Double K-Vacancy Production in Molybdenum by X-Ray Photoionization

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We report the observation of double K-vacancy production in x-ray photoionization of molybdenum. From these data we deduce the relative probabilities for production of double and single K vacancies by photon impact at 50 keV and report the most precise measure of the ratio of double to single K-vacancy production by photon impact in a heavy atom. That ratio provides an important probe of electron-electron correlations in high-Z atoms where theoretical descriptions must consider those correlations simultaneously with relativity. Our results suggest the need for theoretical treatments to properly deal with such systems.

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With the advent of modern synchrotron radiation sources providing intense, collimated beams of tunable monochromatic x rays, there has been increased interest in the investigation of multielectron processes [1]. Beyond the importance of such processes in understanding electron-electron correlations, they have also been implicated in the production of satellite structures in extended x-ray absorption fine structure (EXAFS) and x-ray absorption near-edge structure (XANES) studies of materials [2,3]. The most basic multielectron process is the complete emptying of an atomic K shell in photoabsorption. In this work we used a tunable synchrotron x-ray source and investigated that process by detecting double K-vacancy production in molybdenum using incident photon energies just below and nearly 10 keV above the double-K ionization threshold.

The double photoionization of helium is the simplest example of such "K-vacating" photoabsorption and has been extensively studied ever since the first reported measurement more than 30 years ago [4]. Because of the single-particle nature of the photon-electron dipole operator [5], double ionization would not occur in the absence of the e-e interaction and thus this process serves as an extremely sensitive probe of electron correlations within atoms. There has been considerable progress both experimentally [6] and theoretically [7] in recent years and workers have now turned to methods of investigating such processes in other systems as a more extensive test of the new theories [8]. Most of that effort is directed toward light, few-electron systems such as H^- and Li^+ because it is generally held that the effects of electron-electron correlations are most pronounced in such systems. This is a consequence of the $1/Z$ falloff in the ratio of the electron-electron to the electron-nucleus interactions with increasing atomic number Z. While that argument is certainly valid with regard to energy eigenvalues, it is not necessarily pertinent to double ionization which is instead sensitive to eigenfunctions. Because double ionization proceeds through the Z-independent e-e interaction, the effect of electron-electron correlations has in fact been found to be *constant* with increasing Z [9] and, consequently, more challenging to treat in high-Z systems where relativistic effects simultaneously become important [10]. Here, we used a relatively simple method to isolate the effects of electron-electron correlations in a heavy atom by the creation of double K-vacancy states in x-ray photoionization and subsequent detection through the observation of the K-hypersatellite transitions as those states relax.

The formation and decay of atoms with empty K shells was first considered by Heisenberg [11] during the early development of quantum mechanics. It then became an important subject in nuclear physics because of the predictions of Migdal [12] and Feinberg [13] of the production of such atomic systems in nuclear α and β decay processes. For $Z > 40$, when K fluorescence yields become large, the predominant decay of such states is through the sequential emission of two K x rays. In 1953, Charpak [14] first observed such x-ray cascades following the electron capture (EC) decay of ^{55}Fe by coincident detection of the x rays in a pair of proportional counters. Since that time, many workers have investigated the production and decay of such hollow atoms in α, β, electron capture, and internal conversion (IT) decays of radioactive nuclei [15].

Briand and his co-workers [16] were the first to point out the large energy shifts (from the normal diagram lines) of the $K^{-2} \rightarrow K^{-1}L^{-1}$ transitions which they termed *hypersatellites* in contrast to the more common satellite transitions when there are multiple vacancies in the upper level of the initial state. Using radioactive sources, several atomic structure aspects of such decays have been investigated including the suppression of the $K_{\alpha 1}$ transition [17], relativistic effects [18], and the importance of electron-electron correlations [9].

While such work has been quite illuminating, it has also been somewhat limited because of the necessity of using radioactive sources. Because of the change in nuclear charge in α, β, and EC decays, shakeup and shakeoff processes dominate the production of double K vacancies with such sources. In contrast, in IT decays, the Coulomb field of the nucleus remains essentially unchanged and, especially near threshold, there can be substantial contributions from correlated electron motions. Unfortunately,

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with IT, the exciting photon (in this case virtual) is of *fixed* energy. Previous attempts to study such systems by photoionization using x-ray tubes have been similarly hampered [19,20] because of the limited photon flux and tunability. Our experiment represents the first direct observation of hypersatellite decays with a tunable x-ray source.

The experiment was performed on the 12BM bending magnet beam line operated by the Basic Energy Sciences Synchrotron Radiation Center (BESSRC) at the Advanced Photon Source (APS). Photon beams of 40.2 and 50 keV were obtained using 3rd order reflections from a Si(111) double-crystal monochromator ($\Delta E/E \simeq 2 \times 10^{-4}$) and then collimated with a set of slits to produce a 1×1 mm^2 beam spot at the target. The intense 1st order radiation was absorbed by a $5/16$-inch aluminum filter leaving primarily 3rd order radiation with slight contamination ($<10\%$) from 4th, 5th, and 7th orders. The lower energy used (40.2 keV) is below the double-K ionization threshold of 40.654 keV calculated with the GRASP2 multiconfiguration Dirac-Fock (MCDF) computer code [21]. However, since the K binding energy is 20 keV [22], this photon energy is 200 eV above the 40-keV threshold for the background process of photoabsorption on one atom followed by electron-impact ionization of another atom by the resulting photoelectron. At the higher energy (50 keV), both processes can contribute. Furthermore, this energy is close to that corresponding to the predicted maximum ($\sim$53 keV) in the double photoionization cross section for He-like Mo [23].

The target consisted of a 25-μg/cm^2 film of natural molybdenum deposited on a 5-μg/cm^2 carbon foil and oriented with the surface at an angle of 30° with respect to the incident beam. Two Si(Li) detectors faced each other and were normal to the beam, lying in the same plane as the beam polarization and the target normal. With this geometry, Compton and Rayleigh scattering were suppressed. The crystal of one detector subtended an angle of $\sim$300 msr while the other crystal subtended $\sim$200 msr for a combined angular efficiency of $\sim$4%. Each detector was covered with a 127-μ Kapton filter to suppress high energy photoelectrons produced by the energetic higher-order components of the beam while transmitting the $\sim$17–20 keV Mo $K_{\alpha,\beta}$ fluorescence with $>$99% probability.

Standard coincidence electronics recorded the energies deposited in each detector and the time difference between the detectors for all coincidence events within 4 μsec. This time window was sufficiently broad to encompass the 3.7 μsec revolution period of the positrons in the storage ring. In addition, 1% of all singles were also recorded.

The region of the energy spectrum in each detector corresponding to K x rays is shown in Fig. 1 for those x rays detected in coincidence with K x rays in the other detector. The open circles in each spectrum correspond to "prompt" coincidences. The "delayed" accidental coincidences are shown as filled triangles (connected by solid lines). The delayed spectrum was determined by averaging over many

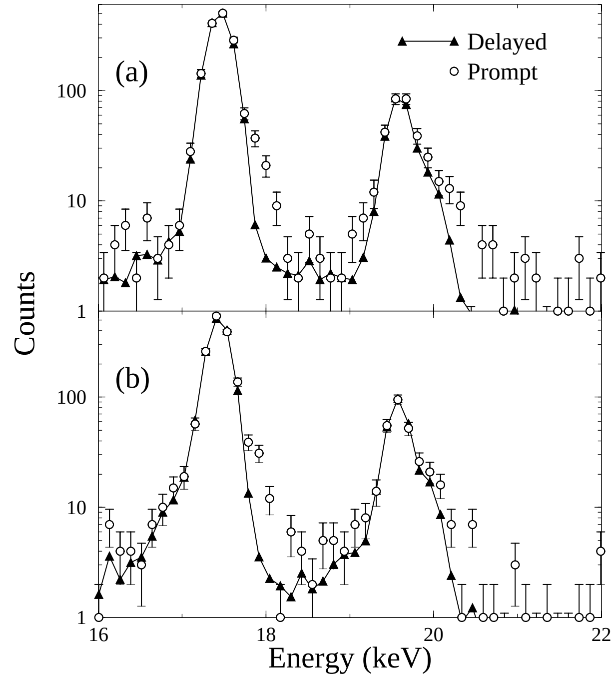

FIG. 1. Energy spectra in each detector for coincidences with $K_{\alpha,\beta}$ x-rays in the other detector. Spectrum for detector "1" is in (a) while that for "2" is in (b). Incident photon energy was 50 keV. Data points (open circles) are for prompt coincidences while the filled triangles connected with the solid line correspond to delayed coincidences.

pulses of the bunched beam and is thus statistically more significant than the prompt with correspondingly smaller errors.

The main features in this region of the spectrum are the K_α and K_β normal diagram lines in Mo at 17.5 and 19.6 keV, respectively. The prompt spectra show a clear excess on the high-energy sides of each peak corresponding to the hypersatellite transitions which, because of the reduced screening in the hollow atom, are systematically shifted up in energy. At the lower subthreshold energy, there was no discernible difference between the prompt and delayed spectra.

The true coincidences were obtained by subtracting the prompt and delayed spectra and one such spectrum is shown in Fig. 2. Because of the low coincidence efficiency ($\sim$4%), the prompt/delayed ratio is near unity and, consequently, the statistical errors resulting from this subtraction are especially large in the regions of the intense diagram lines. To highlight the hypersatellite features, the delayed spectrum for K_α and K_β is shown superimposed and shifted up in energy by 465 and 594 eV, respectively. These are the energy shifts predicted for the hypersatellite transitions by the MCDF calculations of Chen *et al.* [24]. This is merely to guide the eye, as the actual structure of the hypersatellite region is expected to be somewhat modified from that of the diagram lines because of the different energy shifts and intensity ratios of the $K_{\alpha,\beta}$ components

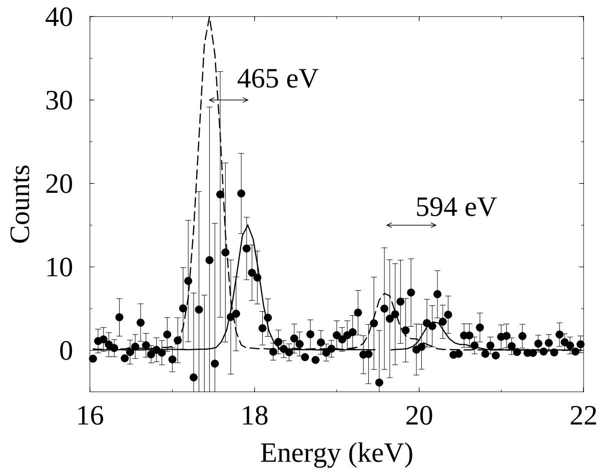

FIG. 2. Energy in detector "1" coincident with K x-rays in detector "2" for true coincidences (i.e., prompt-delayed from Fig. 1a). The delayed peaks have been arbitrarily scaled and superimposed (dashed lines). They have also been shifted up in energy by the theoretical hypersatellite shifts (solid lines) and rescaled to guide the eye.

[25]. To accommodate these shifts, the true coincidences in each detector were determined from such spectra and summed over the regions for K_α^h (17.5–18.4 keV) and K_β^h (19.8–20.7 keV) hypersatellite transitions to yield the quantity I_{2K}. Similar sums were carried out on the singles spectra for the normal $K_{\alpha,\beta}$ diagram lines to yield the integrated intensity I_{1K} for the predominant single-vacancy transitions. These can be related to the corresponding vacancy probabilities through

$$I_{2K} = N_{2K}\,\omega_{2K}\,\omega_{1K}\,\epsilon_1\epsilon_2\,\frac{\Omega_1\Omega_2}{16\pi^2} \qquad (1)$$

and

$$I_{1K} = N_{1K}\,\omega_{1K}\,\frac{\epsilon_1\Omega_1 + \epsilon_2\Omega_2}{4\pi}, \qquad (2)$$

where N_{nK} is the total number of atoms produced with nK vacancies and ω_{nK} is the corresponding fluorescence yield. The absolute detector efficiencies are given by ϵ_i and solid angles by Ω_i. From these relations, the ratio of double/single ionization of the K shell can be expressed as

$$R = \frac{N_{2K}}{N_{1K}} = \frac{4\pi}{\omega_{2K}}\,\frac{I_{2K}}{I_{1K}}\left(\frac{1}{\epsilon_1\Omega_1} + \frac{1}{\epsilon_2\Omega_2}\right). \qquad (3)$$

Although the fluorescence yields for double-K-hole states in light atoms can be substantially higher than those of single-vacancy states, Chen has demonstrated [26] that for $Z > 25$ they are identical to a good approximation. Thus, we assume $\omega_{2K} = \omega_{1K} = 0.764(32)$ in molybdenum [27]. The absolute efficiencies of our detectors have previously been determined to be >99% in this energy range [28]. Combining those measurements with the transmission through the Kapton filters (0.9939) and the Mo target (0.9997) we find an overall mean efficiency of 0.9863 averaged over the hypersatellite region (17.5–20.7 keV). Including these numbers in Eq. (3) with the measured yields, we find $R = 3.4(6) \times 10^{-4}$ for 50 keV incident photon energy.

As discussed earlier, these measurements were carried out in a region where the total energy available to the photoelectrons (~10 keV) is appreciably smaller than the initial photon energy (~50 keV). Furthermore, the photon momentum is small in comparison to the initial momenta of the K electrons in Mo. Thus, the predominant ionization process is photoabsorption and Compton ionization may be neglected. At higher energies, the double photoionization of the K shell has been discussed extensively in a 2-step picture where a fast photoelectron leaves with most of the available energy and then as the core-excited atom relaxes the second electron is shaken up/off leading to the concept of an energy-independent asymptotic limit of the ratio R [29].

This asymptotic ratio is particularly simple to estimate for this experiment because rather than detecting double ionization, we merely detect the presence of two K vacancies. Thus, all final states can be summed over and the usual sum over all states [30] can be reduced to a single term: the probability that the second electron *remains* in the K shell of the relaxed atom [31]. We have performed such an estimate using relativistic wave functions calculated with the GRASP2 code [21] and find this asymptotic ratio to be 3.18×10^{-5} in this case. Because of the relative isolation of K-shell electrons in heavy atoms, this result is not affected very much by the population of outer shell electrons. For example, performing the same calculation with He-like molybdenum yields a value of 3.36×10^{-5}. These values are in good agreement with the Z-scaling laws which have been given by several authors for He-like systems. Using the scaling law suggested by Forrey *et al.* [32] we find a value of 5.1×10^{-5} while the formula suggested by Kornberg and Miraglia [23] yields a value of 4.2×10^{-5}.

It is not surprising that all of these estimates are much smaller (by an order of magnitude) than the experimental result. As discussed earlier, the energies employed in this experiment were well below the asymptotic regime and in fact, using the scaled double photoionization cross sections [23], are very near the peak of that cross section. Hence it is crucial to treat the energy-dependent dynamical double ionization process in a rigorous fashion and this asymptotic value should be viewed only as a lower limit in this regime. At the other extreme, the double ionization of the Mo K shell by impact of 100-MeV α particles has been studied by Boschung *et al.* [33]. Because of the large probability for multiple ionization in a single collision with such strongly ionizing particles, it is well known that such processes lead to substantially more double ionization of the K shell than can be achieved through photoionization.

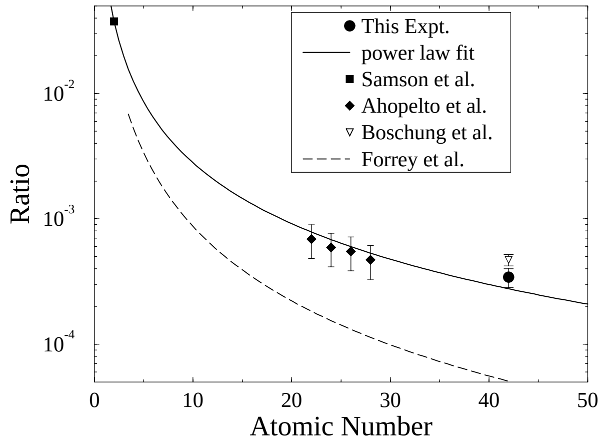

FIG. 3. The ratio of double to single K ionization as a function of atomic number. This experiment (filled circle) is compared to the maximum experimental value in He [35] (filled square), and to the previous photoionization measurements [20] (filled diamonds). Also shown are the power law fit described in text (solid line) and the asymptotic Z-scaling law for double ionization of He-like ions [32] (dashed line). The open triangle shows the α-particle impact result [33] discussed in text.

Those workers reported a value of $4.7(5) \times 10^{-4}$ for that case (see Fig. 3). We also show in Fig. 3 the earlier photoionization results [20] in lighter atoms ($22 \leq Z \leq 28$). Those measurements were also carried out somewhat above threshold but well below the asymptotic regime.

Shake processes lead to a $1/Z^2$ falloff in the double-K ionization probability [34], and that is a predominant characteristic of all of the Z-scaling laws suggested for He-like ions. For comparison, we show in Fig. 3 one of those scaling laws. We have combined our result with the data of Ahopelto *et al.* [20] and the peak ratio in He [35] and best fitted all of these experimental data with a power-law dependence. We find a somewhat weaker $1/Z^{1.61\pm0.05}$ dependence to be more appropriate for these nonasymptotic measurements. While one should not put too much credence in the quantitative value of this exponent, the fit does illustrate the overall trend of the ratio to decrease more slowly than $1/Z^2$.

In conclusion, we have demonstrated that it is now possible, with modern 3rd-generation synchrotron sources, to explore the energy dependence of double K ionization in heavy atoms. Although this problem has been studied extensively in He, little attention has as yet been paid to heavier systems. In particular, the difficulties of simultaneously treating electron-electron correlations and relativity should pose an intriguing challenge.

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