PHYSICAL REVIEW A VOLUME 54, NUMBER 5 NOVEMBER 1996

Decay of hollow atoms above and below a surface

J.-P. Briand,[1] G. Giardino,[1] G. Borsoni,[1] M. Froment,[2] M. Eddrief,[3] C. Sébenne,[3] S. Bardin,[4] and D. Schneider,[4] J. Jin,[5] H. Khemliche,[5] Z. Xie,[5] and M. Prior[5]

[1]*Laboratoire de Physique Atomique et Nucléaire, ERS CNRS 112, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France*

[2]*Laboratoire des Liquides et Electrochimie, UPR CNRS 0015, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France*

[3]*Laboratoire de Physique des Solides, ERS CNRS 113, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France*

[4]*Lawrence Livermore National Laboratory, L-421, P.O. Box 808, Livermore, California 94550*

[5]*Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720*

(Received 13 May 1996)

We present some experiments which demonstrate definitively that the filling of the L shell of argon hollow atoms formed below a surface proceeds, like those formed above a surface, through a cascade of eight *spontaneous* transitions. This result means that the hollow atoms' clock property may be used in both cases to study continuously the approach and penetration of an ion onto a surface as it is experimentally shown. [S1050-2947(96)02510-3]

PACS number(s): 79.20.Rf, 32.30.Rj, 31.50.+w

A recent publication [1] reported experiments which demonstrated the production of fully inverted, excited states of atoms (termed ''hollow atoms'') formed during the interaction of slow, highly charged ions with surfaces. In that case, highly excited states of argon in which electrons filled the M and N shells leaving the K [2] and L shells empty were observed (up to ten inner shell vacancies). More recently hollow atoms have been observed in plasmas produced inside electron cyclotron resonance (ECR) ion sources [3] and by lasers [4].

The removal of all electrons from an inner atomic shell was first observed and studied in the 1970s [5] where double K vacancy states were formed by nuclear excitation or photoionization and led to a sequence of two fast radiative transitions: the hypersatellite-satellite cascade. The double K-vacancy states have also been observed recently in photoexcited lithium (formation of doubly or triply excited states) [6,7]. Hollow atoms, i.e., atoms having a large number of inner vacancies, are now currently prepared in slow ion-surface interactions by filling the outermost shells of, e.g., a fully stripped ion [1,8–13].

Above a surface the electrons are captured, for energetic reasons, at large distances in Rydberg states. Below the surface capture occurs at much closer distances into lower excited states. There are then two different types of hollow atoms that can be observed during the interaction of highly charged ions with surfaces.

As discussed in previous papers [1,14,15] the filling of the eight holes of the L shell of the hollow atom may be used as an atomic internal clock to study the ion-surface interactions. The filling of the L shell of hollow atoms formed *above* a surface takes place through a long cascade of Auger transitions. Below the surface (or at surface) capture occurs at much closer distances and fills excited states of the ions of much lower n states. For light ions, such as N^{6+}, and below the surface, Folkerts and Morgenstern [10] demonstrated that the L shell is partly filled by cascades from the M shell and partly via a direct collisional capture process that they named side feeding. For higher Z ions, like argon, and below a surface, the M shell is filled two or three times faster than the L shell, as experimentally demonstrated [1,14]. While the stepwise filling of the eight L holes has also been experimentally demonstrated [2] one cannot exclude, *a priori*, that a (small) part ($\leqslant$30%) of the L holes is also filled by a side feeding process. The geometrical cross section for capturing electrons into the M and N shells of the ion being, *a priori*, much larger than into the L shell ($\sigma \sim n^4$), this process was first considered for argon ions as negligible compared with the very fast LMM Auger transitions (cascade feeding).

The aim of the first experiment presented in this paper (study of the K and L x rays of Ar^{17+} and Ar^{16+}) is to demonstrate that this L side feeding process may be definitively neglected and, as for above surface hollow atoms, the L shell is mainly filled by an Auger cascade from outer shells. The clock property of the hollow atoms may then be used in the same way for both types of hollow atoms. This property, valid for all types of hollow atoms, is illustrated in a second experiment where the proportion of above and below the surface hollow atoms has been dramatically changed by varying the ion velocity to a very large extent.

The experiments were carried out at two laboratories. At the Lawrence Berkeley National Laboratory, K and L x-ray spectra emitted by Ar^{17+} and Ar^{16+} ions impacting Si-H targets were studied with a low-resolution Si(Li) detector sensitive to x rays down to 200 eV. The 10-keV/q Ar^{17+} ions were produced by the Advanced Electron Cyclotron Resonance (AECR) ion source at the Lawrence Berkeley National Laboratory (LBNL) 88-in. cyclotron. The experiment utilized the joint LBNL-LLNL (Lawrence Livermore National Laboratory) atomic collision physics facilities. In this case we formed, below the surface, hollow atoms having most of their electrons captured in the M and N shells. A second set of experiments was performed in Grenoble on the test ECR ion source of the Laboratoire des Ions Atomes et Agrégats

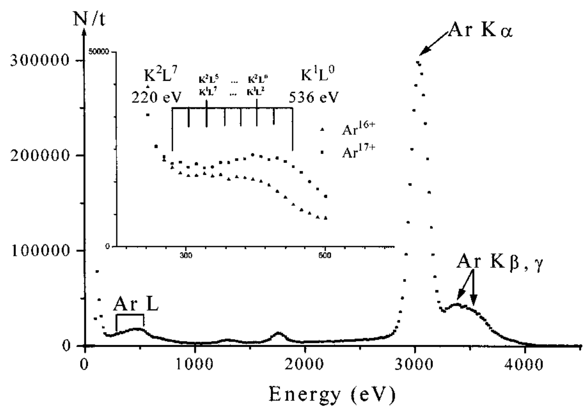

FIG. 1. K and L x-ray spectrum emitted by Ar^{17+} ions of 10 keV/q energy impinging on SiH surfaces and observed with a low-resolution Si(Li) detector. In the upper inset of the figure, a magnification of the L spectrum is presented and compared to the L spectrum of the Ar^{16+} ions impinging on the same surfaces.

(LI2A), where the K x rays were studied with a high-resolution crystal spectrometer. This experiment was carried out at various ion kinetic energies ranging from 2 eV/q up to 10 keV/q (formation of above and below surface hollow atoms). A very flat, well characterized Si surface covered by a single layer of hydrogen, prepared with conventional chemical techniques, was used in both experiments.

Figure 1 shows the K and L x-ray spectra simultaneously observed in the studies at LBNL. The broad $K\alpha$ ''line'' is composed of an array of eight satellite lines ($KL^x, x=1, \ldots, 8$) arising from an $L \rightarrow K$ radiation emitted from ions containing $(x-1)$ spectator electrons. The L x-ray spectrum was observed, also as a very broad ''line,'' which, as in the case of $K\alpha$, is made up of an array of satellite lines arising from $M \rightarrow L$ transitions in the presence of any allowed number of L vacancies. The L x-ray energies range from 220 $(x=7)$ to 536 eV $(x=1)$. The figure also shows a higher-energy broad L x-ray line corresponding to the N(O)$\rightarrow L$ radiative transitions. The approximately flat topped shape of the $M \rightarrow L$ intensity shows that, as for the $K\alpha$ transitions, all the $L^x M \ldots$ satellites are present and hence one observes all possible steps in the L-shell filling process. The most interesting observation from the spectrum of Fig. 1 is the large intensity of the L x rays compared to that of the $K\alpha$ complex $(L/K \geq 12 \pm 2\%)$. This should be compared to the mean fluorescence yields of the K and L shells. The value of the L fluorescence yields for ions having zero to seven L electrons and a certain number of M and N electrons is not as accurately known as that for the K fluorescence yields. The fluorescence yield of the lowest L satellite (one L vacancy and a closed M shell) is experimentally known to be 0.02% [16]. In this case, if the M electrons are not only in the s or p subshells, the L fluorescence yield may be slightly larger. The Auger or radiative transitions corresponding to satellites of the highest energies, i.e., those having many holes in the L shell, are, *a priori*, statistically more intense. The radiative rates are $\sim y \times 2 \times 10^{12}$ s^{-1} (y equals the number of M electrons) [17], whereas the corresponding LMM Auger rates are of the order of 2×10^{15} up to 10^{16} s^{-1} for $3 < y < 8$ [15,18,19]. The fluorescence yields of the L satellites then lie between 0.1% and 0.3%. The K fluorescence yields for all the KL^x satellites have been calculated by Bhalla [20]. They range from 11% $(x=8)$ to 100% $(x=1)$ with a value of $\approx$30% for $(x=5)$, the mean KL^x satellite. Thus, for an equal number of K and L transitions, the ratio of L to K x-ray intensity would be $\approx$1%, i.e., much lower than our experimental value of $12 \pm 2\%$. This means that there are many L transitions for a single K transition (there is only one K vacancy for eight L holes) and that the population of the L shell below the surface follows mainly from Auger cascades from the M shell where the electrons have been captured below the surface (i.e., the L side feeding is negligible). The filling of the L shell of hollow atoms below the surface is then similar to that outside the surface, i.e., through spontaneous Auger cascades from the highly excited states where the electrons are captured in that case.

Figure 1 also shows the comparison between the L x-ray spectra observed with Ar^{16+} and Ar^{17+} impinging on the same target. The most visible difference between the two spectra is a large extension of the intensity towards high energy (about 50 eV) for the Ar^{17+} spectrum relative to that from Ar^{16+}. Since all the L lines of Ar^{17+} are shifted upward about 50 eV by the increased effective nuclear charge, the observed shift suggests that a large number (>30%) of the L x rays is *emitted prior to the filling of the K vacancy* in the case of Ar^{17+}. This observation illustrates the time dependence of the L-shell filling, and is consistent with the observation of a roughly uniform $K\alpha$ satellite intensity distribution (i.e., all L occupation states are observed).

As discussed previously [1,15], the relative intensities of the eight KL^x lines depend only upon the rates at which the outermost shells, collisionally fed, fill the L shell and the L electrons fill the K shell. In an oversimplified view, if the rate of filling of the L shell by the outermost electrons (e.g., $n \geq 3$) is very low compared to the K-filling rate, then as soon as the first electron reaches the L shell, a $K\alpha$ photon may be emitted and the KL^x distribution would peak on the KL^1 component. If, on the other hand, the L-shell filling is very fast compared to the K rate, the KL^x distribution would peak on KL^x satellites with large numbers of L electrons $(x>1)$. The relative intensities of these KL^x lines depend upon the different lifetimes of the states into which the electrons are initially captured. The L-shell filling rates from various outermost shells, previously calculated [1] using the Larkins statistical procedure, have now been accurately cal culated by Desclaux and co-workers [15] and Vaeck and Hansen [18]. These rates, e.g., when the electrons come from the M shell through LMM Auger transitions, are of the order of a few times 10^{16} s^{-1}.

In order to illustrate the use of this atomic clock effect, the x-ray spectrum from Ar^{17+} ions interacting with a Si-H surface has been studied at various energies, i.e., in situations where electron capture occurs into very different n levels. At low collision energies, the hollow atoms are formed outside the surface and, for energetic reasons, high n levels $(n \geq 3)$ are fed. In this case the long series of Auger cascades needed to reach the L shell leads to relatively long lifetimes (slow L-filling rates). At much higher energies, i.e., when the interaction takes place mainly below the surface and where the electrons are captured into the M shell, the L-shell filling rates are much larger and the KL^x distribution is, as observed [1], rather uniform.

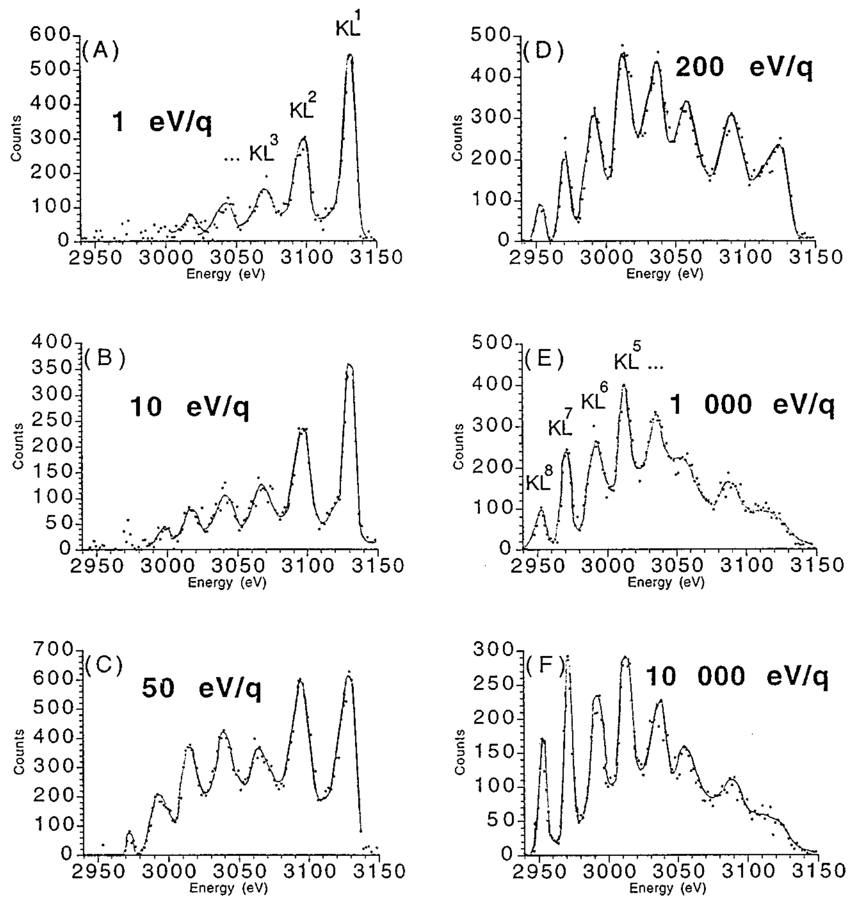

FIG. 2. KL^x satellite spectra observed at high resolution with Ar^{17+} ions of various, imposed energies from 1 up to 10 000 eV/q. [In spectrum (A), the energy of the ions cannot be accurately known due to the image acceleration (or deceleration), which may be as large as a few eV/q.]

The difference in energy between KL^x and KL^{x+1} satellites is of the order of 25 eV and hence is resolvable with a crystal spectrometer of 6-eV resolution, as was used in the Grenoble experiments. Figure 2 presents the array of KL^x satellite lines observed with ions decelerated by varying amounts. The results show the evolution of the spectrum from outside the surface (capture in Rydberg states) to below the surface behavior (capture in M and N shells). Figure 2(F) shows the spectrum observed with ions of 10 keV/q and displays a characteristic below surface array of KL^x satellites [1]. Figures 2(A)–2(E) show the same spectra observed from decelerated ions. The nominal energy of the ions is noted on each spectrum, however, because of acceleration by the image charge, this is inaccurate for the lowest values [Figs. 2(A) and 2(B):1 and 10 eV/q]. In the case presented in Figs. 2(A) and 2(B), the ion cannot penetrate the surface and one observes the characteristic outside decay spectra peaked on KL^1 while Figs. 2(C), 2(D), and 2(E) (50, 200, and 1000 eV/q) show an increasing proportion of the ''at'' or ''below'' surface contribution to the spectrum.

In summary, this work has shown that with third row elements, such as argon, the stepwise decay of hollow atoms formed below a surface constitutes an internal atomic clock of intrinsic properties (i.e., only defined by the ion spectroscopic properties as in the case of ''above'' surface hollow atoms).

This result allows the study of the continuous change of the x-ray spectra emitted by the ions during (i) the approach and touch down of the surface ($0<E<12$ eV/q); (ii) the penetration of the first atomic layer ($12<E<50$ eV/q); (iii) the interaction inside the bulk ($E>50$ eV/q). All three processes have recently been found to be strongly dependent on the nature of the surface [21,22].

The authors express their gratitude to C. Lyneis for his assistance at the LBNL 88-in. cyclotron, and to G. Melin, D. Hitz, and B. Jettkant for their help while working with their Caprice ECR ion source at Grenoble. Work at LBNL received support from the Office of Energy Research, Office of Basic Energy Science, Chemical Science Division, under Contract No. DE-AC03-76SF00098.

[1] J.-P. Briand, L. de Billy, P. Charles, S. Essabaa, P. Briand, R. Geller, J.-P. Desclaux, S. Bliman, and C. Ristori, Phys. Rev. Lett. **65**, 159 (1990).

[2] J. P. Briand, L. de Billy, P. Charles, S. Essabaa, P. Briand, R. Geller, J.-P. Desclaux, S. Bliman, and C. Ristori, Phys. Rev. A **43**, 565 (1991).

[3] J. P. Briand, G. Ban, P. Briand, R. Geller, G. Melin, C. Hill, and H. Haseroth, KVI Report No. 996, 1993 (unpublished).

[4] A. McPherson, R. D. Thompson, A. B. Borlov, M. Boyer, and C. K. Rhodes, Nature (London) **370**, 631 (1994).
[5] J.-P. Briand, P. Chevallier, M. Tavernier, and J.-P. Rozet, Phys. Rev. Lett. **27**, 777 (1971).
[6] A. Müller, G. Hofmann, B. Weissbecker, M. Stenke, K. Tinschert, M. Wagner, and E. Salzborn, Phys. Rev. Lett. **63**, 758 (1989).
[7] L. Kierman, E. T. Kennedy, J. P. Mosnier, J. T. Costello, and B. Sonntag, Phys. Rev. Lett. **72**, 2359 (1994).
[8] F. Meyer, S. H. Oberbury, C. C. Havener, P. A. Zeijlmans van Emmichoven, and D. M. Zehner, Phys. Rev. A **44**, 723 (1991).
[9] J. Burgdörfer, P. Lerner, and F. Meyer, Phys. Rev. A **44**, 5674 (1991).
[10] L. Folkerts and R. Morgenstern, Europhys. Lett. **13**, 377 (1990).
[11] F. Aumayr and HP. Winter, Comments At. Mol. Phys. **29**, 275 (1994).
[12] D. H. Schneider, M. A. Briere, J. M. McDonald, and J. Biersack, Radiat. Eff. Defects Solids **127**, 113 (1993).
[13] R. Köhrbrück, K. Sommer, J. P. Biersack, J. Bleck-Neuhaus, S. Schippers, P. Roncin, D. Lecler, F. Fremont, and N. Stolterfoht, Phys. Rev. A **45**, 4653 (1992).
[14] J.-P. Briand, B. d'Etat-Ban, D. Schmeider, M. A. Briere, V. Decaux, J. W. McDonald, and S. Bardin, Phys. Rev. A **53**, 1 (1996).
[15] B. d'Etat, J.-P. Briand, G. Ban, L. de Billy, J.-P. Desclaux, and P. Briand, Phys. Rev. A **48**, 1098 (1993).
[16] M. O. Krause and J. H. Oliver, J. Phys. Chem. Ref. Data **8**, 329 (1979).
[17] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935).
[18] N. Vaeck and J. Hansen, J. Phys. B **28**, 3523 (1995).
[19] M. H. Chen, B. Crasemann, and H. Mark, At. Data Nucl. Data Tables **24**, 13 (1971).
[20] C. P. Bhalla, Phys. Rev. A **8**, 827 (1973).
[21] J.-P. Briand *et al.* (unpublished).
[22] J.-P. Briand, S. Bardin, D. Schneider, H. Khemliche, J. Jin, and M. Prior (unpublished).