Comment on "Collisional Deexcitation at Ion-Bombarded Surfaces"

In a recent Letter and a previous paper [1] Fine *et al.* report that energy spectra of electrons ejected from NaCl, NaF, and NaI by keV ions have three Auger peaks of similar height at energies agreeing with those from free Na* $2p^5 3s3l$ atoms [2]. This is unlike ion impact of metallic Na, where only one main peak results [3], and unlike electron bombardment of the undamaged salts where no Na-$2p$ Auger structure was visible. From this, Fine *et al.* conclude that the peaks are from Na*, formed by a presumably new class of *collisional* deexcitation process *inside* the solid. Here I question this interpretation and propose that the peaks result from normal (i.e., *noncollisional*) Auger deexcitation of Na* atoms *outside* the solids. Where and how the Na* deexcite are key questions to determine if we are indeed in the presence of a new mechanism then can eventually create defects in insulators.

That deexcitation occurs outside the solid follows from the fact that the observed Auger energies are like those of free Na*, and not like bulk core-exciton Na^{+*} $2p^5 3l$ and Auger energies [4] which vary much among Na halides, unlike those of Ref. [1]. Energy shifts are indeed expected in the solid since the Na* $3l$ orbits overlap with halogen valence orbitals or are even larger than the lattice spacing [5].

How excitation occurs can be described with concepts used successfully to explain other ion-induced $2p$ Auger spectra in solids [6]. Na^{+*} can be sputtered into vacuum due the violent collisions needed to excite Na-$2p$ orbitals. During ejection, its outer-shell population will result from competing electron capture and loss processes with the surface. These are different for the Na halides than for elemental Na, where a sputtered Na$^+$ $2p^5 3s$ will capture an electron resonantly from metal valence states. Only Na* states with an ionization potential I larger than ϕ, the work function of the surface, can survive resonant ionization into the metal conduction band [7]. Including a 1–2 eV image shift near the surface, only $2p^5 3s^2$ and, marginally, $2p^5 3s(^1P)3p$ and $2p^5 3p^2$ can form even for low ϕ surfaces, as observed [3]. In contrast, in insulators there is no continuum of empty states available for resonance ionization. In the Na halides, where sodium exists essentially as Na$^+$, a $2p$-excitation collision will lead to either Na^{++} $2p^5$ or to core excitons Na^{+*} $2p^5 3l$. These ionic configurations will have a long range attractive interaction with the band-gap electron surface state left behind, approaching neutral states that lead to the final Na* $2p^5 3l 3l'$ configurations observed. An electron can be transferred when the states are close or cross, leading to the excited neutral Na*. A crossing requires that the asymptotic ionic curve lies above the neutral curve, i.e., that $A < I$, where I is the energy to ionize the atom and A the energy gained when the electron drops to the affinity level in the solid. For instance, Na* $2p^5 3s^2$ ($I = 7.2$ eV) can be formed if the electron is left in a surface state or trap with $A \sim 2-4$ eV [8], but not if left in a bulk halogen site ($A \sim 9.3$ eV for NaCl [9]), as proposed [1]. It is important to notice that the required band-gap state does not have to be filled or populated before impact since it is created dynamically near the ejection site in the collision cascade. Finally, we note that the observed decrease in Auger intensities with halogen depletion can result from an increased fraction of Na* decays *inside* the solid due to the enhanced valence density around the Na-$2p$ hole.

Thus, observations can be explained by a model that is consistent with previous results and which does not require to postulate a new mechanism in the solid. While this model is similar to the bond-breaking model in SIMS [10], we recall that the ejection of a core-excited atom is not a typical ion sputtering event [6] and that different surface sites may play the dominant role in different ejection processes.

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