$M_{2,3}$ NN Auger emission of K excited with low-energy Ar⁺ and K⁺ projectiles

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We have measured energy distributions of $M_{2,3}$ NN Auger electrons of K produced during low-energy $Ar⁺$ and $K⁺$ bombardment of K-implanted surfaces. The spectra present bandlike and atomiclike components. We have assigned the atomiclike peak to reflected and/or sputtered K atoms in the autoionizing state KL3s²3p⁵4s² (²P) decaying to K⁺. We have not observed any evidence of excitation of autoionizing states of Ar,

Thc Auger electron emission from a solid surface bombarded with noble-gas ions has been studied extensively during the last years.¹⁻⁷ The main points of interest have been the relative importance of different mechanisms responsible for inner-shell excitation and the identification of the features in the electron-energy spectra. Most of these studies have dealt with light metals (especially Mg and Al), and, despite some controversies still remaining, a fairly good consensus on both points has been reached.

Studies of the Auger electron emission of the third-row elements are more scarce. Some authors⁸ have reported derivative spectra⁹ of the elements between Ti and Ge, obtained by bombardment with energetic noble-gas ions (20-200 keV). The use of these derivative spectra allows an easy identification of the peaks, but at the cost of losing spectroscopic details due to poor energy resolution.

In this paper we present a preliminary study of the K Auger emission from K-implanted Be, Mg, Al, and Cu surfaces bombarded with low-energy (0.15 keV) Ar⁺ and K⁺ ions. When bombarding with the $Ar⁺$ projectiles, we have also searched for the existence of autoionizing lines of Ar.

The experiments were performed under ultrahigh-vacuum conditions ($\sim 10^{-10}$ Torr). The K⁺ beam was produced with a thoroughly outgassed K source and focused with an Einzel lens. Typical current densities during the K implantation were on the order of tenths of a μ A/cm², but when recording the spectra the current density was reduced to a few nA/cm2 to preserve the composition of the sample. The $Ar⁺$ beam was produced by an electron-bombardmenttype ion gun, and mass analyzed with a Mien filter. The $Ar⁺$ current density was also in the range of $nA/cm²$.

The electron energy spectra were taken with a hemispherical electrostatic energy analyzer operating at a constant pass energy of 20 eV and an energy resolution of 0.4 eV.

We used high-purity polycrystalline samples of Be, Mg, Al, and Cu, cleaned by sputtering with low-energy noble-gas ions. All thc samples were implanted with 1-keV K. We recorded spectra of electrons emitted under 1 -keV K⁺ bombardment at different stages of the implantation; the K Auger peak grew linearly with implantation dose until saturation started to set in. After implantation the samples remained clean; only Auger signals from K and the substratum could be observed in spectra excited with 3-keV electrons. The atomic concentrations of the contaminants (oxygen and carbon) were below 1%.

Unless otherwisc stated, our results correspond to saturated K-implanted samples. Nevertheless, one must notice that the surface concentration of K atoms depends on the

matrix properties influencing the implantation (namely sputtering yield, reflection coefficient, ion range distribution, diffusion, etc.), so it can be different for each sample.

I. $K^+ \rightarrow K/Be$, Mg, Al, Cu

Figure ¹ shows spectra taken during bombardment of the K-implanted Mg sample with $K⁺$ projectiles at three different impact energies. In the spectrum corresponding to 1-keV impact energy, the K Auger signal is clearly seen above a background of electrons emitted by other mechan-

FIG. 1. Electron-energy spectra taken during bombardment of the K-implanted Mg sample with K^+ projectiles of 1, 0.6, and 0.2 keV. Counts are normalized to a beam current of 10^{-8} A. In the 1-keV-impact-energy spectrum, the lines separating the Auger structure from the secondary electrons {long-dashed line) and the atomiclike component from the bandlike one {short-dashed line) have been drawn only approximately.

isms. The Auger signal is composed of a narrow atomiclike peak superimposed on a broad structure. Following previous work,⁵⁻⁷ we ascribe these features to K atoms with a $3p$ hole decaying in vacuum (reflected and/or sputtered excited atoms) and inside the solid, respectively. It is observed in Fig. ¹ that the shape of the spectra varies strongly with the impact energy. At low impact energies two notable effects occur: The Auger peak becomes stronger than the lowenergy peak of secondary electrons, and the bandlike feature clearly predominates over the atomiclike peak.

Figure 2 shows spectra taken during 1-keV K^+ bombardment of the K-implanted Be, Al, and Cu samples. These spectra, being similar to each other, are quite different from those taken with the Mg sample. Only the atomiclike peak is apparent above the background of secondary electrons, and its intensity, relative to the background, is very small. In addition, the general shape of these spectra does not change with impact energy.

These surprising differences between the Mg substratum and the Be, Al, and Cu substrata are very probably due to different densities of K atoms at the surfaces of each sample. To go further with the study of this point requires a detailed characterization of the distribution of K atoms, which is outside the scope of this work.

Both the position and width of the atomiclike peak depend very little on projectile energy, in the range 0.2-1 keV. The atomiclike peak in the spectra from the Al substratum has a constant full width at half maximum (FWHM) of 0.75 eV; in the case of the Mg substratum the FWHM decreases slightly from 0.9 eV at 1 keV to 0.6 eV at the lowest projectile energies. The energy position of the atomiclike peak does not change with the impact energy, but

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varies with the implantation dose, shifting to low energies. This is due to the change in the work function from that of the "clean" substratum to that of a K surface, similar to our previous observations¹⁰ for the $L_{2,3}$ MM atomiclike peaks of Mg and Al. Taking into account the work functions of the sample and the spectrometer, we have estimated the energy of the emitted electrons with respect to the vacuum level¹⁰ to be 14.2 eV. We thus assign the atomiclike peak to reflected and/or sputtered K atoms in the autoionizing state¹¹ KL $3s²3p⁵4s²$ (²P) decaying to K⁺.

The dependence of the yield of the atomiclike peak on impact energy is shown in Fig. 3 for Be, Mg, and Al substrata. In the spectra of the Be and Al substrata (Fig. 2) the subtraction of the underlying background is straightforward. In the spectra of the Mg substratum separation of the atomiclike peak from the bandlike feature can only be done approximately as suggested in Fig. 1. Since the surface density of K atoms is unknown at present, we cannot compare absolute yields. Rather, we have normalized the yields at 1 keV impact energy to study their relative energy dependences. The three curves show nearly the same slope and a threshold impact energy for excitation somewhat lower than 200 eV. Kith the Mg substratum, which produces the strongest Auger signal, we have observed excitation down to 150-eV impact energy.

The similar behavior of the three curves in Fig. 3 suggests that, in the three cases, excitation of K results from the same mechanism. There are three kinds of collisions which can lead to excitation of the K atoms: (i) asymmetric collisions between a K atom and a substratum atom, (ii) primary symmetric collisions between a K^+ projectile and an implanted K atom, and (iii) secondary symmetric collisions between a recoiling K atom and an implanted K atom. Since no peak appears while bombarding the "clean" sub-

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FIG. 3. Yield of the atomiclike peak vs the K^+ projectile energy for the Be, Mg, and Al substrata. The yields are normalized at 1 keV.

strata, asymmetric collisions can be disregarded as the source of excitation. The relative importance of the other two types of collisions should vary with the concentration of implanted K^{12} . The spectra taken at different stages of the K implantation show a linear increase of the peak intensity with the implantation dose. This linear dependence indicates that, at least before saturation, excitation occurs preferentially in primary symmetric collisions between a K^+ projectile and an implanted K atom.¹³

The excitation of inner-shell electrons in these slow collisions of heavy particles is well described by the electronpromotion model.¹⁴ In the K-K quasimolecule, the $5f\sigma_{\mu}$ molecular orbital (MO) is strongly promoted near a certain internuclear distance R_c , crossing many empty MO's. It is assumed that whenever the nuclei get closer than R_c , one or both electrons in the $5f\sigma_{\mu}$ MO are transferred to empty $MO's$ creating a $3p$ vacancy in one or both collision partners. As a test of the model we can calculate the threshold impact energy for excitation. Following calculations of potential energy curves of the Ar-Ar (Ref. 15) and K⁺-Ar (Ref. 16) quasimolecules, we derived $R_c \sim 2.5a_0$. With this value and a Thomas-Fermi interaction potential we get a threshold impact energy for excitation of 120 eV, which is in very good agreement with our experiments.

II. $Ar^+ \rightarrow K/Mg$

We have also observed excitation of K during bombardment of the Mg substratum with $Ar⁺$ projectiles with energies ranging from 500 to 5 keV. At the highest impact energies the peak, though very weak, is clearly observed above the background; it decreases with decreasing projectile energy and disappears below the noise in the data at an impact energy ~ 800 eV. There is evidence which suggests that in this case excitation occurs mainly in symmetric collisions between K recoils rather than in asymmetric Ar-K collisions. First, we have also observed excitation of K with Ne⁺ and Kr⁺ projectiles, and second, a large implantation dose is required to detect the peak and afterwards it indose is required to detect the peak and afterwards it increases faster than linearly to saturation.¹⁷ A way to find whether the Ar-K or K-K collisions are responsible for the excitation would be to look at the threshold energy, but this is hindered by the weakness of the signal relative to the

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background of secondary electrons.

Autoionization of Ar in collisions with solids has been reported only for the case of 400-keV Ar⁺ transmitted through thin carbon foils. 18 The excitation of Ar autoionizing states $KL 3s^2 3p^4 n 1n' 1'$ could be expected, at the energies used in this work, from the similarity of the Ar-K system to the Ne-Na system, where strong excitation of Ne autoionizing states $K2s^22p^4n1n'1'$ is observed.¹⁰ The strong promotion of the two electrons in the $5f\sigma$ MO of the Ar-K quasimolecule would lead to the formation of one or two vacancies in the $3p$ level of Ar; reflected Ar projectiles with two $3p$ vacancies could then capture two electrons to Rydberg levels forming autoionizing states.¹⁹ Nevertheless, in the range of projectile energy between 0.5 and 4 keV, we did not observe any evidence of autoionization of Ar.

We have verified that the collision kinematics are similar for the Ar-K and Ne-Na pairs. Thus the absence of autoionizing lines of Ar must be related to the electron dynamics. There are two possibilities: (a) $3p$ electrons of Ar are not promoted as predicted by the electron-promotion model, or (b) excitation of the $3p$ electrons of Ar takes place, but formation or decay of the autoionizing states is quenched by some mechanism. The first possibility is unlikely, since electron promotion does occur in the gas-phase K^+ -Ar collisions and in the collision of two K atoms in a solid. The second possibility is more probable, but we do not know at present which particular aspect of the Arsurface interaction, absent or irrelevant in the Ne-surface interaction, is responsible for the quenching of the autoionization of Ar.

In summary, we have presented a preliminary study of the Auger electron spectra from collisions of Ar^+ and K^+ projectiles with different K-implanted surfaces. The spectra show a peak corresponding to the Auger decay of K atoms with a $3p$ hole. The shape and intensity of this peak depend on the kind of projectile and substratum; the understanding of this latter dependence probably requires a detailed characterization of the surface and near-surface concentration of K atoms, which has not been made in this work. We think that a study of the shape of the Auger peak, as a function of the concentration and depth distribution of the implanted atoms, would enlighten the knowledge of the relative role of the atomiclike and bandlike components and serve to test models of the collision cascade.

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