RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 47, NUMBER 2 FEBRUARY 1993

Measurement of autoionization rates for electron emission above a metal surface

J. Das and R. Morgenstern

Kernfysisch Versneller Instituut, University of Groningen, Zernikelaan 25, 9747 AA Groningen, The Netherlands

(Received 23 October 1992)

We present K Auger spectra arising from collisions of N^{6+} ions with a Ni(110) target for different kinetic energies and observation angles. The bulk of the electrons is ascribed to emission below the surface. At very low collision velocities ($v_\perp \leq 10^{-2}$ a.u.) we find a pronounced contribution from electrons emitted prior to impact. The velocity dependence of the above-surface component is used for the experimental determination of the time scales involved in electron emission above the surface. Comparison with theoretical estimates is also presented.

PACS number(s): 34.90+q, 79.20Nc

Neutralization processes that occur during highly charged ion-surface collisions result in the emission of large numbers of electrons. These electrons are characteristic of the neutralization dynamics and provide an insight into the interaction mechanism between highly charged ions and metal surfaces. According to the current scenario, a multiply charged ion approaching a surface is rapidly neutralized by electron capture from the surface. This capture proceeds mainly via resonant neutralization into high-lying states of the projectile, resulting in multiply excited neutral atoms with empty or sparsely populated inner shells—the so-called "hollow" atoms. The deexcitation of these hollow atoms proceeds at first via a cascade of autoionization (AI) processes [1]. However, this sequential Auger decay of multiply excited states is much too slow to allow for a complete relaxation of the projectile to the ground state before it hits the surface. A significant fraction of inner-shell vacancies is therefore carried into the surface and is filled only after the projectile has suffered close encounters with the target atoms [2, 3]. An important parameter, for the validity of this scenario, is the time involved in the Auger cascade above the surface. Although there exist theoretical estimates [4, 5] for these Auger rates there have been no direct experimental measurements so far. In this paper we present a direct determination of the time scales involved during electron emission above the surface.

We have shown in a previous publication [3] that the K Auger electrons emitted during collisions of $N^{q+}(q=6,7)$ with a Ni(110) target arise predominantly from beneath the surface. At very low projectile velocities ($v_\perp \leq 10^{-2}$ a.u.) the K Auger spectra also contain contributions from processes that take place above the surface [2, 6, 7]. Here we present electron spectra arising from collisions of N^{6+} with Ni(110) where the contributions from above-surface and subsurface electrons can be clearly resolved. The high resolution of our electron spectra allows the precise determination of the characteristics of the above-surface peak. By measuring the intensity of this peak as a function of the collision velocity we have been able to experimentally determine the time required for the multiply excited "hollow" atom to decay to the ground state prior to impact.

We have also measured the Doppler shift at different observation angles for both the above-surface and subsurface components of the electron spectra. Electrons emitted above the surface show the characteristic shift associated with electrons that are emitted from the moving projectile before it has undergone appreciable deviation from its initial trajectory. However, the subsurface electrons show Doppler shifts that are different from this characteristic value. This further emphasizes the difference in the spatial origin of the two components of the K Auger spectra.

The electron spectra were measured in a ultrahigh-vacuum μ-metal collision chamber with a base pressure below 2×10^{-8} Pa. 60 keV N^{6+} beams were extracted from the Kernfysisch Versneller Instituut Electron Cyclotron Resonance ion source [8] and then transported to the experimental setup. Floating the complete apparatus on a positive voltage allowed us to decelerate the ion beam from the ECR source to the desired collision energy. The target was a Ni(110) crystal which was sputter cleaned with Ar ions prior to measurement. The electron detector was a 180° spherical electrostatic analyzer equipped with a channeltron and rotatable over a large range of detection angles. The energy resolution of the analyzer is $5 \times 10^{-3}E$ full width at half maximum (FWHM) and its acceptance at the center of the target is $11.2 \times 10^{-8}E$ (sr eV), with E being the energy of the detected electrons in eV. A more detailed description of the apparatus is presented elsewhere [9].

Figure 1 shows a K Auger spectrum measured for 2 keV N^{6+} ions colliding with a Ni(110) target at an incidence angle of 5°. The narrow peak on the low-energy side is assigned to electrons that are emitted above the surface while the remainder of the electron spectrum is due to subsurface electrons. The width of the above-surface peak is much narrower than the subsurface component of the K Auger spectra. The narrow width is an indication that only a small number of initial states contribute to this peak, whereas the subsurface peak contains contributions from a large range of initial states with different M- and L-shell populations [5]. The en-

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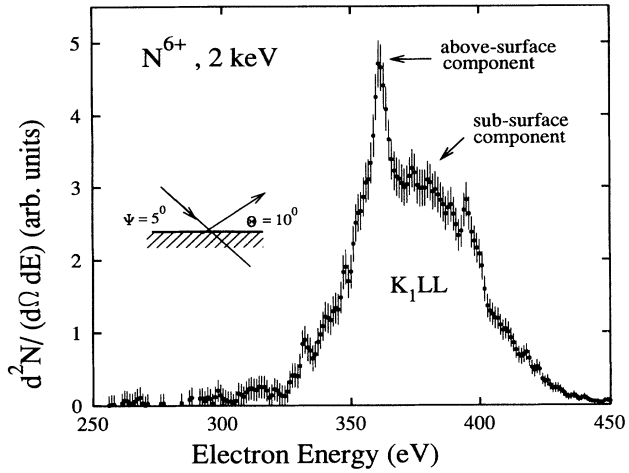

FIG. 1. Background subtracted K Auger spectra arising from collisions of N^{6+} with a Ni(110) target.

ergy position of the above-surface peak is indicative of a sparsely populated L shell [5, 6, 10]. The actual transition energy depends on the exact distribution of the electrons in the different projectile levels and it is difficult to extract the correct configuration from the experimental spectrum. However, it can definitely be said that the main contributions to the above-surface peak are from configurations with only two electrons in the L shell. This is consistent with the fact that, above the surface, the L shell is filled via the AI cascade and the long time scale of the cascade makes a large L shell population unlikely.

The intensity of the above-surface component is critically dependent on the interaction time available to the projectile before colliding with the target surface. Lowering the collision velocity increases the fraction of K vacancies that are filled above the surface, thereby increasing the intensity of the above-surface peak. This enhancement does not, however, continue indefinitely but the intensity of the peak saturates at a certain fraction of the total K Auger intensity. This saturation effect is a direct consequence of the acceleration of the projectile by its image charge [11], which imposes an intrinsic lower bound to the collision velocity. Figure 2 shows the change in the intensity of the above-surface component as the interaction time prior to impact is varied. This velocity dependence of the intensity can be used to directly estimate the time scales involved during electron emission above the surface. For the sake of simplicity the filling of the K vacancy above the surface is described in terms of three states—the initial state where the projectile is a hollow atom with an empty L shell, the intermediate state with at least two electrons in the L shell, and finally the state where the K vacancy has been filled. The population numbers of these states, respectively n_i, n_L and n_K, are determined by the transition rates between them. The following set of coupled differential equations has to be solved in order to determine the time evolution of the population numbers:

$$\frac{dn_i}{dt} = -\Gamma_{\rm av} n_i, \tag{1a}$$

$$\frac{dn_L}{dt} = \Gamma_{\rm av} n_i - \Gamma_k n_L, \tag{1b}$$

$$\frac{dn_K}{dt} = \Gamma_k n_L, \tag{1c}$$

where Γ_k is the Auger transition rate of the KLL process. $\Gamma_{\rm av}$ is the average L-shell filling rate and is a measure of the time required by the AI cascade to populate the L shell to the minimum level required for a KLL process. The assumption here is that, above the surface, there is no direct electron transfer into the inner shells. The ratio R of the intensity, $I_{\rm AS}$, of the above-surface component to the the total K Auger intensity $I_{\rm tot}$ can then be written as

$$R = \frac{I_{\rm as}}{I_{\rm tot}} = 1 + \frac{\Gamma_k}{\Gamma_{\rm av} - \Gamma_k} e^{-\Gamma_{\rm av} t} - \frac{\Gamma_{\rm av}}{\Gamma_{\rm av} - \Gamma_k} e^{-\Gamma_k t}, \tag{2}$$

where t is the total interaction time above the surface. In terms of the perpendicular velocity $v_\perp$ of the projectile, Eq. (2) can be written as

$$R = 1 + \frac{\Gamma_k}{\Gamma_{\rm av} - \Gamma_k} e^{-\frac{\Gamma_{\rm av} d}{v_\perp}} - \frac{\Gamma_{\rm av}}{\Gamma_{\rm av} - \Gamma_k} e^{-\frac{\Gamma_k d}{v_\perp}}, \tag{3}$$

where d is the distance from the surface where the Auger cascade is initiated. In order to extract the transition rates from Eq. (3) we need to know the exact energy gain $E_{\rm im}$ due to the image acceleration and the distance d. Winter [11] has experimentally determined $E_{\rm im}$ and for a projectile with initial charge state $q = 6$, $E_{im} = 17$ eV. Simulations performed by Burgdörfer and co-workers [4, 12] using the classical overbarrier model show that for N^{6+} the image acceleration is switched off at a distance of 13 a.u. from the surface due to a complete neutralization of the projectile. It should be noted that this distance is different from the characteristic distance for the onset of electron capture. In the case of N^{6+} the first electrons

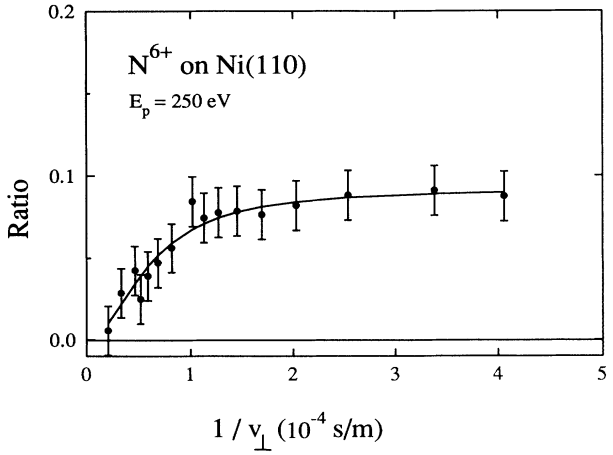

FIG. 2. Ratio of the intensity of the above-surface component and the total K Auger intensity as a function of the vertical velocity $v_\perp$. The primary energy E_p of the beam was 250 eV and the velocity was changed by adjusting the angle of incidence on the surface.

are captured when the projectile is at a distance of 19.1 a.u. from the surface but a reduced image acceleration continues until its effective charge goes to zero. The solid curve in Fig. 2 is a fit to data points using Eq. (3) with $\Gamma_{av}d$ and $\Gamma_k d$ as free parameters. The above-mentioned value for the energy gain due to image acceleration has been used as an input. It is clear from Fig. 2 that this simple picture reproduces the general trend of the data points rather well. The fit results in $\Gamma_k d = 1.3 \times 10^4$ m/s and $\Gamma_{av}d = 4.5 \times 10^3$ m/s. In order to extract the actual decay rates we have assumed that the Auger cascade starts at an intermediate distance between the point of first electron capture and the point where the image acceleration is switched off. Using $d = 16$ a.u. we have $\Gamma_{av} = 5 \times 10^{12}$ s^{-1} and $\Gamma_k = 1.5 \times 10^{13}$ s^{-1}. The result for Γ_{av} is in agreement with theoretical estimates [4] that require time scales of the order of 10^{-12} to 10^{-13} s for the completion of the AI cascade. It should be noted that the experimentally determined value for Γ_k is lower than the value of the same $\Gamma(= 3.4 \times 10^{14}$ s$^{-1})$ determined for subsurface Auger processes [3]. We ascribe this difference to the different L shell populations during electron emission above and below the surface. Calculations performed by Hansen, Schraa, and Vaeck [5] show that the average transition rate of configurations with two L-shell electrons is 2.6×10^{13} s^{-1}, while that of configurations with six electrons in the L shell is 1.7×10^{14} s^{-1}. This is consistent with the fact that the measured value for Γ_k is lower in the case of above-surface processes where the L shell is sparsely populated.

Measurement of the Doppler shift of the Auger electrons allows one to probe the emitter velocity at the time of electron emission. Previously we have reported [3] that the subsurface electrons show Doppler shifts that are not consistent with the original projectile velocity. This was taken to be an indication that interactions with the target atoms lead to a change in the projectile velocity, resulting in the measured deviations. If this is indeed true, then electrons that are emitted prior to collision with the surface should show no such deviation. Figure 3 shows the Doppler-shift measurements for both the above-surface and subsurface components of the K Auger electrons. The solid curve is a calculation of the Doppler shift, assuming that the electrons are emitted while the projectile is still in its initial trajectory. The dashed curve in the lower part of Fig. 3 is a least-squares fit to the measured data with the energy of the projectile as a free parameter. The fit results in an energy of 1.5 keV, which is clearly lower than the initial value of 2 keV. Figure 3 clearly demonstrates that the above-surface electrons show the characteristic Doppler shift associated with 2 keV N^{6+} projectiles, in contrast to the behavior of the subsurface component.

In conclusion it can be said that the experimental results and the predictions of Eq. (3) are in reasonable agreement with each other. The simple scenario used to derive Eq. (3) is a good approximation of the AI cascade and allows the direct determination of the time scales involved during electron emission above the surface. The measured Auger rates indicate that the L shell is sparsely populated during electron emission above the surface. The average L-shell filling rate is long compared to the time ($\approx 10^{-14}$ s) available to the projectile before it collides with the surface and results in only a small fraction of the K vacancies being filled above the surface. This is consistent with the fact that the measured electron spectrum consists mainly of electrons coming from below the surface.

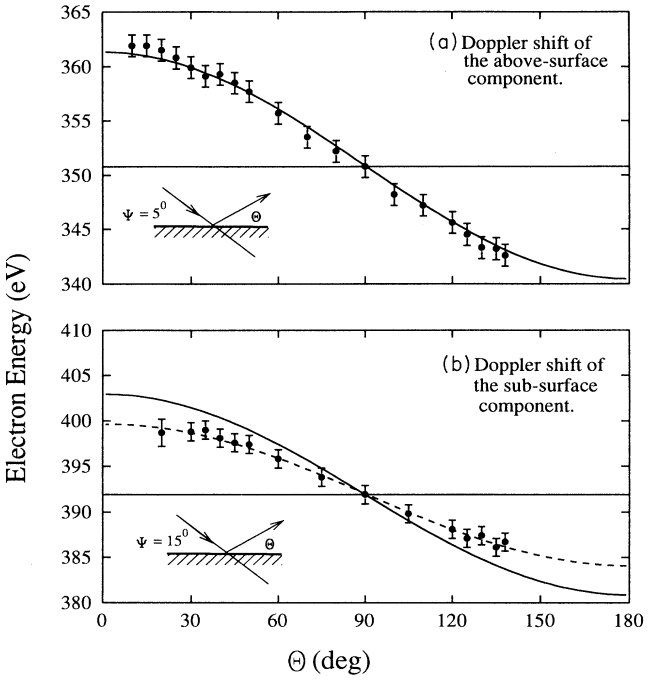

FIG. 3. (a) Position of the centroid of the above-surface component of the K_1LL peak in N^{6+} as a function of the detection angle θ. (b) Position of the half maximum at the high-energy side of the subsurface component of the K_1LL peak in N^{6+} as a function of the detection angle θ. The solid curves are a calculation of the Doppler shift, assuming the decay occurs while the projectile is still in its initial trajectory while the dashed curve is a least-squares fit to the measured data with the energy of the projectile as a free parameter.

We would like to thank J. Eilander, R. Kremers, and J. Sijbring for their excellent technical support. This work is part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie" (FOM) with financial support from the "Nederlandse Organisatie voor Wetenschappelijk Onderzoek" (NWO).

[1] U. A. Arifov, E. S. Mukhamadiev, and E. S. Parilis, Zh. Tekh. Fiz. **43**, 181 (1973) [Sov. Phys. Tech. Phys. **18**, 118 (1973)].

[2] F. W. Meyer, S. H. Overbury, C. C. Havener, P. A. Zeijlmans van Emmichoven, and D. M. Zehner, Phys. Rev. Lett. **67**, 723 (1991).

[3] J. Das, L. Folkerts, and R. Morgenstern, Phys. Rev. A **45**, 4669 (1992).

[4] J. Burgdörfer, P. Lerner, and F. W. Meyer, Phys. Rev. A **44**, 5674 (1991); F. W. Meyer, S. H. Overbury, C. C. Havener, P. A. Zeijmans van Emmichoven, J. Burdörfer, and D. M. Zehner, *ibid.* **44**, 7214 (1991).
[5] J. E. Hansen, O. Schraa, and N. Vaeck, Phys. Scr. **T36**, 1 (1992).
[6] H. J. Andrä, A. Simionovici, T. Lamy, A. Brenac, G. Lamboley, J. J. Bonet, A. Fleury, M. Bonnefoy, M. Chassevent, S. Andriamonje, and A. Pesnelle, Suppl. Z. Phys. D **21**, S135 (1991).
[7] R. Morgenstern and J. Das, Phys. Scr. (to be published).
[8] A. G. Drentje and J. Sijbring, in Oak Ridge National Laboratory Report No. Conf. 9011136 (unpublished), p.17.
[9] S. T. De Zwart, A. G. Drentje, A. L. Boers, and R. Morgenstern, Surf. Sci. **217**, 298 (1989).
[10] J. Das and R. Morgenstern, in *Atomic Physics of Highly Charged Ions, Manhattan, Kansas, 1992*, Proceedings of the Sixth International Conference on the Physics of Highly Charged Ions, edited by C. L. Cocke and M. Stöckli (AIP, New York, in press).
[11] H. Winter, Europhys. Lett. **18**, 207 (1992).
[12] J. Burgdörfer and F. W. Meyer, Phys. Rev. A (to be published).