Inner-Shell Electron Promotion in Low Energy Li $^+$-Al(100) Collisions

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A previously unobserved inelastic excitation mechanism is reported for alkali ions scattered from a metal surface. Li $1s$ holes are generated via electron promotion during hard binary collisions with surface Al atoms. Excited Li then resonantly neutralizes to form Li$^*(1s\,2s^2)$. These particles autoionize above the surface and are thus detected as ions. At large scattering angles, the majority of the singly scattered Li$^+$ ions participate in this promotion process for incident energies of ~ 3 keV and higher.

Electronic processes that occur during ion-surface collisions are important in many areas of physics, such as bombardment-activated chemistry and ion scattering spectroscopy [1]. However, little is known about specific mechanisms and their relative importance. The present study details a rather intricate process with several novel components. In scattering Li$^+$ from Al(100), $1s$ core electrons from the projectile are promoted above the Fermi level during hard binary collisions. The promotion energy is absorbed by both the rebounding Li projectile and the recoiling Al atom. The creation of an inner-shell vacancy in the projectile opens new channels for electronic transitions and charge exchange. Of primary importance is the formation of excited Li$^*(1s\,2s^2)$ neutrals, which autoionize *en route* to the analyzer and are thus measured as ions. This process is demonstrated via measurements of scattered ions as well as of the electrons emitted from the autoionization.

Spectra of scattered ions and secondary electrons were collected in an ultrahigh vacuum chamber equipped with a ^{7}Li$^+$ source (Kimball Physics) and a hemispherical electrostatic energy analyzer (Comstock). The incident beam energy ranged from 0.4 to 5 keV, with an energy spread of $< 0.2\%$ and a spot size of < 1 mm^2. Scattered ion energy spectra were collected with the incoming beam at normal incidence and the analyzer positioned 12° off normal towards the [011] azimuth, which gives a scattering angle of $\Psi = 168°$. For the electron spectra, the sample was rotated such that the analyzer was normal to the surface. The resolution of the analyzer was scaled to 1% of the beam energy for scattered ion spectra and set to 3 eV for electron spectra. The angular acceptance of the analyzer was $\pm 2°$. The Al(100) sample was prepared by reiteratively sputtering with grazing incidence 2 keV Ar$^+$, normal incidence 0.5 keV Ar$^+$, and annealing to $\sim 420°$C. The purity and order of the surface were verified with Auger electron spectroscopy and low energy electron diffraction (LEED). Polar scans of singly scattered ^{7}Li$^+$ ions, which are more sensitive to surface order than LEED [2], were used as a final measure of surface quality. Damage due to the ion beam was kept within an acceptable level by signal averaging several spectra, each collected from an unexposed spot on a newly prepared sample.

Representative scattered ion energy spectra are shown in Fig. 1. The energy scale is given with respect to that calculated from the binary collision model (BCM), which assumes a perfectly elastic collision between an ion and an unbound target atom. Two peaks, labeled $P1$ and $P2$, are evident in most of the spectra. The higher energy peak, $P1$, is the only feature visible at the lowest incident energy. The lower energy peak, $P2$, emerges as the incident energy increases, and eventually dominates the spectra. Since $P2$ is observed only above a certain threshold incident energy, $P1$ is attributed to single scattering from Al. Both $P1$ and $P2$ broaden and shift further away from the BCM energy with increasing in-
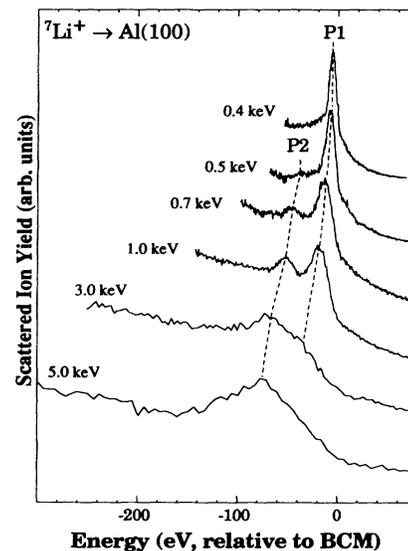

FIG. 1. Ion scattering spectra for normal incidence ^{7}Li$^+$ ions backscattered from Al(100) with various incident energies, as indicated. The maximum intensities of the spectra are normalized to each other and consecutive spectra are displaced by the distance indicated by tick marks on the right vertical axis. The energy scale is set to zero at the BCM energy for ^{7}Li scattered elastically from ^{27}Al.
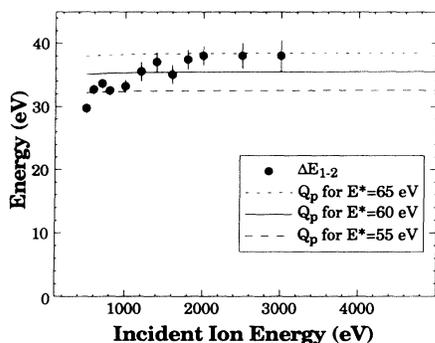
FIG. 2. The measured energy separation between $P1$ and $P2$, ΔE_{1-2}, and the inelastic loss for Li, Q_p, calculated for a few values of E^* as a function of incident ion energy.

cident energy. This is due to the dissipation of energy by the continuous interaction of the projectile with the crystal electrons, an effect which is known to increase with projectile energy [3].

The positions of $P1$ and $P2$ were determined by fitting the peaks with Gaussian line shapes after removing the multiple scattering background, as described elsewhere [4]. Note that spectra collected with incident energies above 3 keV were not fit, as the two peaks are not resolved. The energy separation between the peak positions of $P1$ and $P2$ determined from these fits, ΔE_{1-2}, is shown as a function of incident energy in Fig. 2.

While $P1$ is associated with single scattering from Al, $P2$ cannot be explained within the context of elastic scattering. $P2$ is not due to single scattering from another element, because ΔE_{1-2} would then scale directly with incident energy. For the same reason, it is unlikely that $P2$ is due to a highly probable multiple scattering trajectory. Monte Carlo simulations, which are described elsewhere [4], were performed as a further test. Simulations corresponding to a representative set of the experimental spectra consistently failed to produce more than a single peak.

Since the above considerations show that $P2$ is not produced by elastic scattering, it must be the result of an inelastic loss associated with single scattering. There are, however, no electronic transitions in the Li-Al system with energies comparable to the observed values for ΔE_{1-2}. For instance, the binding energy of the lowest lying core level of Al, which is the $2p$, is 73 eV. The smallest core level excitation of Li involves the $1s$, which requires 59 eV. Also, the surface and bulk plasmon energies of Al are ~ 10 and ~ 15 eV, respectively, which are too small to account for ΔE_{1-2}.

The energy lost by a rebounding projectile, however, does not necessarily represent the total excitation energy, as a substantial fraction of the excitation energy can be absorbed by the recoiling target atom. The inelastic loss experienced by the projectile, Q_p, for a given excitation energy, E^*, can be estimated as follows. For a given incident energy and scattering angle, the final energy of the
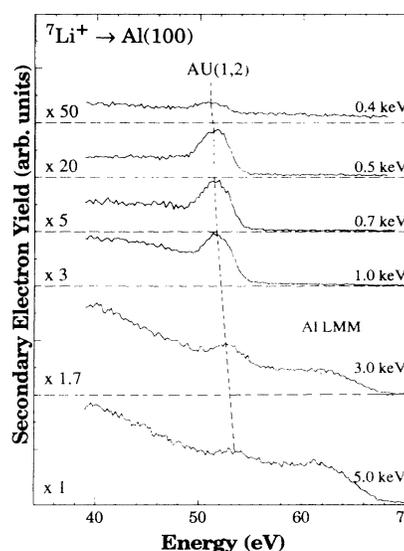

FIG. 3. Energy spectra of secondary electrons emitted along the surface normal during bombardment by $^7Li^+$ ions. Spectra are normalized to ion beam flux. Scaling factors are shown on the left. Broken lines indicate zero intensity for the spectra that are displaced.

projectile is calculated using conservation of energy and momentum for both an elastic binary collision and a partially inelastic binary collision, in which the total kinetic energy is reduced by E^*. The value for Q_p is then the difference between these two energies. This method assumes that extraneous inelastic losses prior to the collision are small compared to the incident energy, and that energy losses occurring after the collision do not depend on whether or not the collision was elastic. The set of curves plotted in Fig. 2 were produced by applying this method to the present system for a few values of E^*. Comparing the calculated value of Q_p to ΔE_{1-2}, shows that E^* is on the order of 60 eV, which is significantly larger than ΔE_{1-2}, and is on the order of the energy required to promote a Li $1s$ electron.

The electronic aspects of the scattering process were investigated by collecting spectra of the electrons emitted with $^7Li^+$ ions impinging on the surface, as shown in Fig. 3. Two features are evident in these spectra. The lower peak, marked AU(1,2), is attributed to the autoionization of $Li^*(1s\,2s^2)$ [5,6]. The other peak, which is only present at the higher incident energies, is due to the emission of substrate Al LMM Auger electrons. The energy scale for these spectra is given with respect to the vacuum level of the sample, which was calibrated by setting the low energy secondary electron cutoff to zero.

The AU(1,2) peak is identified by comparison to published data on the electrons ejected in the $Li^*(1s\,2s^2)$ $\rightarrow Li^+(1s^2)+e^-$ autoionization process. Gas-phase studies show that these electrons have 51 eV of kinetic energy [5]. Likewise, spectra of electrons produced by 2 keV Li^+ impinging on Li-covered W(110) exhibit an

AU(1,2) peak at $\sim$51 eV above the secondary electron cutoff [6]. In the present study, the energy of the AU(1,2) peak ranges from 51 ± 0.5 eV for a 0.5 keV incident beam to 53.5 ± 0.5 eV for the 5.0 keV beam. The response of the AU(1,2) peak to changes in the ion incident energy is largely explained by a Doppler shift due to the motion of the scattered Li projectiles.

A quick way to estimate the magnitude of this effect is to compare the final energy of AU(1,2) electrons that are emitted in the direction of motion from a Li* moving towards the analyzer at the BCM energy for single scattering. Using this approximation, the observed AU(1,2) peak energy increases by 1.7 eV for the spectra collected with 0.5 keV ions and 5.4 eV for the spectra collected with 5.0 keV ions. The predicted shift in the AU(1,2) peak over this range is thus 3.7 eV, which is slightly larger than the observed shift of $\sim$2.5 eV. It is expected that this calculation will overestimate the effect, however, as the detected AU(1,2) electrons are emitted not only from Li* singly scattered toward the analyzer, but also from Li* traveling in other directions and with smaller velocities. The fact that the peak position shifts with incident ion energy provides evidence that the AU(1,2) electrons originate from a moving source and not from the Al substrate.

The presence of $Li^*(1s\,2s^2)$ in the scattered particle yield indicates that an inner-shell hole is created during the Li-Al collision process. The correlation between the appearance of the AU(1,2) and $P2$ signals strongly suggests that they are related. Furthermore, the minimum excitation energy required to promote a Li $1s$ electron to the Al(100) Fermi level is 59.6 eV [7], which is in good agreement with the values of E^* that compare favorably to the data. Note that the actual final state may be centered a few eV above the Fermi level, depending on the density of empty states and the transition matrix.

The coincidence of the formation of $Li^*(1s\,2s^2)$ and the inelastic loss feature associated with a $\sim$60 eV excitation energy leads to the following interpretation. As a Li^+ ion approaches the surface, the $2s$ level broadens and shifts to become resonant with the Al conduction band [8]. This well-known mechanism for charge exchange does not involve any alteration of the kinetic energy of the projectile. During a hard collision, some Li $1s$ electrons are then promoted to unoccupied states above the Fermi level. Such an excitation does require energy, which results in a measurable reduction in the kinetic energy of the scattered particles. Finally, removal of a $1s$ electron shifts the Li electron affinity level down, so that the $2s$ now becomes fully occupied via resonant charge exchange. Thus, Li leaves the surface as $Li^*(1s\,2s^2)$, which subsequently autoionizes.

At this point, the identification of $P2$ as a loss feature associated with the promotion of Li $1s$ electrons to empty states above the Fermi level has been established. There are, however, some minor differences between the measured values for $\Delta E_{1\text{-}2}$ and values of Q_p calculated with $E^* = 60$ eV. One difference is that $\Delta E_{1\text{-}2}$ increases more rapidly with energy than does Q_p. This is due, at least in part, to differences in the continuous inelastic losses experienced by Li* and ground state Li. After losing a $1s$ electron, the Li nucleus is less screened, which results in a stronger Coulombic interaction between the Li projectile and the crystal. Excited Li* particles therefore experience larger dissipative forces than their ground state counterparts. Because the rate of energy dissipated via the Coulombic interaction also increases with the speed of the projectile [3], the additional continuous energy loss caused by the $1s$ hole becomes more significant at higher energies.

While differences in the energy dissipated after the collision account for an increase in $\Delta E_{1\text{-}2}$ with incident energy, they do not explain why $\Delta E_{1\text{-}2}$ falls below the minimum energy required to promote a Li $1s$ electron. The apparent discrepancy between $\Delta E_{1\text{-}2}$ and Q_p at energies near the onset of the excitation occurs because the difference between the peak centers is not an accurate reflection of the discrete inelastic loss in this region. There is a distribution of collision energies as a result of inelastic losses experienced along the incoming trajectory. Near the onset of $P2$, the promotion probability is a rapidly increasing function of the collision energy, so that Li particles at the higher end of the distribution are more likely to undergo Li $1s$ promotions than those at the lower end. The net effect is that the inelastic loss associated with the promotion preferentially reduces the higher side of $P1$ and thus augments the higher side of $P2$, so that the separation between $P1$ and $P2$ near the onset is actually smaller than the inelastic loss.

The fact that the inner-shell occupation of an ion can be altered in the low energy ion scattering regime has some important consequences in the interpretation of previously published work. For example, the site-specific neutralization reported in Ref. [9] can be better understood in light of the present results. That study showed that for 3 keV Li^+ scattered from Na-covered Al(100), the ion yield from multiple scattering decreased with Na coverage, while the ion yield for single scattering from Al was relatively unaffected. Also, no single scattering from Na was observed. These results were interpreted within the context of resonant neutralization, and were consequently thought to be an effect of a varying local electrostatic potential. Given the present data, however, it is seen that the peak that was relatively unaffected by Na coverage was $P2$. The Al single scattering peak, which appeared as a shoulder on $P2$ in the data of Ref. [9], actually did decrease in intensity with Na coverage. In more recent experiments, which employed a range of ion energies, it is found that both Na and K adsorption do preferentially suppress the $P1$ signal over $P2$ [4].

The combined results of these two studies leads to some additional important conclusions. First, the site-specific

neutralization observed in Ref. [9] is due primarily to the preferential formation of autoionizing Li states during Li-Al collisions, as compared to Li-Na collisions. This can be understood from an atomic perspective, as a level crossing from Li $1s$ to Al $3p$ does occur, while no such crossing exists for the Li-Na system [4]. This is analogous to a phenomenon seen in He$^+$ scattering in which the probability of reionization of He scattered from composite surfaces depends on the target atom species [10,11]. Second, the fact that the intensity of $P2$ is relatively unaffected by alkali adsorption confirms that Li is leaving the surface in an excited state and that the autoionization process contributes to the measured ion yield. If Li* were to relax to its ground state at or below the surface, it would be subject to the same resonant neutralization mechanisms as projectiles that did not have a $1s$ vacancy, and the resistance to alkali-induced neutralization would not have been observed.

The present study was successful because it was able to track inelastic losses with ion scattering spectroscopy and electronic processes with secondary electron spectra. Very few studies have monitored both. Furthermore, prevalent ion scattering procedures are generally not well suited for detecting discrete inelastic losses. Employment of high energy resolution and large scattering angles were essential in detecting and tracking the inelastic loss through this energy range. The extent to which an autoionization process is responsible for detected alkali ion yields is, in general, unknown at this point. In light of the present results, however, it is possible that it may even be a majority process for several systems. The results of previous [12–16] and future research on charge exchange between surfaces and low energy alkali ions should, therefore, be interpreted with consideration of the possible effects of inner-shell excitations.

[1] J. Los and J. J. C. Geerlings, Phys. Rep. 190, 133 (1990).

[2] J. A. Yarmoff and R. S. Williams, Surf. Sci. 165, L73 (1986).

[3] A. Närmann, W. Heiland, R. Moneal, F. Flores, and P. M. Echenque, Phys. Rev. B 44, 2003 (1991).

[4] K. A. H. German, C. B. Weare, and J. A. Yarmoff (to be published).

[5] M. Rødbro, R. Bruch, and P. Bisgaard, J. Phys. B 12, 2413 (1979).

[6] H. Brenten, H. Müller, and V. Kempter, Z. Phys. D 22, 563 (1992).

[7] Ionization of ground state Li^0 from the $1s$ level requires 64.0 eV [C. E. Moore, in *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) (U.S. GPO, Washington, DC, 1971)] and the Al(100) work function is 4.41 eV [J. K. Grepstad, P. O. Gartland, and B. J. Slagsvold, Surf. Sci. 57, 348 (1976)]. The energy difference between Li $1s$ and the Al(100) Fermi level is therefore 59.6 eV.

[8] J. J. C. Geerlings, J. Los, J. P. Gauyacq, and N. M. Temme, Surf. Sci. 172, 257 (1986).

[9] K. A. H. German, C. B. Weare, P. R. Varekamp, J. N. Andersen, and J. A. Yarmoff, Phys. Rev. Lett. 70, 3510 (1993).

[10] R. Souda, T. Aizawa, C. Oshima, S. Otani, and Y. Ishizawa, Phys. Rev. B 40, 4119 (1989).

[11] F. Shoji, K. Kashihara, T. Hanawa, and K. Oura, Nucl. Instrum. Methods Phys. Res., Sect. B 47, 1 (1990).

[12] L. Jiang, Y. D. Li, and B. E. Koel, Phys. Rev. Lett. 70, 2649 (1993).

[13] M. J. Ashwin and D. P. Woodruff, Surf. Sci. 244, 247 (1991).

[14] A. J. Algra, E. van Loenen, E. P. T. M. Suurmeijer, and A. L. Boers, Radiat. Eff. 60, 173 (1982).

[15] J. J. C. Geerlings, L. F. T. Kwakman, and J. Los, Surf. Sci. 184, 305 (1987).

[16] G. A. Kimmel, D. M. Goodstein, Z. H. Levine, and B. H. Cooper, Phys. Rev. B 43, 9403 (1991).