Evolution from Threshold of a Hollow Atom's X-Ray Emission Spectrum: The Cu $K^h\alpha_{1,2}$ Hypersatellites

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The first pure high-resolution photoexcited $K^h\alpha_{1,2}$ hypersatellite spectrum from a hollow Cu atom is measured. Its $K^h\alpha_2$-$K\alpha_1$ shift and the $K^h\alpha_{1,2}$ lines' splitting, widths, and intensity ratio are accurately determined. Such spectra are uniquely suited to study relativistic correlation effects, transition from LS to intermediate coupling, and the Breit-Wigner interaction. The threshold energy and the spectrum's evolution with excitation energy are also measured. The roles of relativity and Breit interaction are explored by comparison with *ab initio* Dirac-Fock calculations.

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The electronic excitation and deexcitation processes of an atom in the isothermal regime, high above the excitation threshold, are separate and consecutive. They have been successfully interpreted within the standard independent-electron, frozen-core, sudden (IFS) approximation. Near threshold, however, the two processes occur on comparable time scales, merging into a single complex process [1]. The slow, adiabatic kinetics renders electronic correlations highly important in this regime, invalidating, in principle, the IFS approximation. X-ray satellite (S) and hypersatellite (HS) spectra, originating in multielectronic transitions, have long been recognized as subjects of choice for studying correlation effects and near threshold phenomena [1,2]. Among these, the $K^h\alpha_{1,2}$ hypersatellites, originating in the $1s^{-2} \rightarrow 1s^{-1}2p^{-1}$ transition, are unique in several respects. The involvement of a K shell renders relativistic effects on the intrashell correlations very important, in contrast with transitions involving higher shells (e.g., conventional $K\alpha_{3,4}$ satellites) where such effects are almost always too small to observe [3]. Furthermore, the HS spectra depend sensitively on the coupling. For example, the $^3P_1$ triplet transition, yielding the $K^h\alpha_1$ line, is dipole forbidden in pure LS and allowed only in intermediate coupling [4]. The $K^h\alpha_2/K^h\alpha_1$ intensity ratio (denote R) is therefore a sensitive probe of the coupling [5]. This is of particular interest in the $3d$ transition elements where the coupling varies strongly with Z from an almost pure LS at $Z \approx 20$ to a pronouncedly intermediate at $Z \approx 30$ [6]. In addition, the Breit-Wigner interaction, the least studied of all atomic interactions, can be investigated almost only in HS spectra [7], where it should strongly influence the transition energies and R [6,8]. Finally, HS are the simplest transitions in a hollow atom [9], i.e., an atom where an entire inner shell is empty, while the outer ones are populated. Such atoms became a focus of interest lately as model systems for atoms very far from stability [10], and for studies of ultrafast dynamics in chemistry, biology, and materials sciences [11]. Kiernan *et al.* [12] recently pioneered the preparation of hollow atoms by the controllable process of photoionization rather than by the ill-controlled electron pickup by highly stripped ions. The very few photoionized hollow atom studies to date address low-Z atoms (mostly He and Li) at excitation energies high above threshold.

Photoexcited HS measurements were strongly inhibited by the low HS intensities [13,14], e.g., $I(K^h\alpha_{1,2})/I(K\alpha_{1,2}) \sim 10^{-4}$ for Cu in the isothermal regime, and much lower near threshold. Heavy-ion-excited HS spectra are much more intense, but also strongly contaminated by additional multielectronic transitions [2,15]. Moreover, the various effects discussed above are reflected in the energies, intensities, and splittings of the individual lines, requiring well-resolved HS spectra. These are obtainable only with crystal spectrometers, whose narrow bandpass means an intrinsically low throughput. For near-threshold studies the exciting x-ray beam need not only be intense but also energy tunable. Because of these extremely challenging experimental requirements, very few *resolved* HS studies were published to date [16]. Even these few deal exclusively with the isothermal regime. The present study provides the first isothermal-regime, high-resolution *pure* Cu $K^h\alpha_{1,2}$ HS spectrum, as well as the first measurement of the HS's evolution from threshold to saturation in any atom.

The measurements were done at the X25 wiggler beam line, NSLS, Brookhaven National Laboratory, with a polycrystalline Cu foil sample. A Si(111) two-crystal monochromator of ~6 eV bandpass provided an incident flux of $\sim 10^{12}$ photons/sec. The emission spectra were recorded by a Johann spectrometer with a spherically bent Si(444) analyzer on a horizontal Rowland circle of 1 m diameter. The high Bragg angle, 72°, yielded a high ($\leq$1 eV) energy resolution. The analyzer's large, 75 mm, diameter provided high throughput. Incidence and detection angles were fixed at 45° to the sample's surface. This 90° geometry and the use of a high-resolution Ge detector greatly reduced the background. The spectrometer's energy was calibrated using a tungsten sample with [17]

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$E_{\mathrm{W}\,L\alpha_2} = 8335.2 \pm 0.1$ eV. The spectra were corrected for sample absorption of both incident and emitted x rays and for the energy variation of the efficiency of the incident beam monitor. Off-peak, and below-threshold backgrounds were measured and subtracted off the data. For further details, see Refs. [3,18].

Figure 1(a) shows the Cu $K^h\alpha_{1,2}$ spectrum, measured at $E_{\mathrm{excitation}} = 20$ keV. A good fit (solid line) is obtained with a single Voigt function (dashed lines) for each emission line. The residuals [Fig. 1(b)] are almost everywhere below $\pm 2\sigma$, where σ is the measurement error. This indicates a pure Lorentzian shape for each HS line and no detectable admixture with spectator transitions having additional holes at higher shells. Such admixture was found to be considerable in heavy-ion-excited HS spectra [9,15] and even in photoexcited Cu $K\alpha_{1,2}$, where $3d^{-1}$ spectator transitions account for ~30% of the intensity [19].

The *correlated* HS lines (CHS, $K^h\alpha\alpha$), originating in a simultaneous *two* electron-one photon $1s^{-2} \rightarrow 2s^{-1}2p^{-1}$ deexcitation, should be over 1000-fold weaker for Cu than the HS lines [20]. Nevertheless, their only published high-resolution study [16] reports intensities (at 16 193 ± 10 and 16 236 ± 10 eV) roughly equal to those of the HS lines. We measured, under identical conditions, the CHS and the HS spectral ranges, using the Si(888) and Si(444) reflections, respectively. For best statistics, white-beam excitation was used yielding 220 counts/sec at the $K^h\alpha_2$ peak, ~50-fold higher than for monochromatic excitation at 20 keV. These scans, shown in Figs. 1(c) and 1(d) on the same intensity scale, fail to detect any CHS lines. In contrast with the previous measurement [16], this places an upper limit of $I(\mathrm{CHS})/I(\mathrm{HS}) < 10^{-3}$ in agreement with theory [20] ($\sim 5 \times 10^{-4}$) and previous low-resolution, heavy-ion-excited measurements for neighboring Ni and Fe [21] ($\sim 2 \times 10^{-4}$).

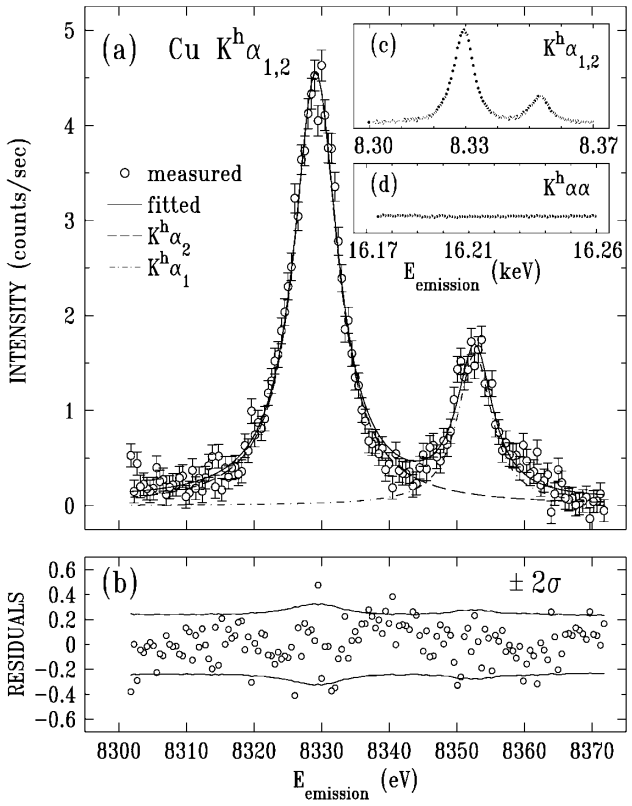

FIG. 1. (a) The measured (circles) and Voigt function fitted (lines) Cu $K^h\alpha_{1,2}$ spectrum measured at $E_{\mathrm{excitation}} = 20$ keV. (b) Fit residuals. (c) and (d) White-beam-excited scans of the hypersatellite and correlated hypersatellite regions. The latter are below the detectability limit.

Table I lists values obtained from the fit in Fig. 1(a). The measured shift $\Delta = E(K^h\alpha_2) - E(K\alpha_1)$ and splitting $\delta = E(K^h\alpha_2) - E(K^h\alpha_1)$ allow for the first time to make a detailed comparison with the different calculations. Nonrelativistic Hartree-Fock and Hartree-Fock-Slater calculations [4] (not listed) overestimate Δ by ~30 eV, indicating the importance of relativistic effects here. Nestor's early relativistic Dirac-Fock (DF) calculation [4] reduces this to ≤10 eV, the remaining discrepancy being assigned to correlation effects [4]. Of the three relativistic calculations in Table I Chen, Crasemann, and Mark's (CCM's) [8] and our [22] multiconfigurational DF ones, which include the Breit interaction, agree better with Δ than does Åberg and Suvanen's (ÅS's) [5], which neglects them in the mixing calculations [8]. This is more pronounced for δ, where both our and CCM's results are within 1σ of the measured value, but ÅS's deviates by $\sim 5\sigma$. The linewidths, $\Gamma_{1,2}$, are ~3 times larger than that of $K\alpha_1$ [20]. The only previously reported Γ_2, MCB's, is significantly lower than ours, possibly due to over correction for their considerably lower resolution, or their ion-bombardment excitation mode. While MCB's empirical prediction [23] agrees

TABLE I. Values obtained from the fit in Fig. 1. Γ is the full width at half maximum. $\Delta = E(K^h\alpha_2)$-$E(K\alpha_1)$, $\delta = E(K^h\alpha_2)$-$E(K^h\alpha_1)$, and $R = I(K^h\alpha_1)/I(K^h\alpha_2)$. The numbers in parentheses are the uncertainties in the last digit of the respective values.

Source	Δ (eV)	δ (eV)	Γ_2 (eV)	Γ_1 (eV)	R
		Experiment			
Present	281.4(3)	23.5(4)	7.7(8)	6.2(8)	0.28(2)
SKS[a]	283.0(30)	21.0(40)			0.27(7)
B[b]	283.0(30)				
MCB[c]			5.3(5)		
		Theory			
Present	281.8	23.7			0.32
CCM[d]	282.2	23.8			0.32
ÅS[e]	280.0	25.6			
MCB[f]			5.7		

[a]Salem, Kumar, and Scott, Ref. [16].
[b]Briand *et al.*, Ref. [4].
[c]Mossé, Chevallier, and Briand, Ref. [26].
[d]Chen, Craseman, and Mark, Ref. [8].
[e]Åberg and Suvanen, Ref. [5].
[f]MCB's [26] semiempirical formula [23].

with our Γ_1, it underestimates our Γ_2 by ~30%. A similar ~50% underestimation was found for the electron-excited HS lines of Na [24].

While the relativistic DF calculations successfully reproduced the measured Δ and δ, they slightly (10–15%) overestimate R, albeit by only $\sim 2\sigma$. This indicates that the intermediate coupling is mostly accounted for properly. Non-relativistic calculations, or those excluding Breit interaction, yield larger, 20%–30%, overestimations [8]. Measurements at both lower- and higher-Z elements are clearly called for to determine the Z evolution of these quantities and for testing the theoretically predicted trend.

The HS intensity evolution from threshold is shown in Fig. 2. Since the Cu $K\alpha_1$ intensity was not directly measurable by our setup, the measured $K^h\alpha_2$ intensity was first divided by the measured W $L\alpha_2$ intensity at each $E_{\text{excitation}}$. The ratio was then multiplied by the calculated W $L\alpha_2$/Cu $K\alpha$ intensity ratio [25]. The resultant values are plotted in Fig. 2(a). The finer scan in Fig. 2(b) yields $E_{\text{threshold}} = 18.352 \pm 0.015$ keV, in excellent agreement with our $Z + 1$ approximated [4] $E^{Z+1}_{\text{threshold}} = 18.345$ keV and, to a lesser extent, with our DF calculated [27] $E^{\text{DF}}_{\text{threshold}} = 18.378$ keV. Since only one of the K electrons is photoionized directly, the second is a shake-off electron excited solely through intrashell correlations. Shake theory [28] predicts, albeit in the sudden limit, a strongly increasing shake-off/shake-up ratio with increasing Z and decreasing n, the shake electron's shell. Trends in recent DF calculations for Ar and Kr [29] indicate <1% shake-*up* contributions in our case ($Z = 29$, $n = 1$). Indeed, the intensity's smooth rise from zero at threshold (Fig. 2), typical of a shake-*off* process, corroborates experimentally this long-standing prediction. The absence of an observable jump, the signature of shake-up [30], in Fig. 2(b) places an experimental upper limit of <3% on shake-up contributions here.

$I(K^h\alpha)/I(K\alpha)$ in Fig. 2(a) does not saturate even at 25 keV, our upper measurement limit. This extended range, by far the largest observed for any line to date, much exceeds the ~1 keV saturation range found for the Cu $K\alpha_{3,4}$ satellites [3]. Both HS and S originate in a $2p \rightarrow 1s$ transition, following a direct photoionization of a single K electron, and a shake-off of an additional single electron. Thus, the different saturation ranges must originate in the different shells of the shake electron and the correspondingly different correlations: KK *intra*shell ones for HS and KL *inter*shell ones for S. Elucidation and quantification of these differences must await currently unavailable adiabatic-regime theoretical calculations of sufficient detail.

Thomas's [31] time-dependent perturbation theory of shake processes near threshold accounted successfully for the measured photoelectron spectra of Ne and Ar [32]. Assuming a convenient *ad hoc* error function time dependence for the Hamiltonian, and a constant velocity for the ejected electron, the Thomas model yields in closed form

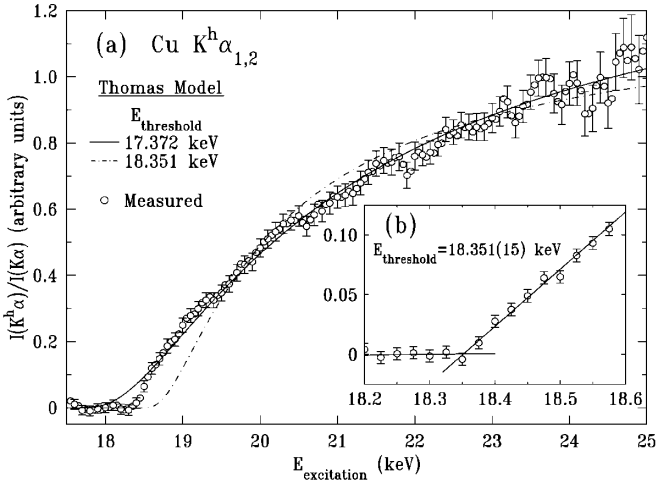

FIG. 2. (a) The measured (circles) relative $K^h\alpha/K\alpha$ intensity ratio's evolution from threshold (~18.352 keV). Fits to the Thomas model (see text) are shown in lines. (b) The near-threshold region.

$$I(K^h\alpha)/I(K\alpha) = I_\infty \exp[-(r^2\Delta E^2)/(15.32\varepsilon)]. \quad (1)$$

Here r is the radius, in Å, of the shake-off shell $1s$. $\varepsilon = E_{\text{excitation}} - E_{\text{threshold}}$ is the excess excitation energy. The shake-up energy, $\Delta E = 9366.3$ eV, is calculated from the $Z + 1$ approximated [4] 9658.6 eV Zn K binding energy [17], reduced by 2% [33]. The best fit [solid line in Fig. 2(a)], yields $r = 0.024$ Å and $E^{\text{Thomas}}_{\text{threshold}} = 17.372$ keV. Although r is close to our DF calculated [22] 0.028 Å, the curve deviates significantly from the measured values near threshold. Also, $E_{\text{threshold}}$ is underestimated by 1 keV. Fixing $E_{\text{threshold}}$ at the measured 18.352 keV (dot-dashed line) yields even larger deviations, and a significantly lower $r = 0.016$ Å. Similar discrepancies were found for Cu $K\alpha_{3,4}$ satellites [3]. Foregoing the *ad hoc* choice of an error function time dependence for the Hamiltonian entails a numerical, rather than a closed form [31], calculation of $I(K^h\alpha)/I(K\alpha)$. It may, however, yield a better agreement with both the HS and the S measurements [3].

Finally, we measured also HS spectra ~350 eV (the closest allowed by the available incident intensity) and ~6 keV above threshold. They were found to be identical within the experimental errors, indicating a fast *shape* saturation for the spectrum near threshold. This was also found for Cu $K\alpha_{3,4}$ satellites [3], where the shape saturates within ≤50 eV of the threshold.

The clean, well-resolved Cu $K^h\alpha_{1,2}$ spectra presented here, allows us for the first time to derive the various physically important quantities to an accuracy sufficient for studying the effects of relativity, intermediate coupling, and Breit interaction. A comparison of the experimental δ, Γ, Δ, and R with calculations indicates that both relativity and the Breit interaction need to be taken into account. However, the former's contribution is significantly higher

than that of the later. R indicates some remaining discrepancy even with the best DF calculations. The HS intensity is found to increase smoothly from threshold, typical of a shake-off process, over the largest energy range measured to date. The Thomas model is found to be at odds with the measured intensity evolution and a more sophisticated theoretical treatment is called for. HS measurements for neighboring $3d$ transition elements, now in progress, will hopefully shed more light on the remaining discrepancies and, in particular, on the coupling variation with Z.

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