X-ray emission from slow highly charged Ar ions interacting with a Ge surface

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We have measured K x-ray spectra and yields from Ar^{17+} ions slowly approaching a single-crystal Ge surface. The yields were measured as a function of the projectile velocity component perpendicular to the surface. From the data a characteristic time of approximately 1 psec was extracted for the in-flight filling above the surface of the Ar K vacancy.

I. INTRODUCTION

Our understanding about the collision dynamics of very slow, highly charged ions approaching a surface is still relatively incomplete. The reason for this is that until recently, no ion sources were available which could produce this ion species. On the other hand, the interaction between slow, highly charged ions and surfaces is interesting because at very low collision energies the ions capture electrons from the surface very efficiently into very-high-n states. The capture process is thought to commence at relatively large distances above the surface [1]. Since the surface offers a huge source of electrons, the ion can assume a highly, multiply excited state with many electrons in high-n states and essentially empty inner shells.

At present very little is known about the decay mechanism of such a highly excited state. It is believed that these states decay predominantly by a large number of Auger cascade transitions before the innermost vacancy is filled [1]. As long as the ion is above the surface, the collision dynamics involve a continuous filling of high-n states by the capture process and a gradual filling of the medium and inner shells by the Auger cascades. The transition time of the Auger cascades is not a well-known quantity at all. Thus, it is not yet clear whether the filling time is dominated by the cascading time or by the time of the last transition directly filling the innermost vacancy. In the former case, the filling of the innermost vacancy may occur with significant delay relative to the time when the capture process started. In the latter case, in contrast, the innermost vacancy would be filled on a much shorter time scale.

Once the ion reaches the inside of the solid, the dynamics of the collision is expected to change significantly. Inside the solid the average internuclear distance between the ion and the crystal atoms is small compared to the distance at which the capture starts above the surface. Therefore, inside the solid strong capture to relatively low-n states takes place [2] and the innermost vacancy can be filled almost instantaneously by a direct transition of a captured electron without going through a large number of Auger cascades.

With the development of powerful ion sources [3–5] it has become possible to study experimentally the interaction between slow, highly charged ions and surfaces. Meyer *et al.* [6] have studied the K-vacancy filling rate in initially H-like ions with $Z=7-9$ interacting with a Au surface by measuring KLL Auger electrons emitted by the ions. They concluded that most of the Auger electrons are emitted by the ion on the path approaching the surface rather than by reflected ions. However, it is not clear whether these results indicate a filling time of the K vacancy shorter then the time of flight above the surface or simply that very few ions are reflected by the surface. De Zwart [7] reported similar results for the emission of L Auger electrons from Ar^{9+} ions interacting with a W surface. From these data Andrä [1] extracted a relatively short L-vacancy filling time of approximately 5×10^{-14} sec. A very similar time for filling the K vacancy in H-like O interacting with a W surface was found by Folkerts and Morgenstern [8], who measured KLL and LMM Auger electrons emitted by the O ions.

The interaction of highly charged ions has also been studied by measuring the x rays emitted by the ions. Donets measured K x-ray spectra from 16-keV Ar^{17+} ions interacting with a Be surface and obtained information about the average L-shell population of the Ar ions at the instant of x-ray emission [9]. Briand *et al.* [2] obtained more detailed information on the L-shell population by measuring Ar $K\alpha$ x rays in high resolution using a crystal spectrometer. Similar experiments were performed in low resolution by Andriamonje *et al.* [10] and Andrä [11] in high resolution by Bonnet *et al.* [12] and Andrä [11] in which evidence for x-ray emission above the surface was obtained. X rays emitted above the surface appear to be particularly interesting because these x rays contain the information about the characteristics of an ion - surface interaction i.e., the population of very-high-n states and the subsequent deexcitation presumably via a large number of cascade transitions. The x rays emitted inside the solid, in contrast, reflect to a larger extent the characteristics of an ion-solid interaction, i.e., the population of lower-n states and the deexcitation probably involving a

smaller number of cascade transitions.

In this work we report on evidence for K x-ray emission above the surface in collisions of Ar^{17+} ions with a Ge target. From the data we deduce a characteristic time for the in-flight filling of the K vacancy initially present in the ion.

II. EXPERIMENT

The experimental set up is schematically shown in Fig. 1. The experiment was performed at the Cryogenic Electron Beam Ion Source CRYEBIS at Kansas State University. The details of the CRYEBIS are described elsewhere [5]. A H-like Ar beam was extracted from the source at 3 kV, corresponding to a projectile energy of 51 keV. Ar^{17+} ions were selected by a 90° magnet. The beam was collimated to a size of less than 1×1 mm^2 and focused by an electrostatic lens onto a single-crystal Ge target. With the target taken out the beam intensity could be monitored with a microchannel plate detector (MCP). The beam intensity was in the order of 10^5 particles/sec averaged over the entire cycle (preparation of Ar^{17+} ions and extraction). The x rays were measured with a Si(Li) detector which viewed the collision region at an angle of 90° with respect to the beam axis. The energy resolution was 180 eV at 5.9 KeV, and a solid angle of 2×10^{-3} sr was subtended. The x-ray count rate was typically 5/sec averaged and 500/sec instantaneously during the extraction period. Each x-ray spectrum was obtained in approximately 1 h. After each run the beam intensity was monitored. No change in beam intensity was observed.

The projectile velocity component perpendicular to the Ge surface v_p was varied by rotating the target by an angle θ with respect to the beam axis. An angular range of 3° (near grazing incidence) to 60° was covered. If the projectile velocity is constant and the surface flat, v_p is related to θ by $v_p=v_0\sin(\theta)$, where v_0 is the magnitude of the total projectile velocity vector. However, there are uncertainties inherent in this assumption. First, to the Ar^{17+} ion, there is strong image potential as it approaches the surface. The energy associated with this potential at a distance of 20 Å above a perfect conductor would be 104 eV, which is almost as large as the vertical translational energy of an ion approaching with constant vector velocity at $\theta=3°$. The actual potential experienced by the ion approaching a Ge surface is not known, but from the above estimate we expect that the assumption of constant vector velocity may not be reliable for the smallest angles.

Second, the surface must be flat. The target is a single Ge crystal, initially flat, but we did not have the facilities to either clean, diagnose, or maintain the surface cleanliness. The target vacuum was typically 5×10^{-7} mbar. This lack of cleanliness would be expected to have two possible effects. First, an average variation in the growth of an oxide layer would wash out the θ dependence of the x-ray yields and spectral shape. However, since the in-flight neutralization begins at a large distance ($\simeq$50 Å) from the surface, the variations in the thickness of an oxide layer would have to be an appreciable fraction of this distance to have a large effect, which we believe unlikely. Second, the presence of a contaminant or oxide layer changes the work function ϕ and thus the neutralization distance d_0. Since the relationship between the two is approximately $d_0=Z/\phi$ (classical barrier model), a factor-of 2 change in ϕ would make a factor-of-2 change in our assigned time scale (see Sec. IV). One must bear this relationship in mind when evaluating the quantitative precision of the time constants we deduce from the data analysis.

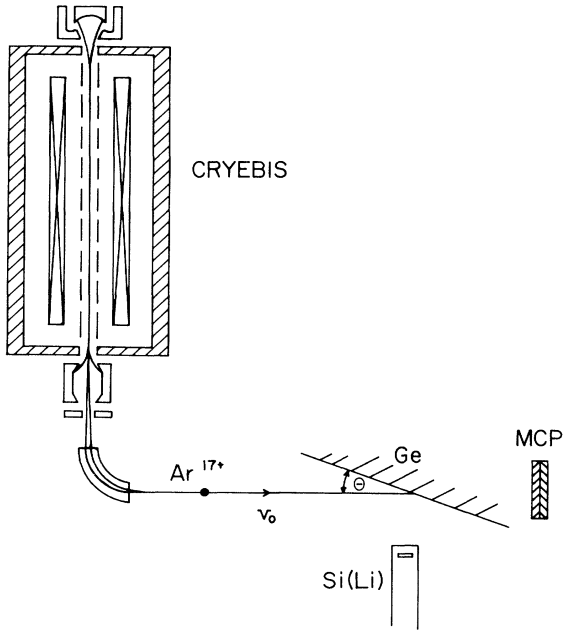

FIG. 1. Schematic experimental setup.

III. DATA ANALYSIS

In Fig. 2 x-ray spectra are shown for angles of 3° (top) and 60° (bottom). For a constant vector velocity these angles correspond to vertical energies of 140 eV and 38.2 keV, respectively. In these spectra the Ar $K\alpha$ line at about 3 keV can be resolved from a second line at around 3.5 keV containing $K\beta$ and higher transitions. Significant differences between the two spectra can be observed. The $K\beta$ line in the 3° spectrum is shifted towards higher energies by about 150 eV with respect to its counterpart in the 60° spectrum. The corresponding shift for the $K\alpha$ line is only about 30 eV. Furthermore, we find that, after normalizing the spectra to beam intensity and data-collection time, the x-ray yield at 3° is increased by about 40% compared to the 60° spectrum. Both the increase in absolute yield and the shift to higher energies is observed to change systematically with decreasing θ. Furthermore, it should be noted that the width of the lines of about 300 eV full width at half maximum (FWHM) for the $K\alpha$ line and 450 eV FWHM for the $K\beta$ line is significantly broader than the expected detector resolution of 130 eV FWHM at 3.1 keV and 140 eV FWHM at 3.5 keV. The 60° spectrum is very similar to

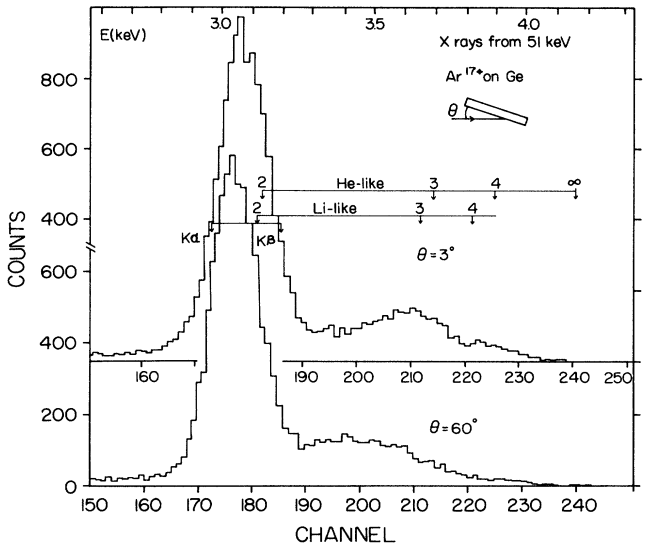

FIG. 2. Total x-ray spectra for angles of 3° (top) and 60° (bottom). The arrows indicate calculated x-ray energies for He-like and Li-like transitions and for various n states. The arrows labeled $K\alpha$ and $K\beta$ show the x-ray energies for neutral Ar.

spectra taken for Ar^{17+} ions interacting with various surfaces at comparable vertical energies [2,9,10,13].

The large width of the x-ray lines suggests that the x rays are emitted from Ar ions with a broad spectrum of L- (and M-) shell populations. The observed shift to higher x-ray energies with decreasing θ means that for small θ the x-ray spectra are dominated by decays of ions with more L vacancies than for large θ. For small θ the centroid energy of the $K\alpha$ line agrees with calculated x-ray energies [14] for configurations with approximately three to four L electrons, depending on the M-shell population. For large θ the centroid energy is consistent with an L population of about five.

This change in the L-shell population is consistent with the physical picture of the ion-surface interaction described above. With decreasing θ, the ions spend an increasing amount of time above the surface within the capture distance. Therefore, with decreasing θ we expect an increasing fraction of the K vacancies to be filled in flight above the surface. Furthermore, above the surface an electron can, in our model, reach the L shell of the ion only by cascading down from a high-n state. At the time an x ray is emitted, we expect a relatively small L-shell population. Once the ion enters the surface, the L shell fills on a time scale comparable to the L-K transition time [2] because of the relatively strong capture directly to low-n states. Therefore, the x-ray spectrum for the x rays emitted inside the solid should show the presence of a large number of L electrons.

Following the above picture, we attempt to identify in our spectra two components, one from radiation in flight, "above surface," and one from radiation "inside" the solid, and to extract their relative strengths as functions of θ. At the largest angle (60°) studied here, the time of flight of the projectile over d_0 is 10^{-14} sec, where d_0 was estimated to be 50Å by calculating the appropriate neutralization rates [1]. This is approximately the same time as the decay time for a $K\alpha$ transition. However, we expect the time for the cascade transitions from a high-n state to the L shell, which above the surface precede the filling of the K vacancy, to be much longer than the $K\alpha$ transition time. We therefore assume that at 60° essentially all x rays are emitted inside the solid, an assumption consistent with the later results of our model. To faciliate evaluation of the model, we fitted the 60° spectrum, which we took to be the "inside" spectrum, with three Gaussian functions for $K\alpha$, $K\beta$, and $K\gamma$ transitions. This spectrum, along with the fit, is shown in Fig. 3 (a). The fitting parameters (x-ray energies and widths) are listed in Table I. The fitted x-ray energies agree with those reported by Donets [9] for 16-keV Ar^{17+} ions colliding with a Be target.

At 3° we expect that x rays emitted both inside the solid and above the surface contribute to the spectra. An "above-surface" spectrum should thus be obtainable by subtracting the "inside" spectrum, i.e., the 60° spectrum, from the 3° spectrum. However, it is not correct to subtract the entire 60° spectrum, because at 3° a significant fraction of the K vacancies initially present in the projectile may be filled above the surface. In that case, the absolute yield of the "inside" spectrum should be smaller at 3° than at 60°. The fraction to be subtracted was determined by making it small enough so that the difference spectrum did not become negative at any energy and big enough that the difference spectrum did not contain the previously determined lines from the "inside" spectrum. With this method we find that the fraction of projectile K vacancies being filled inside the solid has a value of 0.85 at 3°.

In Fig. 3b a difference spectrum between the 3° spectrum and 85% of the 60° spectrum is shown. This "above-surface" spectrum was characterized by fitting it

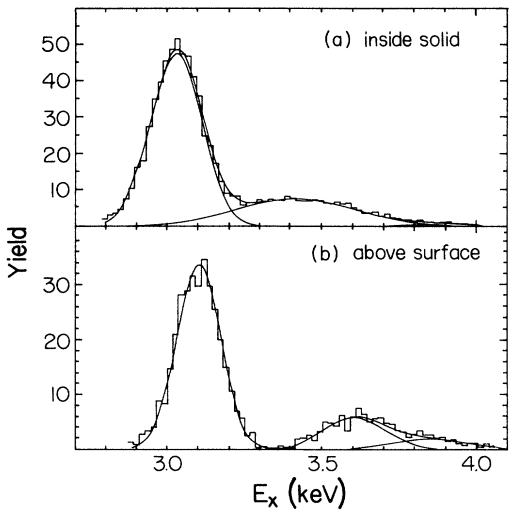

FIG. 3. Spectra of the x rays emitted inside the solid (top) and emitted above the surface (bottom). The curves are a fit with Gaussian functions to the spectra.

TABLE I. Fitting parameters for the inside and above-surface spectra (see text).

Transition	Energy inside solid (eV)	Width inside solid (FWHM) (eV)	Energy above surface (eV)	Width above surface (FWHM) (eV)
$K\alpha$	3025	195	3101	166
$K\beta$	3414	467	3610	231
$K\gamma$			3847	276

with three Gaussian functions for the $K\alpha$, $K\beta$, and $K\gamma$ transitions. For the $K\gamma$ line, the fitting parameters are not very meaningful because of the weak intensity of this line. Here we used the energy and the width of this line as fixed parameters common to the "inside" and "above-surface" spectra. The fitting parameters for both the "inside" and the "above-surface" spectra are listed in Table I. The x-ray energies of the $K\alpha$ and the $K\beta$ lines agree well with averaged theoretical energies for Li-like transitions (3104 and 3618 eV, respectively). A comparison with the "inside" spectrum shows that the average L-shell population must be significantly larger (by about two or three electrons) for the "inside" spectrum. Furthermore, the lines are clearly broader than in the "above-surface" spectrum, which may be taken as an indication that the "inside" spectrum has contributions from a broader range of L-shell populations.

The x-ray yields of the "inside" and "above-surface" fractions can now be obtained for each θ by fitting the normalized total spectra with the line positions and widths of Table I common to all θ. For both the "inside" and "above-surface" lines, the ratios between the areas of the $K\alpha$ and the $K\beta$ lines were kept constant for all θ in this fitting routine. In order to check the internal consistency of our procedure, we performed these fits by allowing the intensities of all five of the contributing (Gaussian) lines listed in Table I to vary, rather than just two parameters corresponding to "inside" and "above-surface" fractions. The results of the five-parameter fit showed that the relative intensities of those lines that made up the "inside" spectrum and of those lines that made up the "above-surface" lines remain approximately constant for all θ. This result gives us confidence that the two-component decomposition of the spectrum is internally consistent.

In Fig. 4 we compare the spectra along with these fits for 3° and 30°. A significant increase in the intensity of the "above-surface" fraction is observed in the 3° spectrum. At the same time the intensity of the "inside" fraction is slightly decreased, even though the effect is not as strong as for the "above-surface" fraction.

IV. RESULTS AND DISCUSSION

In the following we will discuss the x-ray yields obtained from the data analysis described above as a function of the time τ the projectiles spend above the surface after the neutralization process has started. In our model we make the approximation that the neutralization process takes place rapidly at a well-defined distance above the surface, rather than proceeding continuously within a certain distance. With the assumption of constant vector velocity of the beam, τ is then related to θ by

$$\tau = d_0/[\sqrt{(2E/M)}\sin\theta] , \quad (1)$$

where E is the total projectile energy of 51 keV and M is the projectile mass. We take d_0 to be 50 Å [1,2].

In Fig. 5 the total x-ray yield is plotted versus τ. An almost linear increase in the total x-ray yield with increasing τ can be observed. Only the data point at 200 fsec ($\theta = 3°$) deviates significantly from this linear dependence. The reason for this might be that ions are accelerated by the image potential towards the surface, in which case the time of flight would be shorter than 200 fsec. At the longest time the yield has increased by about 40% as compared to the shortest time studied here.

In Fig. 6 the open circles show the $K\alpha$ yield for the "above-surface" fraction. In Fig. 7 the same yields are shown for the $K\beta$ transitions. A sharp increase in the yield of the "above-surface" fraction with increasing time can be observed for both the $K\alpha$ and the $K\beta$ line. The yield of the "inside" fraction (solid symbols), in contrast, slightly decreases with increasing time.

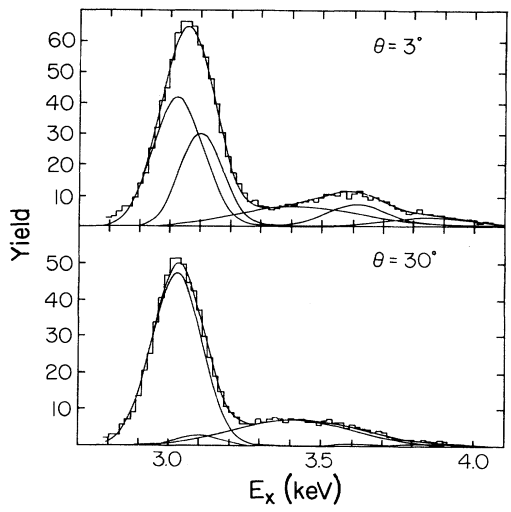

FIG. 4. Total x-ray spectra for angles of 3° (top) and 30° (bottom). The curves are fits with Gaussian functions for the inside and above-surface fractions. For the centroid energies and the widths, the parameters obtained from the fits shown in Fig. 3, which are listed in Table I, were used as fixed parameters for all angles and only the areas were fitted.

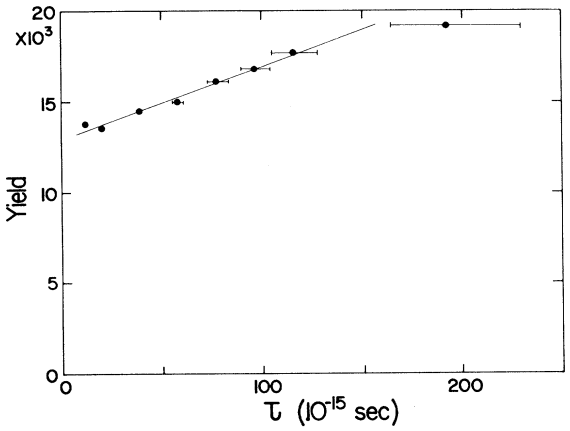

FIG. 5. Total x-ray yield as a function of the time the projectiles spend above the surface (see text). The line is to guide the eye.

These dependences of the x-ray yields are consistent with the general picture of the neutralization process described in the literature [1] and above. As the neutralization process starts above the surface there is a certain probability for an x ray to be emitted above the surface, which is proportional to the time the ion spends above the surface. Consequently, the number of K vacancies which survive this time and reach the solid decreases and so does the yield of the "inside" fraction. It is interesting, however, that the increase in the "above-surface" fraction is much larger than the decrease in the "inside" fraction or, in other words, that the total x-ray yield increases. Since the number of initial K vacancies is constant (one per ion), this means that the fluorescence yield for the "above-surface" fraction must be significantly larger than for the "inside" fraction.

The K x-ray yield per incident Ar ion of the "above-surface" fraction, $Y_a(\tau)$, can be written as

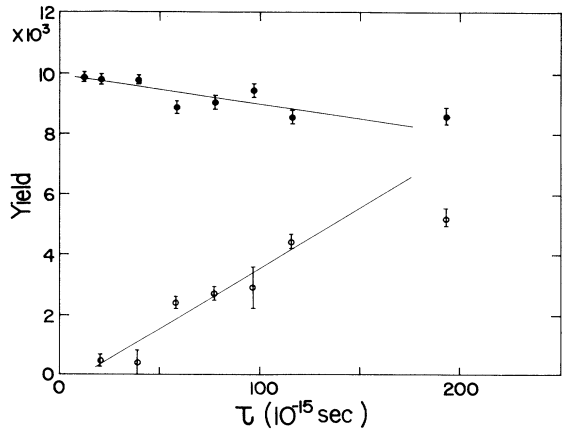

FIG. 6. Same as Fig. 5 for the $K\alpha$ x rays. The solid symbols are the fraction of x rays decaying inside the solid and the open symbols the fraction of x rays decaying above the surface. The lines show linear least-squares fits to the data.

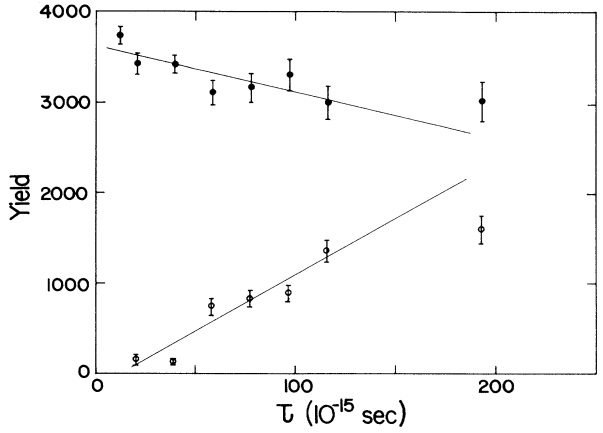

FIG. 7. Same as Fig. 6 for the $K\beta$ x rays.

$$Y_a(\tau)=f_a(\tau)\omega_a \ , \tag{2}$$

where $f_a(\tau)$ is the fraction of initial Ar K vacancies being filled above the surface and ω_a is the fluorescence yield for the "above-surface" fraction. With $f_a(\tau)$ given by

$$f_a(\tau)=(1-e^{\lambda\tau})\simeq\lambda\tau \ , \tag{3}$$

one obtains

$$Y_a(\tau)=\lambda\omega_a\tau \ , \tag{4}$$

where λ is the rate at which electrons fill the K vacancy above the surface. Analogously, the yield for the "inside" fraction is given by

$$Y_i(\tau)=(1-\lambda\tau)\omega_i \ , \tag{5}$$

where ω_i is the fluorescence yield for the "inside" fraction. From Eqs. (4) and (5) one can see that there is a linear dependence of the "inside" and "above-surface" yields on τ. The ratio between the slope and the offset of the straight line for the "inside" fraction gives λ. Furthermore, the ratio between the slopes of the "above-surface" and "inside" fractions yields the ratio of their fluorescence yields R_ω. With the coefficients obtained from a linear least-squares fit to the data of Fig. 6 and 7, we find a characteristic cascading time $\tau_K=1/\lambda$ of 1.0 ± 0.5 psec for the $K\alpha$ x rays and 0.7 ± 0.35 psec for the $K\beta$ x rays. For R_ω a value of 4 ± 2 is found for the $K\alpha$ x rays and 2.4 ± 1.2 for the $K\beta$ x rays. These numbers are also listed in Table II. In these fits the data points at 200 fsec were omitted because of the uncertainty in τ.

According to calculations by Bhalla [14], the fluorescence yield for the $K\alpha$ transition is not very sensitive to the L-shell configuration for populations down to three L

TABLE II. Total cascading time τ and ratio of fluorescence yields between the above-surface and inside fraction R_ω for the $K\alpha$ and $K\beta$ transitions.

Transition	τ (sec)	R_ω
$K\alpha$	0.96×10^{-12}	4.0
$K\beta$	0.71×10^{-12}	2.40

electrons. For smaller L-shell populations the fluorescence yield strongly increases and depends sensitively on the specific configuration. Those configurations, which have a lifetime longer than the projectiles time of flight above the surface (2×10^{-13} sec at 3°), will not decay above the surface, and, once the ion reaches the solid, a new configuration (with a larger L population) is formed within a very short time. Therefore, the "above-surface" fluorescence yield for these configurations is essentially zero. Assuming a statistical distribution of the L-shell electrons and taking the fluorescence yields of configurations with lifetimes longer than 2×10^{-13} sec to be zero, we calculate the fluorescence yield for Li-like states to be approximately 0.25. For He-like states we find, with the same assumptions, an average fluorescence yield of 0.38. With these numbers,and assuming equal contributions from one-L-electron and two-L-electron states to the "above-surface" spectrum, we expect ω_a to be near 0.31. For the "inside" spectrum (three or four L electrons), we find ω_i to be approximately 0.15. This yields $R_\omega \simeq 2$, which is within the error of the value determined experimentally.

The cascading time obtained in this work is significantly longer than the one Andrä [1] extracted from the data of de Zwart [7] (5×10^{-14} sec) for Ar^{9+} + W in which L Auger electrons were detected. Of course, the system studied by de Zwart is different both in the projectile and the target from the system studied in the present work. The charge state can affect both the n distribution of the states into which the electrons are captured and the cascade mechanism in the deexcitation process. For high-n states the binding energy of an Ar^{9+} ion is significantly smaller than for an Ar^{17+} ion. Therefore, electrons may be resonantly captured into lower-n states in the case of the Ar^{9+} ions. Since the transition rates for a single cascade step are expected to strongly decrease with increasing n, this might explain the shorter total cascading time found for Ar^{9+} ions. Furthermore, the n distribution is also determined by the work function ϕ of the target material. For Ge and W, ϕ is almost identical (4.4 eV). However, due to the uncertainty of the cleanliness of the surface used in this work, the actual work function is not known. For a smaller work function the n distribution would be shifted to lower n's, which would decrease the total cascading time. Finally, it should also be kept in mind that the work function also determines the distance at which the neutralization process starts, which introduces an uncertainty in the time scale assigned to the angle of the surface rotation. Therefore, both the difference in charge state and in the target material in de Zwart's and our work are possible explanations for the different time constants.

V. CONCLUSIONS

We have studied K x-ray emission from initially H-like Ar ions interacting with a single-crystal Ge target. With decreasing vertical projectile velocities an increasing fraction of x rays emitted above the surface was observed. These x rays are emitted from states with L-shell populations of approximately one to two, whereas the L-shell population of the states decaying inside the solid is larger by about two electrons. From the data we have extracted a characteristic time for the above-surface filling of the K shell of approximately one psec. Uncertainties attend this number from both the model and the experiment. The model is quite simplified, assumes constant vector velocity of the beam, and neglects possible ion reflections from the surface. In the experiment a controlled clean surface could not be established or maintained. Nevertheless, we believe that the approximate value of the extracted filling time constant is significant. This time is orders of magnitudes longer than the K x-ray transition time for an excited state typically populated in a high-energy ion-atom collision. The reason for this anomalously long time is that, in highly charged ions slowly approaching a surface, very highly excited states are populated with a large number of electrons in very-high-n states and (except for the initial electrons) empty inner shells. Such states decay predominantly via a large number of slow cascading steps, and it is this cascading which dominates the filling time.

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