Electron Bihole Complex Formation in Neutralization of Ne^+ on LiF(001)

H. Khemliche, J. Villette, A. G. Borisov, A. Momeni, and P. Roncin,*
Laboratoire des Collisions Atomiques et Moléculaires (CNRS UMR 8625), Bat. 351, Université Paris Sud,
F-91405, Orsay Cedex, France
(Received 28 December 2000)

Neutralization of low keV Ne^+ ions at a LiF(001) surface is studied in a grazing incidence geometry. The combination of energy loss and electron spectroscopy in coincidence reveals two neutralization channels of comparable importance. Besides the Auger process, the Ne^+ neutralization can proceed via peculiar target excitation, corresponding to the formation of an electron bihole complex termed trion.

DOI: 10.1103/PhysRevLett.86.5699 PACS numbers: 34.50.Bw, 34.50.Dy, 63.20.–e, 79.20.Rf

When an atomic projectile is brought in front of a target surface its electronic states couple with those of the surface, giving rise to electronic transitions. The one-electron resonant charge transfer corresponds to an electronic transition between the projectile and target states of the same energy. Owing to the low binding energy of the projectile states, the resonant charge transfer process dominates, e.g., negative ion formation and alkali ion neutralization on metal surfaces [1]. For noble gaz ions such as He^+ or Ne^+, electronic relaxation to the neutral ground state usually involves multielectronic transitions. A typical example is the Auger process, where a conduction electron is transferred to the projectile state of larger binding energy. The excess energy is transferred to another conduction electron which can be emitted from the target [2–4]. For a long time such a process has been thought to be the dominant multielectron process. However, recent experimental [5,6] and theoretical [7,8] studies brought clear evidence that the energy released by the electron capture is not necessarily transferred to an electron-hole pair, but can be efficiently absorbed by a many-body target excitation, such as a bulk or surface plasmon in the case of metals. For insulators, target electronic excitations play a crucial role in surface modifications. For ionic crystals, understanding how the potential energy brought by the projectile is deposited into the target material is of paramount importance. Indeed, particle induced formation of excited states such as self-trapped excitons is known to play a major role in target sputtering and secondary ion emission [9–14],

In this paper, we present results of the detailed study of the neutralization of Ne^+ ions in grazing angle collision on an insulator LiF(001) surface. The combination of energy loss and electron spectroscopy in coincidence reveals that two processes of comparable importance contribute to the projectile neutralization. One is the Auger capture process leading to electron emission from the target. The other corresponds to an electron capture combined with a peculiar target excitation, where two adjacent holes in the valence band accommodate an excited electron to form a trion. This can be viewed as the bound counterpart of the Auger capture since both processes differ only by the energy gained by one of the target electrons. In spite of the challenge that such three-body bound states represent for theory [15,16], their experimental study has been carried only in conditions where a core-level vacancy is being filled by an interatomic Auger decay (see, e.g., [17]).

The main part of the experimental setup [18] is composed of 16 microchannel plate detectors mounted on a hemisphere surrounding the target and placed in a UHV chamber. The chopped incident atom or ion beam is sent at grazing incidence angle onto the LiF(001) target oriented along a high index direction. The scattered beam passes a slit perpendicular to the surface plane where it is charge-state analyzed by a set of plates parallel to the slit. The coordinates of the projectile's impact onto a two-dimensional position-sensitive microchannel plate detector provide the scattering angle and the charge state. Electrons emitted from the target drift freely to the 16 hemisphere detectors where they are accelerated to 400 eV just before striking the microchannel plates. The energies of all detected particles are determined independently by their time of flight referred only to the chopper signal. The LiF(001) surface is prepared by cycles of grazing sputtering by 5 keV Ar^+ ions and annealing at 400 °C. During the experiment, the target temperature is kept above 250 °C to avoid charging effects.

The experiments have been performed for $He^{0,+}$ and $Ne^{0,+}$ projectiles at collision energies between 500 eV to 3 keV. For the sake of clarity, only the results obtained with Ne at 2 keV ($v = 0.06$ a.u.) are detailed. For Ne^+ projectiles, scattered Ne^0 particles are observed but most of the Ne^+ ions do not neutralize [19]. As already observed [20,21], the energy losses of the scattered Ne^+ ions indicate an elastic scattering process (with respect to electron excitation). It is mainly due to the large band gap of the LiF crystal that prevents low energy electronic excitations. Consistently the Ne^+ scattered ions are not correlated with electron emission. Taking into account the localization of the valence band electrons at F^- lattice sites, Hecht *et al.* [19] proposed that neutralization occurs via an interatomic Auger process involving the Ne^+ projectile and two neighbor F^- sites of the crystal. The Ne^+

projectile captures a $2p$ electron from one F^- site while a $2p$ electron of another F^- site is emitted in the field of the two holes left at the surface. Figure 1 displays the evolution with the angle of incidence of the total fraction of scattered neutral particles. The rapid increase from 30% to 55% outlines the high sensitivity of the neutralization probability to the distance of closest approach.

Depending on the angle of incidence, the energy spectrum of the emitted electrons peaks between 1 and 2 eV. Owing to the negative electron affinity of the LiF crystal with a conduction band starting 2 eV above the vacuum level, these low energy electrons can be emitted only to the vacuum side [22]. However, even after an account of the actual detection efficiency [22,23], Fig. 1 shows that most of the neutralization is not correlated with electron emission, indicating the presence of two neutralization processes. The first one is associated with electron emission and is responsible for the rapid increase of the neutral fraction with the incidence angle, suggesting that this first process occurs close to the surface around the turning point of the projectile trajectory. The second one is not associated with electron emission and its contribution hardly depends on the angle of incidence.

Figure 2a shows that the mean energy loss associated with these processes depends on the incidence angle and that the energy loss of scattered Ne^0 particles is systematically smaller when no electron is emitted. Since the conduction band starts 2 eV above the vacuum level, this smaller energy loss indicates a possible transition towards states below the vacuum level rather than to the conduction band.

To derive the electronic energy defect associated with the neutralization processes, the elastic contributions have to be properly subtracted. The first contribution is associated with the recoil of the target atoms during the short distance core-core collisions involved in the scattering process. It was measured directly with a pulsed neutral Ne^0 beam, and the values agree well with recent measurements and classical trajectory simulations [21,24]. The second elastic contribution is the energy loss to the excitation of optical phonons via the long-range electrostatic coupling with the ion charge [20]. For incident Ne^+ projectiles, the energy loss of the scattered Ne^+ is merely the sum of both contributions [20,21] allowing a straightforward evaluation. As the neutral fraction is small, neutralization occurs on average at the apex of the trajectory and, therefore, the energy loss to optical phonons of scattered Ne^0 is only half that of scattered Ne^+ ions. Finally, the kinetic energy E_e of the emitted electrons can be subtracted to determine the energy loss associated with the emission of threshold (zero energy) electrons. The resulting inelastic energy losses associated with the two neutralization processes are displayed in Fig. 2b. Within the error bars, these electronic energy defects do not depend on the angle of incidence, so that mean values of 7.5 ± 1 and 4 ± 1 eV can be derived for the two processes.

This indicates that, in addition to the $I_{\mathrm{Ne}} = 21.6$ eV potential energy brought by the Ne^+ projectile, an energy of 7.5 eV is taken from the projectile kinetic energy to emit a threshold electron. So 29.1 eV energy is actually

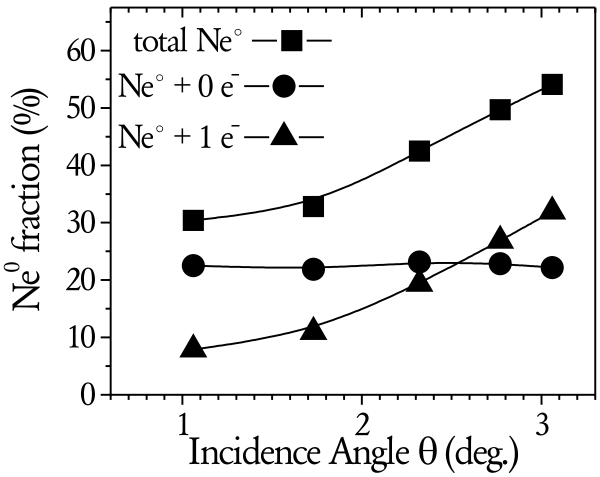

FIG. 1. For collision of 2 keV Ne^+ ions on LiF(001), the incidence angle dependence of the total neutral fraction (■) is split into the neutral fractions associated (▲) or not (•) with electron emission.

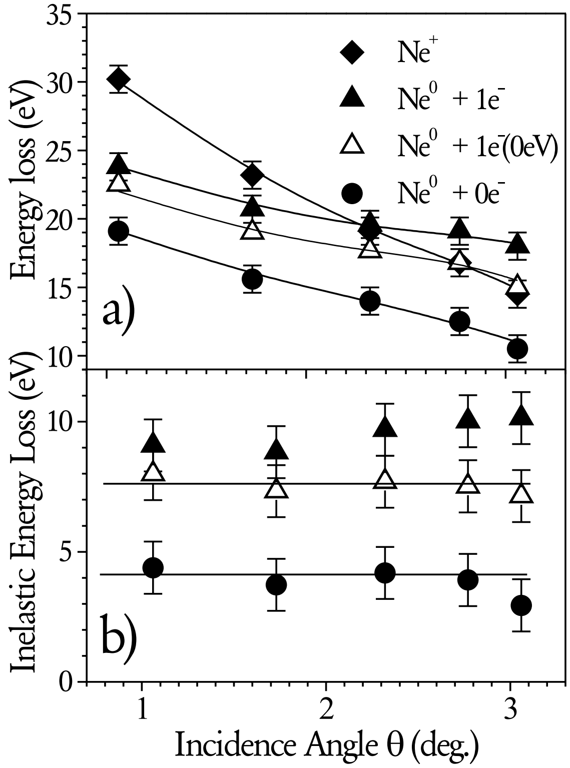

FIG. 2. Mean energy loss of the three channels observed, Ne^+ (◆), Ne^0 associated (▲), and Ne^0 not associated (•) with electron emission. (a) Raw data and (b) inelastic energy losses after correction of the elastic contributions. Open triangles (△) correspond to the subtraction of the observed mean electron energy. The lines through the data are to guide the eye.

required to create two holes on the surface and to emit a zero energy electron. This energy can be decomposed into twice the value of the valence electron binding energy in a LiF crystal (I_{LiF}) plus the hole-hole interaction energy $E_{h\text{-}h}$. By assuming $I_{\mathrm{LiF}} \approx 13$ eV [22,25], a value of

$$E_{h\text{-}h} = I_{\mathrm{Ne}} + 7.5 - 2I_{\mathrm{LiF}} = 3.1 \pm 1 \text{ eV}$$

is determined. This value is consistent with theoretical data for bulk NaF [26] and provides the typical magnitude of the hole-hole interaction energy in the ionic crystal. Neglecting screening effects, this Coulomb energy corresponds to a hole-hole separation of 8 a.u., close to the 7.6 a.u. lattice constant. Alternatively, considering the distance of 5.4 a.u. between closest neighbors, such a Coulomb energy is obtained by introducing a screening factor of 0.7, which seems quite reasonable considering the electronic part of the dielectric constant of the LiF crystal, $\epsilon_\infty = 1.96$. Thus, our results give first direct evidence that the two holes are created within a unit cell, confirming the interpretation in terms of interatomic Auger process [19] involving neighbor F^- sites.

The inelastic energy loss of the neutralization process that is not correlated with electron emission is close to 4 eV (Fig. 2b). Quasiresonant neutralization from the $F^-(2s)$ and $F^-(2p)$ states would yield, respectively, an energy loss of 14.4 eV or an energy gain of 8.6 eV (an energy loss of -8.6 eV in the present notation). Therefore, the observed energy loss of 4 eV indicates a transfer-excitation process, where one electron is captured from the $F^-(2p)$ valence band while an excitation energy,

$$E_{\mathrm{ex}} = I_{\mathrm{Ne}} - I_{\mathrm{LiF}} + 4 \text{ eV} = 12.6 \text{ eV},$$

is left on the target. Since the crystal ions are too slow to respond on the time scale of the electron transfer to the Ne^+ projectile, E_{ex} is necessarily absorbed by an electronic excitation of the target.

Since the excitation energy E_{ex} is not observed in the energy loss spectrum of scattered Ne^+ ions and the capture (Ne^0 formation) is not observed without electron excitation or emission, the excitation and the electron capture processes are fully correlated. It seems difficult to imagine that the electron capture and the target excitation could remain correlated while taking place far away from each other. In addition, one would have to explain how the energy can be stored in between these sites. Note also that in the same scattering conditions almost no electronic excitation is observed for Ne^0 projectiles [27]. Both processes necessarily take place within neighboring lattice sites. The observed neutralization without electron emission therefore appears as the bound counterpart of the Auger process. The electron transfer from the F^- site to the Ne^+ projectile is accompanied by the excitation of a $2p$ electron of the neighbor F^- site, not to the continuum above the vacuum level but to a bound state of the potential created by the two holes. The interpretation is then consistent with the quantum defect theory, which states that no discontinuity occurs on both sides of a threshold.

The combination of two holes binding an excited electron in a sort of excited quasimolecule is mentioned in the literature as an electron bihole complex or trion [28]. Comparing the energy losses associated with Ne^+ neutralization without electron emission or with emission of a zero energy electron (Fig. 2a) yields 3.5 ± 1 eV as a mean binding energy of the electron in the two hole potential. Note that this procedure bypasses all the elastic corrections and takes into account the same transient final state of the two holes (at neighbor sites) in both cases. This is substantially larger than the 1 eV measured for individual surface excitons [22], indicating a different nature of the excited state. Indeed, in the present case, an electron is bound by the field of two positive charges (holes), compared to only one for the surface exciton.

So far the proposed theory does not explain the mechanism of the inelastic energy transfer where, in addition to the 21.6 eV potential energy brought by the projectile, 7.5 eV has to be taken from the kinetic energy of the projectile to emit a threshold electron or, correspondingly, 4 eV to form a trion. The explanation comes from the analysis of the Hartree-Fock calculation performed for the Ne^0 atom approaching the F^- site of the LiF(001) surface along the surface normal (Z-axis). As the Ne^0-F^- distance is reduced, the adiabatic state associated at infinite separation with the $Ne^0 2p$ ($F^- 2p$) orbitals are demoted (promoted). This effect is particularly strong for $2p_Z$ orbitals, which are oriented along the molecular axis. Considering an electron transfer between the $F^- 2p_Z$ and the $Ne^0 2p_Z$ adiabatic states, the energy gained during this transition, $\Delta E = E(Ne^0 2p_Z) - E(F^- 2p_Z)$ increases as the separation Z between the two atoms is reduced. Figure 3 shows that the 7.5 eV additional energy needed to emit a

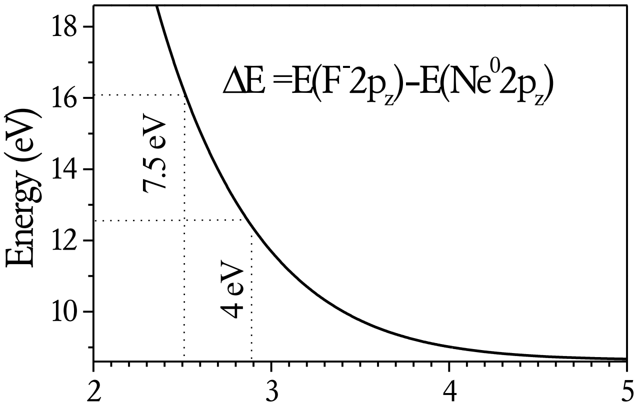

FIG. 3. Evolution of the binding energy difference between the target $F^-(2p_Z)$ and the projectile $Ne^0(2p_Z)$ orbitals. The two horizontal dotted lines correspond to the measured inelastic energy losses for the emission of threshold electrons and for the population of trions.

threshold electron is reached at about $Z_e = 2.5$ a.u., while the 4 eV needed to form a trion is reached at a noticeably larger distance, $Z_t = 2.9$ a.u.

This explains why the efficiency of the Ne^+ neutralization channel with trion formation is much less sensitive to the incidence angle than the Auger channel. Indeed, as follows from a classical trajectory simulation based on the binary interaction potentials derived from the Hartree-Fock calculation, the $Z_t = 2.9$ a.u. distance to the surface is always reached by the projectile under our scattering conditions. At the same time the $Z_e = 2.5$ a.u. distance turns out to be close to the trajectory apex so that increasing the scattering angle opens up the neutralization channel associated with electron emission.

For He^+ projectiles the ionization potential is larger by 3 eV and the energy defects for trion formation or Auger neutralization are reduced by the same amount, making the trion formation a quasiresonant process. For collision of 1 keV He^+ ions at 1.1° incidence, we observe that almost 80% of the projectiles are neutralized, in good agreement with [19]. As for Ne^+ at such grazing incidence, our data point to the trion formation as the dominant neutralization channel, so that overall almost 60% of the scattering events give rise to the formation of a trion on the surface.

In conclusion, we have presented results of the experimental study of Ne^+ and He^+ neutralization at a LiF(001) surface. Our results demonstrate that electron capture from the valence band is not necessarily accompanied by electron emission as in the standard Auger neutralization picture. In fact the potential energy gained by the electron transfer from the valence band to the projectile can be stored in an excited state at the surface, corresponding to an electron bihole complex or trion. Interestingly, this quasimolecular exciton is very loosely bound since the electronic binding energy is very close to the hole-hole repulsion. Finally, the mechanism of energy transfer between the projectile motion and electronic transitions can be rationalized in terms of adiabatic orbital energy difference in the Ne-F^- collisional complex.

Contrary to metal targets, the hole-hole interaction in the ionic crystal is only partly screened with definite consequences on the energy balance for successive electron removal from the valence band. This aspect should play an important role in the neutralization dynamics of highly charged ions at ionic crystal surfaces [13]. From the surface point of view, the density of holes created and their mobility should drastically influence the so-called potential sputtering process, which is seen to be the base for applications, such as selective removal of insulating layers or nanoscale surface modifications.

The authors are indebted to J. P. Gauyacq for fruitful discussions throughout this project.

---

*Corresponding author.
Electronic address: roncin@lcam.u-psud.fr

[1] J. Los and J. J. C. Geerlings, Phys. Rep. **190**, 133 (1990).
[2] H. D. Hagstrum, Phys. Rev. **96**, 336 (1954).
[3] P. Eeken, J. M. Fluit, A. Niehaus, and I. Urazgil'din, Surf. Sci. **273**, 160 (1992).
[4] V. Kempter, Comments At. Mol. Phys **34**, 11 (1998).
[5] P. Riccardi *et al.,* Phys. Rev. Lett. **84**, 378 (2000).
[6] R. A. Baragiola, in *Low Energy Ion-Surface Interactions,* edited by J. W. Rabalais (Wiley, New York, 1994).
[7] N. Lorente and R. Monreal, Phys. Rev. B **53**, 9622 (1996); Surf. Sci. **370**, 324 (1997).
[8] P. M. Echenique, F. Flores, and R. H. Ritchie, in *Solid State Physics: Advances in Research and Applications,* edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1990), Vol. 43, p. 229.
[9] G. Hayderer *et al.,* Phys. Rev. Lett. **83**, 3948 (1999).
[10] P. Varga and U. Diebold, in *Low Energy Ion-Surface Interactions,* edited by J. W. Rabalais (Wiley, New York, 1994).
[11] N. Seifert *et al.,* Phys. Rev. B **51**, 12 202 (1995).
[12] T. Neidhart *et al.,* Phys. Rev. Lett. **74**, 5280 (1995).
[13] See e.g., A. Arnau *et al.,* Surf. Sci. Rep. **27**, 113 (1997).
[14] Z. Sroubek and H. Oechsner, Surf. Sci. **311**, 263 (1994).
[15] J. P. Gallinar, Phys. Rev. B **35**, 6464 (1987).
[16] M. Shibata *et al.,* Phys. Rev. B **42**, 2432 (1990).
[17] T. Ishii *et al.,* Phys. Rev. B **33**, 5664 (1986).
[18] V. A. Morosov *et al.,* Rev. Sci. Instrum. **67**, 2163 (1996).
[19] T. Hecht *et al.,* Phys. Lett. A **220**, 102 (1996).
[20] A. G. Borisov *et al.,* Phys. Rev. Lett. **83**, 5378 (1999).
[21] J. Villette *et al.,* Phys. Rev. Lett. **85**, 3137 (2000).
[22] P. Roncin *et al.,* Phys. Rev. Lett. **83**, 864 (1999).
[23] J. Villette *et al.,* Rev. Sci. Instrum. **71**, 2367 (2000).
[24] A. Mertens and H. Winter, Phys. Rev. Lett. **85**, 2825 (2000).
[25] D. Ochs *et al.,* Surf. Sci. **383**, 162 (1997).
[26] T. A. Green and D. R. Jennison, Phys. Rev. B **36**, 6112 (1987).
[27] A. Momeni *et al.* (to be published).
[28] A. Thilagam, Phys. Rev. B **55**, 7804 (1997).