Electron Capture from Occupied Surface States within the Band Gap of LiF(100)

Q. Yan and F. W. Meyer

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6372

Abstract: Measurements of scattered neutral fractions for Na, K, and Cs multicharged ions grazingly incident on Li(100) as function of projectile velocity suggest that near resonant processes are active in the final neutral formation, involving occupied surface states within the band gap of the alkali halide target. Observed scattered negative fractions for incident O, F, and B projectiles are consistent with such a scenario as well. A model treatment of the projectile charge fraction velocity dependence is utilized to deduce from the experimental data a work function and Fermi energy of 3.8 eV and 0.8 eV, respectively, for this surface band. Measurements of the parallel velocity dependence of the image charge acceleration of Ne^{6+} grazingly incident on LiF(100) in the range 0.1 - 0.52 a.u. are shown to provide further support for the presence of a band of surface states having the above parameters.

The interaction of multicharged ions with alkali halide surfaces has recently become the focus of intensified study [1-5]. Despite the increased activity, a level of understanding of the underlying physics comparable to that achieved for metal targets[6] has not yet been reached. For example, in the area of negative ion formation, the target states involved are still the subject of active discussion. Measurements by R. Souda et al.[7] suggest that negative ion formation occurs preferentially during interactions with states localized at the alkali lattice sites, while results of Auth et al.[4] have been interpreted in terms of binary interactions with the halogen sites. In addition, some complimentary insulator studies have arrived at seemingly contradictory conclusions, adding to the puzzle. For example, measurements by Auth et al.[3] of image charge acceleration of multicharged Xe ions in front of a LiF surface suggested significant projectile neutralization (i.e. "hollow atom" production) prior to impact on the LiF surface. First measurements of KLL Auger spectra for N^{6+} incident on LiF(100) reported by Limburg[2], on the other hand, indicated an absence of features associated with above surface KLL emission, casting doubt on the existence of "hollow atoms" above such surfaces.

Scattered neutral and negative ion formation from incident positive ions during grazing interactions with metal targets have been shown to depend sensitively on the work function of the target[8]. In order to probe the alkali halide target for the presence of occupied surface states correlated with the Li lattice sites, which have been predicted to lie in the upper half of the LiF band gap [9], we have made analogous measurements of scattered neutral fractions for Na, K, and Cs ions, and scattered negative ion fractions for O, F, and B projectiles incident on LiF(100). We have found evidence in both sets of measurements for the possible involvement of surface states during the final phase of the ion surface interaction, in which the dominant scattered charge states are determined. A model treatment of the velocity dependence of the measured scattered charge fractions is used to deduce more detailed information about these occupied states within the band gap of LiF. The possible role of such states in above-surface neutralization has been investigated via first measurements of the parallel velocity dependence of the image acceleration energy gain of Ne^{6+} grazingly incident on LiF(100).

The apparatus used for the present measurements has been previously described [10,11]. The target sample was cleaved from a LiF single crystal in air and quickly put into a UHV chamber having a base pressure of 3×10^{10} mbar. Surface preparation consisted of 30 min. annealing cycles at a temperature of roughly 400°C. The sample temperature was kept at about 300°C during the measurement in order to avoid target charging. The surface quality was checked by verifying the presence of characteristic banana shaped channeling patterns for ions grazingly incident along low index channeling directions. The charge state distribution of the scattered (reflected) projectiles was measured by selecting a thin vertical slice of the scattered beam with movable slits, which was then dispersed by charge state across the face of a 40 mm diameter two dimensional position sensitive detector (PSD) using a pair of electrostatic deflection plates. The zero degree position on the PSD and the angle of incidence on the LiF sample were accurately determined by monitoring with the PSD a photon beam produced by illuminating the ion collimation section upstream of the sample with a UV light source, and registering its shift after specular reflection from the LiF sample. Beam intensities on target were kept sufficiently low to avoid significant defect formation as well as to avoid count rate saturation of the PSD.

Fig.1 shows measured scattered neutral fractions for multicharged Cs, K, and Na ions grazingly incident on LiF(100) as function of projectile velocity. It is noted that the measured neutral fractions were largely independent of initial projectile charge for these measurements. As can be seen from the figure, the scattered neutral fraction for the Na projectiles exceeds ~60% at the lowest investigated velocities and, for the K projectiles as well, decreases with increasing velocity over the whole velocity range investigated. For the Cs projectiles, the neutral fraction goes through a local maximum of ~18% at a velocity of 0.16 a.u.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
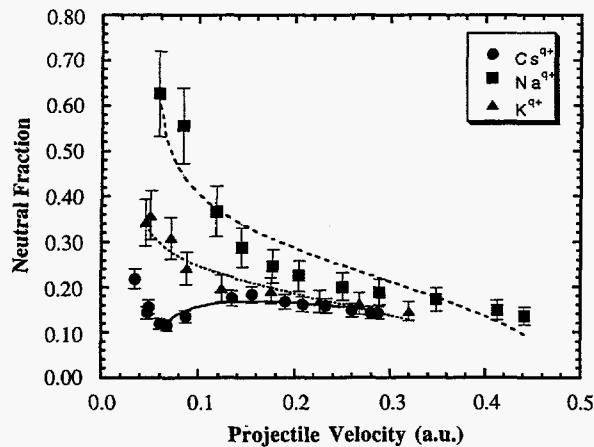
DISCLAIMER

Fig.1 Projectile velocity dependence of the scattered neutral fractions for multicharged Cs, K, and Na projectiles grazingly incident on LiF(100). The lines are fitted curves based on Eq.2.
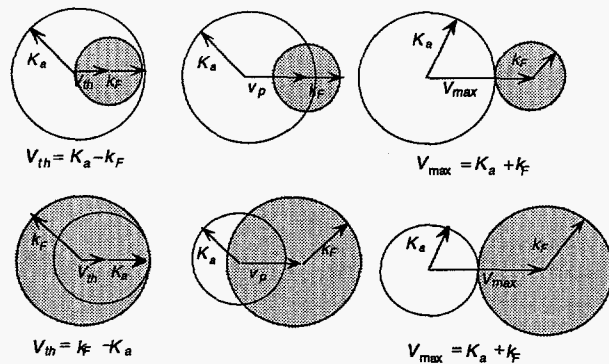

Fig.2 Schematic diagrams of the geometric overlaps of occupied surface states (represented by Fermi disk of radius k_F) in resonance with projectile atomic level (represented by the circle with radius of K_a as defined in the text) for different projectile velocities.

The velocity dependence of the scattered alkali neutral fractions is strongly suggestive of the involvement of a resonant electron transfer process in the formation of the dominant scattered charge fraction during the final phase of the ion surface interaction. Since electronic transitions between the LiF valence band and the alkali neutral atomic levels would be clearly non-resonant (by at least 7 eV), we speculate that the resonant transitions involve occupied surface states located in the upper half of the LiF band gap.

Such occupied states may result from a modification at the surface of the bulk ionic bonding structure arising from transfer of the Li 2s electrons to the F sites to form the valence band, due to absence of one of the F bonding sites at the surface. Since at the surface the number of nearest F neighbors that each Li atom shares its 2s electron with is reduced from 6 to 5, roughly 1/6 electrons per surface Li site are not bound to F sites and may therefore contribute to the surface density of occupied states. This crude initial estimate gives a 2-D surface band Fermi energy of ~0.5 eV or, equivalently, a Fermi velocity k_F of 0.19 a.u. which is based on the relationship between the 2-D electron density, n and, the Fermi energy, $E_F = \pi n \hbar^2 / m$. Since k_F is small compared to the reciprocal lattice vector $g = 2\pi / a = 1.2$ a.u., the electron energies of the surface band can be approximated as $E \approx E_b + k^2 / 2$, where E_b is the energy at the bottom of the band.

In order to further analyze our experimental data, we make the assumption that the measured scattered neutral fractions are proportional to the density of occupied surface states in resonance with the image shifted projectile neutral level at the "freezing"[13] distance. The resonance condition is obtained by matching the energy E of the surface state wavefunction in the rest frame of the moving projectile with the energy E_a of the relevant atomic level. As explained in greater detail in Ref.[5], under the assumption that only the leading term in the summation over the 2-D reciprocal lattice contributes to the surface state wavefunction at the relevant above-surface distances, the resonance condition takes the form:

$$E - v_p \mathbf{k} + \tfrac{1}{2} v_p^2 = E_a \qquad (1)$$

where v_p is the projectile velocity and $\mathbf{k}$ is the reduced wavevector at the surface. Substituting for E the approximate form deduced above for the electron energies in the surface band, Eq (1) can be rewritten as $(\mathbf{k} - v_p)^2 = K_a$ with $K_a \equiv \sqrt{2|E_a - E_b|}$. The density of occupied surface states satisfying this resonance condition is proportional to the geometric overlap between a circle of radius K_a and a disk of radius k_F, the "Fermi velocity" of the surface band, shifted by projectile velocity v_p in the momentum plane parallel to the surface. The velocity dependence of the scattered neutral fractions for incident alkali projectiles can now be easily visualized by reference to the diagrams shown in figure 2. For $K_a < k_F$ (i.e., atomic level below the top of the occupied surface band), from initial complete overlap with occupied states, the neutral fraction will decrease monotonically with increasing parallel velocity at a threshold of ionization $V_{th} = k_F - K_a$, falling to zero above $V_{max} = K_a + k_F$. The velocity dependences of the measured scattered neutral Na and K fractions display such behavior. For $K_a > k_F$ (i.e., atomic level above the top of the occupied surface band), the neutral fraction will start to increase from zero when the surface band electrons are first brought into resonance at a threshold velocity of $V_{th} = K_a - k_F$, reach a maximum, and then decrease as the overlap decreases again. At a velocity $V_{max} = K_a + k_F$ the overlap, and therefore the neutral fraction go to zero. The

velocity dependence of the Cs neutral fraction appears to exhibit such a behavior. In either case, the geometric overlap, Γ, is given by the following expression:

$$\Gamma = \arccos(\frac{E_g + \frac{1}{2}v_p^2}{K_a v_p}) / \pi \qquad (2)$$

where E_g is called the "energy gap", i.e. the difference between the target Fermi level and the shifted atomic level in question. The energy gap is given by $E_g = \Phi - E_a = \Phi - \left| E_a^\infty + \Delta E_a \right|$, with Φ the workfunction of the target, E_a^∞ and ΔE_a the unperturbed binding energy and image shift of the relevant atomic level, respectively. Within this framework, therefore, the detailed parallel velocity dependence of the neutral charge fraction can provide information on the location of the target Fermi level in relation to the relevant projectile levels as well as k_F, the "Fermi velocity" of the surface band.

Using this simple two dimensional model, fits to the data shown in Fig. 1 based on equation (2) give "energy gaps" of 0.4±0.2 eV, 0.2±0.2 eV, and 0.34±0.01 eV for the Na, K, and Cs neutrals, respectively (for reasons discussed in Ref.[5], the Cs data below v_p=0.065 a.u. were excluded from the above fits). Using the known neutral binding energies of Na and K, both of which give negative E_g, and recalling that neutral levels are shifted upward by the image interaction, an *upper* limit of the target work function of 4.2 eV is then suggested by the data. A surface band Fermi energy of 0.8±0.3 eV is also deduced from these fits. This value is consistent with our initial crude estimate above, and serves as a posteriori justification of the simple relation employed for the surface band electron energies.

In order to obtain a *lower* bound to our surface band Fermi level estimate and also to check the internal consistency of our approach, we have also measured the velocity dependences of negative ion formation. Figure 3 shows our results of the scattered negative ion fractions for grazingly incident O, F, and B ions in the projectile velocity range 0.12 - 0.56 a.u. Fractions for all three projectile species show characteristic kinematic resonance peak shapes, with maxima for incident F and O projectiles approaching 80% and 60%, respectively, in good agreement with the measurements of Auth et al.[4], and for incident B projectiles approaching 3%. Using equation (1) in a similar manner as described in previous paragraphs, we obtain for fitted values of the energy gap between the surface-band Fermi-level and atomic affinity levels 0.4±0.1 eV, 0.9±0.1 eV, and 1.4±0.1 eV for the F, O, and B projectiles, respectively. In addition, a Fermi energy of 0.7±0.2 eV is obtained from these fits. In view of the fact that even the F negative ion fractions are fitted by a positive energy gap, indicating a Fermi level lying below the F affinity level, a *lower* bound of the work function magnitude of ~3.8 eV is inferred, resulting that negative ion levels are shifted downward by the image interaction.
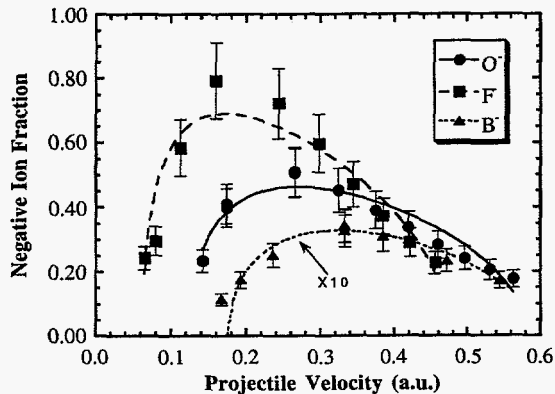

Fig.3 Projectile velocity dependence of the scattered 1⁻ fractions for multicharged F, O, and B projectiles grazingly incident on LiF(100). The lines are fitted curves based on Eq .2
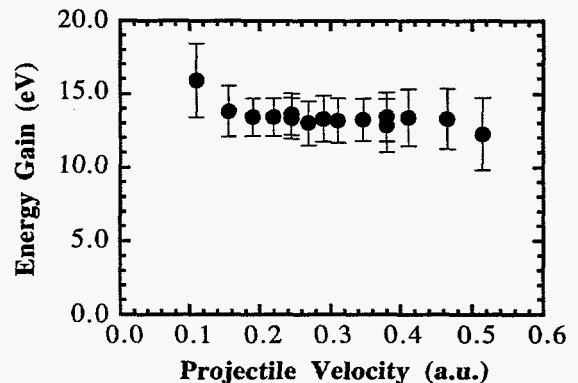
Fig.4 Parallel velocity dependence of the image acceleration energy gain of Ne^{6+} incident on LiF(100) at 0.3°±0.05°.

To further explore the role of resonant electron transfer between occupied surface states and projectile atomic levels, we also investigated the parallel velocity dependence of the energy gain due to image acceleration experienced by a multicharged ion on its approach to the surface. Figure 4 shows the parallel velocity dependence of the image acceleration energy gain of Ne^{6+} incident on LiF(100) at 0.3°±0.05°. The extreme grazing incidence angle assured that even at the highest measured parallel velocities, the change in perpendicular energy due to image acceleration along the incident trajectory could be reliably determined. As can be seen from the figure, the energy gain is almost independent of projectile parallel velocity. This behaviour is in contrast to theoretical predictions[14] for interaction with the LiF valence band, which show a significant decrease of the energy gain over this velocity range, as a result of the strong frequency

dependence of the LiF dielectric function in the vicinity of the resonance near 38 meV, but is similar to that found for measurements on Au(110). Recently published simulation studies [15] have concluded that such insensitivity to parallel velocity may indeed be expected in the case of metal targets. For such targets the energy gain has been shown [15] to be closely approximated by an expression based on the stepwise over-the-barrier neutralization of the projectile during its approach to the surface ("staircase" model): $\Delta E_{im} \approx \frac{\Phi}{2\sqrt{2}}[\frac{2}{3}q^{3/2} - \frac{3}{4}q^{1/2} + 0.521]$, where q is the charge of the projectile. With the observed metal-like parallel velocity dependence serving as justification, we fit recent energy gain measurements[16] for multicharged Cs^{q+}(3<q<24) ions incident on LiF using this expression, and obtained an effective workfunction of ~4.0 eV, suggesting that above surface neutralization of multicharged ions on their approach trajectory may be a sensitive probe of loosely bound occupied surface states as well. More detailed simulations of the energy gains as function of the density of states, carried out at a perpendicular velocity of 0.01 a.u., gave results very similar to the "staircase" model even with a factor of 5 reduction in Fermi energy from typical metal values of 5-6 eV. On the other hand, simulations of the above surface KLL yields for the experimental conditions of Limburg et al.[2], carried out over the same range of Fermi energies, showed an almost 1000 fold decrease, and suggest the possibility that the density of occupied surface states may be insufficient to "fuel" the complete autoionization cascacade. It is noted that, while Auth et al. [3] were able to reproduce reasonably well their measured energy gains using the overbarrier staircase model originally developed for a jellium like target, a work function value corresponding to the top of the valence band (12 eV), and the appropriate dielectric response of LiF, they did not investigate the parallel velocity dependence which suggested the alternative picture discussed above.

In summary, the velocity dependences of the various charge fraction measurements suggest the presence of an occupied LiF surface band lying within 3.8 to 4.2 eV of the vacuum level and having Fermi energy about 0.7 eV. Possible origins for such occupied surface states include the break of the lattice symmetry and the reduced Madelung potential at the top atomic layer. Surface states may also result from intrinsic Li enrichment at the surface due to small differences in the free energies of formation of cation and anion vacancies in ionic crystals [17]. Evidence for intrinsic Li enrichment at a LiF surface had been observed in sputter depth profiling studies [18] even at elevated sample temperatures approaching 400°C as well as in electron loss measurement [19]. Under such a scenario, at sufficiently high sample temperatures, the surface stochiometry returns to the bulk value as the excess Li on the surface is preferentially vaporized. We have seen some evidence for Li surface enrichment in O⁻ fraction measurements performed of sample temperature. Above 400°C a significant drop of the scattered negative ion fraction (about 25%) was observed under well defined specular reflection conditions. A similar decrease of the O⁻ fraction was observed with a NaF(100) sample for temperatures exceeding 250°C. For both alkali halide targets, the onset of significant and irreversible surface roughening at yet higher temperatures degraded specular reflection conditions and prevented a more extensive mapping of the negative ion fraction decrease.

References
[1]   M. Vana et al., Europhys. Lett. **29**, 5560 (1995); Nucl. Instrum. Methods. B100}, 284(1995).
[2]   J. Limburg, et al., Phys. Rev. Lett. **75**, 217 (1995).
[3]   C. Auth, et al., Phys. Rev. Lett. **74**, 5244 (1995).
[4]   C. Auth, et al., Phys. Rev. Lett. **75**, 2292 (1995).
[5]   Q. Yan, J. Burgdörfer, and F. W. Meyer, submitted to Phys. Rev. Lett.
[6]   J. Burgdörfer et al., Phys. Rev. A **44**, 5647 (1991).
[7]   R. Souda et al., Surf. Sci. **324**, L349 (1995).
[8]   J.N.M. Van Wunnik et al., Surf. Sci. **131**, 17 (1983).
[9]   J. D. Levine and P. Mark, Phys. Rev. **144**, 751 (1966).
[10]   L. Folkerts et al., Phys. Rev. Lett. **72**, 2204 (1995).
[11]   F. W. Meyer et al., Nucl. Instrum. and Methods. **B100**, 366 (1995).
[12]   M. Prutton, *Introduction to Surface Physics*, Clarendon Press, Oxford, 1992.
[13]   J. Burgdörfer, in *Progress in Atomic and Molecular Physics*, ed. C. D. Lin (World Scientific, Singapore, 1993) p. 517.
[14]   L. Hägg, C. Reinhold, and J. Burgdörfer, submitted to Phys. Rev. A.
[15]   C. Lemell et al., Phys. Rev. A **15**, 880 (1996).
[16]   Q. Yan, et al., to be submitted to Phys. Rev. A.
[17]   N. F. Mott and M. J. Littleton, Trans. Far. Soc.,**34**, 485 (1938); K. L. Kliewer and J. S. Koehler, Phys. Rev. **140**, A1226 (1965).
[18]   P. Wurz and C. H. Becker, Surf. Sci. **224**, 559 (1989).
[19]   G. Roy, G. Singh, and T. E. Gallon, Surf. Sci. **152/153**, 1042 (1985).