Auger) and the filling of the L shell (via, e.g., LMM Auger). When simultaneously many M ($N,\ldots$) electrons and many L holes are available, the LMM Auger channel dominates the filling of the K shell by at least a factor of 20 [$\Gamma=0.07$ eV for heliumlike $(1s)(2p)\,{}^1P_1\rightarrow(2s)^2\,{}^1S_0$ state;[14] $\Gamma\sim1.4$ eV when the ion is surrounded by eight M electrons]. When considering states with more M and N electrons[9] this enhancement factor can reach values up to 50 ($\Gamma\sim2$-3 eV).

(ii) As shown in Fig. 3, the decrease of the Γ_{LMM} partial width and the increase of $\Gamma_{L\rightarrow K}$ with the number of L electrons lead to a relatively constant total width ($0.7 < \Gamma < 1.2$ eV) for any state of the cascade filling up the L shell. The filling up of the L shell then proceeds via eight steps of roughly constant lifetimes. Since the fluorescence yield is always very small ($\omega\sim2\%$-4%),

this explains why all KL^n lines appear and have roughly constant intensities (Fig. 2). This long series of transitions for filling up the L shell thus extends the survival of the K hole over a relatively long period of time.

(iii) The lifetime of each of the KL^nM^m states is of the order of $(6 \pm 2) \times 10^{-16}$ s. At the considered ion velocity (1.2×10^6 m s^{-1}) the mean length of a trajectory for the filling of one L hole is equal to 7 ± 2.5 Å. Thus, the KL^n lines constitute some time markers of the cascade or "boundary marks" along the ion trajectory inside the solid.

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