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Role of *d* screening in ion-excited electron emission from Ca

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We report an analysis of the electron emission spectrum from Ca metal excited by rare-gas ion bombardment recorded at high-energy resolution. Energy considerations, assisted by electron-energy-loss measurements, indicate that the electron emission from Ca is dominated by the decay of neutral excited atoms from $3p^5 3d 4s^2$ states. The spectrum is explained in terms of initial $3p$ bombardment induced ionization followed by $3d$ neutralization as a result of d electron screening involving electrons from the conduction band in the solid. On emerging from the surface most Ca atoms are in the lowest $3p^5 3d 4s^2$ multiplets (^3P and ^3F) leading to electron emission via autoionization at energies well below that observed in resonant photoemission from Ca atoms. The results give insight into the relationship between the d-screened core hole state in Ca and multiplets of core excited atomic states. [S0163-1829(97)04705-X]

INTRODUCTION

In this paper information is revealed on ion-induced inner shell ionization and screening of ionized atoms in the presence of strong electron-hole coupling. The atomic ground state of Ca is alkaline earth in character (outer configuration $3p^6 4s^2$) with the $3d$ state, accessed by a $4s^2 \rightarrow 3d4s$ valence excitation, weakly localized. However, a $3p \rightarrow 3d$ excitation results in a collapsed $3d$ state characterized both by large hole-electron exchange interaction and strong configurational interaction.[1] A richness of spectral structure is revealed in resonant photoemission with the most intense $3p^5 4s^2 3d\ ^1P \rightarrow 3p^6 4s^1 + e$ channel accompanied by many satellites in accord with the presence of complex many-body effects.

The conduction band of metallic Ca is mainly sp like in character,[2] but optical properties[3–5] are strongly influenced by the presence of flat empty d bands within a few eV of the Fermi level. Electron-energy-loss spectra from Ca metal are characterized by a double plasmon structure; a sharp feature at energy loss $\Delta E = 3.5$ eV is associated with interband transitions driving the real part of the dielectric function ε_1 to near zero over a small energy range, while conventional plasmon behavior is observed at $\Delta E = 7.4$ eV, close to the free-electron plasmon value. In Ca metal and its alloys the main photon excited $3p \rightarrow 3d\ ^1P$ transition ($h\nu = 31.1$ eV in the free atom) broadens into a wide resonance above the $3p$ ionization threshold and also exhibits resonant photoemission.[6,7]

Ion-excited Auger spectra from solids have revealed emission from neutral core excited atoms[8,9] but have not, in general, resolved multiplet structure. In this paper we use ion excitation of clean metallic Ca to report the decay of atomic $3p^5 4s^2 3d$ states not normally observed in photon spectroscopy, and to gain insight into how d screening of core holes contributes to the neutralization of ions created in alkaline earths and the lower part of transition-metal series. Previous ion-excited Auger studies of Ca (Ref. 7) yielded broad structureless emission in the region of the $M_{45}VV$ spectrum observed under electron emission. Here we combine high spectral resolution with an experimental geometry which favors direct ejection of excited atoms/ions from the surface and so emphasizes emission from core-excited atoms directly sputtered from the surface rather than from within the solid. The spectra are interpreted in terms of decay predominantly from a $3p^5 4s^2 3d\ ^3P$ multiplet state whose properties have been separately identified in electron-energy-loss spectra. This state arises from highly efficient neutralization of $3p$ core ionized atoms by metal electrons.

EXPERIMENTAL

Details of the experimental apparatus have been published previously.[10,11] The ions were incident at a glancing angle of 20° and electrons collected at an emergence angle of 15° to the surface, i.e., a strongly forward scattering geometry was used. The shapes of the spectral peaks were not strongly dependent on incidence angle in the range 25° to 10° but the background increased with decrease in the incidence glancing angle, implying an increase in the broad Auger spectrum from the metal.

The target was prepared by subliming Ca metal from a heated tungsten spiral onto a titanium plate. The condition of the target was monitored at regular intervals using electron-excited Auger emission spectroscopy and ion-excited measurements were recorded when only metallic Ca peaks were present and oxygen peaks were not. Ne, Ar, and Kr ions were used to excite the target and no significant differences were observed in the emitted electron-energy spectra. The values quoted for peak energies are averaged over all three incident ion species. In all three cases Ca spectra could be observed with incidence energies as low as 1 keV although the best spectra were obtained at incidence energies of 4 to 5 keV. Electron spectra characteristic of the incident gases were observed, but the Ne peaks were very small even at 5 keV incidence energy. Spectra are presented after subtraction of a smooth background curve as described in Ref. 10.

The spectrometer was a concentric hemispherical analyzer operated in a constant pass energy mode. The instrumental full width at half maximum (fwhm) was constant over the energy range 10 to 20 eV with a value ~0.4 eV, this compares with a value for the fwhm of the narrowest peak in the

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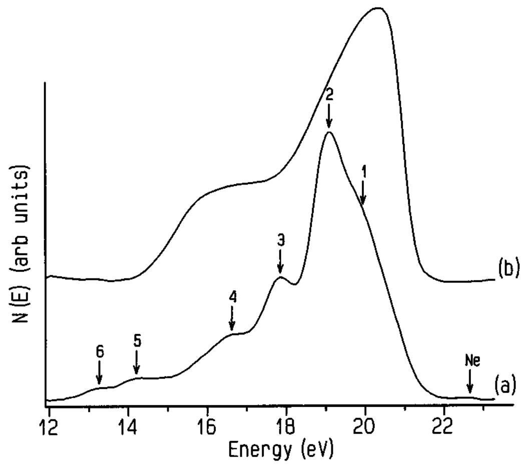

FIG. 1. The low-energy electron spectra of Ca metal after subtraction of a smooth background, (a) excited by 5 keV Ne ions, (b) excited by 500 eV electrons. Peak assignments are shown in Table II with energies determined from an average of 14 runs.

electron spectrum, peak 3 in Fig. 1, of ~0.6 eV. Data were recorded by averaging the signal over typically 50 sweeps to reduce noise. Values for the peak energies were obtained after successive peak by peak background subtraction and the values shown in Table II are the averages of 14 measurements. Standard deviations of the average energies were ~0.1 eV except for peak 4 where the standard deviation was 0.2 eV.

The energy calibration of electron spectrometers presents quite a difficult problem, especially at these low energies where there are no agreed standard peaks. The following method of calibration was adopted. It was assumed that the response of the spectrometer could be represented by a linear relationship of the form

$$E_{\mathrm{TRUE}}=\alpha E_{\mathrm{MEASURED}}+\beta,$$

where E_{TRUE} is the electron energy relative to the vacuum level. This relationship was confirmed by measuring a series of elastic peak energies in the range 10–25 eV and a graph of mean filament potential with respect to ground against measured energy gave a straight line and fixed α as 0.997. To find β, a fixed potential V_c was applied to the surface and the onset energy of emergent electrons measured. Since these should have an energy of V_c with respect to the target vacuum level, and since α had been determined, the value of β could be found (0.33 eV). The onset could be located to better than 0.2 eV and V_c values of 5 and 10 V gave the same value of β within this uncertainty.

RESULTS AND DISCUSSION

Figure 1 shows electron emission from clean Ca metal under ion bombardment and under electron bombardment after the subtraction of a smooth background. The electron-excited spectrum has typical $M_{23}VV$ Auger character with emission commencing at $I_{3p}-\phi$ when referenced to the vacuum level; I_{3p} is the $3p$ metal ionization energy relative to E_F, with a $3p_{3/2}$ value of 25.1 eV,[12] and ϕ is the spectrometer work function, which might be expected to be ~4 eV. The profile has breadth of order twice the Ca conduction band breadth[2] and is consistent with a weighted convolution of the density of states with an additional loss feature corresponding to the low energy-loss feature in Fig. 2.

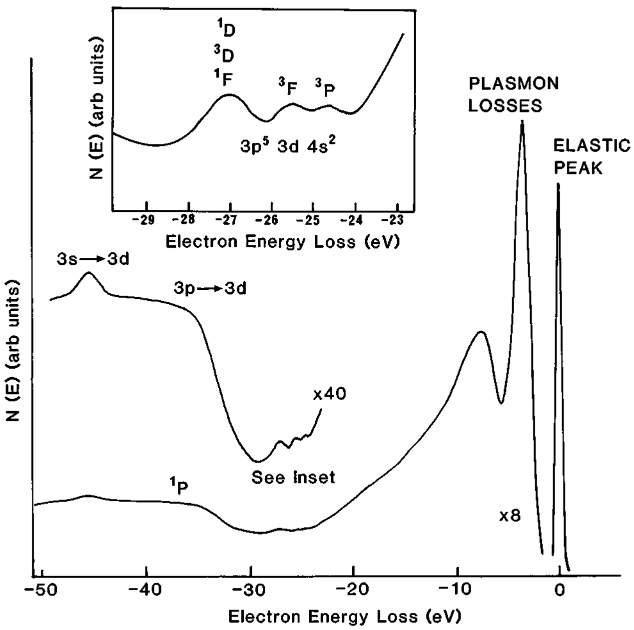

FIG. 2. The electron-energy-loss spectrum of Ca metal obtained using 200 eV primary electrons. The inset shows the results of a separate measurement made at higher gain in the energy loss range 23–29 eV.

The ion-excited spectrum is much sharper and may be resolved into a number of components. The experimental geometry strongly favors core ionization of atoms in the surface layer followed by rapid ejection from the surface. Furthermore, emission by neutral excited atoms is dominant over emission from the conduction band sensed in electron bombardment. Although it is clear that the two main peaks at 20.1 and 19.1 eV could be atomic in origin, their classification is not immediately obvious since they do not correspond either to free atom $M_{23}N_1N_1$ Auger emission as seen by Bizau *et al.*[1] in the energy range 13–16 eV or to excited neutral states observed in resonant photoemission with main peaks at 25 eV kinetic energy.

A clue to the origin of the emission is to be found in the electron energy-loss spectrum of Ca metal in the reflection mode for a primary energy $E_p=200$ eV, as shown in Fig. 2. This spectrum is characterized by a double plasmon structure, as previously discussed, and a broad peak at $\Delta E=35$ eV corresponding to giant resonance excitation into the $3p^5 3d\ ^1P$ state, whose decay gives rise to resonant emission in both Ca metal and Ca alloys such as CaMg and CaAl.[7] At energies around the onset of $3p$ ionization three weak but sharp features are resolved—see the inset of Fig. 2. Using empirical free Ca atom data[13] and relativistic Dirac-Fock calculations the peaks can be identified as electron-induced excitations into $3p^5 3d 4s^2$ multiplet states. The lowest ($\Delta E=24.4$ eV) corresponds to ^3P, the next to ^3F and the third to an amalgam of ^1D, ^3F, and ^1F. These features do not appear in photoabsorption because of the restrictive dipole selection rules ($\Delta L=\pm 1$, $\Delta S=0$) for LS coupling for this system, and

TABLE I. $3p \rightarrow 3d$ excitation energies.

Final state Multiplet	Ca free atom Experiment (Ref. 10) eV	Ca free atom Theory[a] eV	Ca metal Experiment eV
^3P	24.8	24.7	24.4
^3F		25.8	25.4
^1D	27.1	27.6	26.9
^1F		27.6	
^3D		27.7	
^1P	31.4	36.7[b]	~35

[a] Single configurational relativistic Dirac-Fock calculation using the program of Grant (Ref. 14).

[b] Multiconfigurational calculations are required to reproduce the properties of this less localized state.

TABLE II. Electron emission channels. Autoionization energies are predicted from the ^3P excitation energy of Sugar and Corliss (Ref. 11) and the theoretical value for ^3F (Table I) along with the CaII excitation energies of Ref. 11. Predicted Auger energies are from Bizau *et al.* (Ref. 1).

Autoionization	Predicted eV	Observed eV	Peak
$3p^5 3d 4s^2\ ^3F \rightarrow 3p^6 4s + e$	19.7	20.1	1
$3p^5 3d 4s^2\ ^3P \rightarrow 3p^6 4s + e$	18.7	19.1	2
$3p^5 3d 4s^2\ ^3F \rightarrow 3p^6 3d + e$	18.0		
$3p^5 3d 4s^2\ ^3P \rightarrow 3p^6 3d + e$	17.0	17.7	3
$3p^5 3d 4s^2\ ^3F \rightarrow 3p^6 4p + e$	16.6	16.3	4
$3p^5 3d 4s^2\ ^3P \rightarrow 3p^6 4p + e$	15.6		
Auger emission			
$3p^5 4s^2 \rightarrow 3p^6 + e$	16.4	16.3	4
$3p^5 4s^2 \rightarrow 3p^6 + e$	13.0–14.6	13.3, 14.2	5, 6

are only weakly excited by electrons. These excited states are highly localized in the condensed phase with excitation energies closely similar to those of the free atom (Table I): furthermore, the attractive exchange interaction pulls these energy levels below the Fermi level. This provides the key to understanding the ion-excited electron emission.

The interaction of ions with metallic systems such as Ca, Sr, Ba, and lower transition metals differs fundamentally from resonant photon and electron excitation. In the latter two cases direct quasiatomic excitation to configurations such as $3p^5 3d$ in Ca is competitive with direct ionization although photon selection rules and the nature of inelastic electron-scattering cross sections limit the accessibility of many multiplets.[6,7] In contrast we propose that in the case of ion impact there is a three-stage process of ionization, neutralization by conduction electrons leading to sputtered atoms dominantly in a single $3p^5 3d 4s^2$ multiplet state, and subsequent electron emission above the surface. In atom collisions quasimolecules form diabatically leading to level crossings which result in inner shell ionizations (from the Ca $3p$ level in this case). The fact that the results obtained are insensitive to the bombarding ion suggests that Ca-Ca collisions may be responsible for the ionization, but whatever the mechanism, the final state of the promoted electron cannot be d-like due to symmetry considerations. The diabatic collision of Ca atoms leads to electron promotion into a $5f\sigma$ state,[15] which is different in symmetry from molecular states involving $3d$ electrons and so the collision unambiguously leads to ionization rather than excitation. However, the metallic environment rapidly screens the ion created. It is well known that core holes in Ca, Sr, and Ba are d screened[16,17] resulting in large extra atomic relaxations due to the small radius of the ''Bohr orbit'' of the screening electron—a kind of ''superscreening''. The only screening final states that are accessible correspond to $3p^5 3d$ multiplets that lie below the Fermi level. Thus, this energy constraint excludes the dominant states seen by photons or electrons ^1P, with ^1D, ^3D, and ^1F also doubtful. Efficient screening seeks the lowest possible state (^3P) which will be the initial state for the main feature (peak 2 in Fig. 1) with ^3F giving rise to peak 1. After the neutral excited species emerges from the surface, it will mainly decay from $3p^5 3d 4s^2$ to $3p^6 4s^1 + e$ due to the comparable spatial scales of the $3p$ and collapsed $3d$ charge distributions. This implies emission at energies $\Delta E - I^{\mathrm{ATOM}}_{\mathrm{Ca}4s}$, where ΔE is the $3p \rightarrow 3d$ excitation energy and $\Delta I^{\mathrm{ATOM}}_{\mathrm{Ca}4s} = 6.1$ eV,[12] is the $4s$ ionization of the Ca atom (Table II). Alternative decay channels to $3p^6 3d^1 + e$ lie 1.7 eV below the main spectral features[13] suggesting that peak 3 has the same ^3P initial state as peak 2 with the corresponding feature for ^3F being unresolved under peak 2. Peak 4 at lower energy may be a shake up satellite corresponding to a $3p^6 4p$ final state, but may also contain contributions from satellite Auger decay of some unneutralized Ca^+. The very weak peaks 5 and 6 may be either Auger or autoionization shake ups.

Recent work on ion-excited emission from Ti (Ref. 10) suggested a mechanism very similar to that presented here. However, in Ca we are able to identify unambiguously the multiplets that provide the initial state for emission. In Sc, Ti, V, and Cr many $3p^5 3d^{n+1}$ multiplets are accessible according to the screening mechanism outlined here: a comprehensive study of emission for these systems is in progress. Although the mechanism of neutralization investigated here concerns a metallic system, it is of some interest to relate this work to recent controversy on ion-induced electron emission from alkali halides over the question of whether emission is occurring outside the surface or in the surface.[18–20] In the Ca case the results obtained have suggested that the neutralization of core-ionized atoms by conduction electrons at the surface leads dominantly to the ^3P multiplet of the $3p^5 3d 4s^2$ configuration in excited atoms which sputter away from the surface and subsequently decay.

Although this paper is principally about ion-induced electron emission, it also provides better understanding of screening of core holes created by photons or electrons in systems with strong Coulomb and exchange coupling to conduction electrons. The situation is reminiscent of the contrast between the $3d$ x-ray photoemission (XPS) and x-ray absorption (XAS) in La: $3d^9 4f^1$ final states are observed in both spectroscopies due to f screening accompanying photoionization.[21] XPS accesses a wide range of multiplets with emphasis on those at lower energy, while XAS reveals a limited number of multiplet states mainly at higher energy due to dipole selection rules. In Ca ion-induced ionization reveals strong preference for the lowest possible d screening multiplet. The $3p$ XPS ionization energies are slightly larger in energy than the ^3P excitation energy, so that, in the spirit of the excited atom model of d screening in photoemission,[16,17] a reduction in binding energy representative of the lower energy $3p^53d$ multiplets is achieved.

CONCLUSIONS

In summary, it has been shown that ion-induced electron emission from Ca metal is dominated by atomic autoionization from neutral $3p^53d4s^2$ multiplets with excitation energies below that of the $3p$ ionization energy of Ca metal, states which are not accessed in resonant photoemission. The results imply a three stage process: (1) $3p$ ionization induced by ion collision, (2) neutralization by d screening in or near the surface, ending mainly in the lowest energy ^3P multiplet 6 eV below the principal atomic photoabsorption final state ^1P, and (3) if the atoms escape from the surface, electron emission leading to a singly ionized $3p^64s^1$ or $3p^63d^1$ Ca$^+$ final state. These results give insights into the nature of d-electron screening in the presence of strong electron-hole coupling. The d-screened $3p$ hole mimics low-energy $3p^53d$ multiplet states which are then accessed when a neutralized atom leaves the surface.

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