Evidence for the Stopping of Slow Ions by Excitations of Optical Phonons in Insulators

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(Received 26 May 1999)

The energy loss of Ne^+ ions with keV energies scattered under grazing incidence from a LiF(001) surface is studied with a time-of-flight technique. Since charge exchange in front of the wide-band-gap insulator is widely suppressed, the energy loss of slow ions moving in front of the solid can be investigated under specific interaction conditions. From the theoretical analysis of data we find evidence for an energy loss mechanism based on the excitations of optical phonons in the insulator.

PACS numbers: 79.20.Rf, 34.50.Bw

When atomic particles collide with solid matter, excitations in projectile and target give rise to stopping phenomena. For slow ions electronic excitations, charge exchange, and binary collisions with target atoms ("nuclear stopping") clearly dominate the dissipation of energy in ion-solid collisions [1]. Whereas nuclear stopping can be described in a straightforward manner, the treatment of electronic processes is a more intricate subject. For metal targets, considerable progress in the theoretical description of electronic stopping has been achieved over about the last decade [2]. Excitation of electron-hole pairs is the primary mechanism for electronic stopping of slow ions, i.e., projectiles with velocities $v \ll v_0$ (v_0 = Bohr velocity = 1 atomic unit = 1 a.u.). In the framework of corresponding theories, characteristic features for the stopping of slow ions by metal targets, e.g., a linear dependence of the stopping power $-dE/dx$ on the projectile velocity v or oscillations of $-dE/dx$ with atomic number of the projectiles Z_1 ("Z_1 oscillations"), can be described on a quantitative level [3].

An interesting aspect concerning the stopping of slow ions is the role of collective excitations. Whereas at higher projectile velocities excitations of plasmons (typical energies $\hbar\omega \approx 10$ eV) result in substantial contributions to energy loss [2,4], these excitations will have small effects on the stopping of slow ions [5]. From a theoretical analysis Echenique and Howie [6] concluded that at low velocities only collective excitations at low frequencies, as, e.g., optical phonons in ionic insulators (typical energies $\hbar\omega_{\mathrm{ph}} \approx$ some 10 meV [7]) will contribute. In order to observe this mode of stopping, other sources for dissipation of energy of slow ions (single excitations, charge exchange, nuclear stopping) has to be reduced. To our knowledge, corresponding experimental work has not been reported so far.

In this Letter, we report on joint experimental and theoretical studies where unequivocal evidence for the stopping of slow ions in front of an ionic insulator by excitation of optical phonons is obtained. We will demonstrate that under specific experimental conditions for collisions of ions with solid matter, the excitations of phonons clearly dominate the stopping process. Our experiments are performed with Ne^+ ions at keV energies ($v \leq 0.1$ a.u.) scattered under grazing angles of incidence (typically $\Phi_{\mathrm{in}} \approx 1°$) from a clean and flat LiF(001) surface. Under these scattering conditions ("planar surface channeling" [8]) trajectories for projectiles result from a sequence of small-angle scattering in collisions with target atoms. This means large impact parameters and, consequently, a small energy transfer (energy loss $\Delta E < 1$ eV) to the nuclear motion via short range interactions.

The use of an ionic insulator (LiF) implies important features for our studies that clearly differ from those of a metal:

(1) For wide-band-gap insulators as LiF (binding energy of electrons at the top of the valence band $E_b \approx 12$ eV, band gap $E_g \approx 14$ eV [9]) direct electronic excitations by slow ions can be excluded.

(2) A further consequence of the electronic structure of LiF is a substantial suppression of any type of charge exchange. In particular, "Auger neutralization" (AN) is widely suppressed, because final states can be found only in the band gap. Then substantial fractions of Ne^+ ions can be scattered from a LiF surface without undergoing charge exchange, i.e., the charge state of the incident Ne^+ ion is preserved and defined over the complete trajectory [10].

(3) LiF is a good example of an ionic crystal with Li^+ and F^- ions at the lattice sites. It is characterized by acoustical and optical phonon branches. The optical phonons couple efficiently to the long ranged Coulomb

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field of the projectile owing to the dipole moment resulting from opposite displacements of positive and negative charges at lattice sites. This is in contrast to metals where only short ranged interactions contribute to the energy transfer between projectile and lattice, since long ranged interactions are efficiently screened.

In our studies we make profit of these specific features and measure with a time-of-flight (TOF) setup the energy of Ne^+ ions scattered from the surface of the wide-band-gap insulator LiF. The grazing scattering of projectiles from the surface proceeds under UHV conditions (base pressure: upper 10^{-10} mbar range) with the target at a temperature of about 300 °C in order to avoid a macroscopic charging up by projectiles. The incident ion beam is chopped by electric field plates, scattered from the target surface, and hits a channel plate 1.03 m distant from the target after about 10 μs. Pulses from the detector serve for the "start," and the "stop" signal is obtained from the delayed beam chopper signal. The overall energy resolution [comprising an energy width of the filament/hollow cathode ion source (SO55, HVEE) of about 1 eV] achieved with our setup is some eV.

In Fig. 1 we display typical TOF spectra (converted to an energy scale) for 2 keV Ne^+ ions scattered under $\Phi_{in} \approx 0.75°$ from a LiF(100) surface. The data plotted by full circles represent spectra obtained in separate measurements for the incoming beam (no target in beam) and for the scattered beam. The scattered beam contains a fraction of about 30% neutralized projectiles (Ne^0) [10]. A spectrum for projectiles that have undergone charge exchange is separated by means of electric field plates (open circles). Main sources of errors in our investigation are identified to be shifts in the signal from the delay generator (controlled by time measurements), the calibration of the time scale, variations of the projectile energy owing to fluctuations of the discharge in the ion source, and a slight decrease of the flight path with increasing angles of scattering. These sources are taken into account by the error bars shown. The overall consistency of data is sufficient in order to demonstrate evidence for projectile energy losses dominated by optical phonon excitations.

Since the energy spectra are quite symmetrically in shape, mean and most probable energy losses are the same in view of the quality of data. The contributions to the spectra owing to Ne^0 atoms will be discussed below. In Fig. 2 we present for three selected energies (1.5, 4, and 5 keV) the energy loss as a function of the angle of incidence Φ_{in}. The angles are deduced from an analysis of angular distributions for scattered projectiles. An important finding in our experiments is that the energy loss ΔE decreases with increasing energy and with increasing angle.

As we pointed out above, the energy loss owing to small angle scattering with lattice atoms is expected to play a negligible role under our conditions for scattering. For channeling these losses are estimated to sub-eV, in clear disagreement to about 20–35 eV as observed here. Furthermore, for short range collisions between projectiles and target atoms, the energy loss should increase with projectile energy and angle of scattering. This is not observed in the data displayed in Fig. 2.

The curves in Fig. 2 represent calculations of the energy loss of a projectile with charge Q on the basis of a surface response formalism. This formalism has been successfully applied to treat electronic excitations [1–3,11], Auger-type processes [12,13], formation of wake potentials [14], etc. We use the surface response function

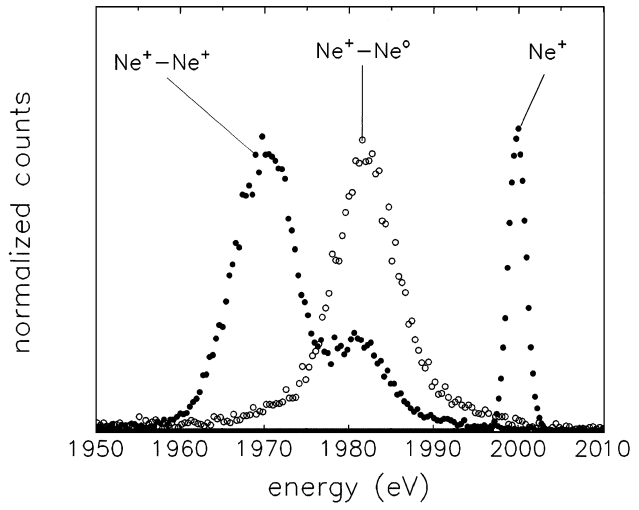

FIG. 1. TOF spectra (converted to projectile energies) for incident 2 keV Ne^+ ions (full circles), emerging Ne^+ ions (full circles) after scattering, and emerging Ne^0 ions (open circles). The spectra are arbitrarily normalized to the same heights of the maxima.

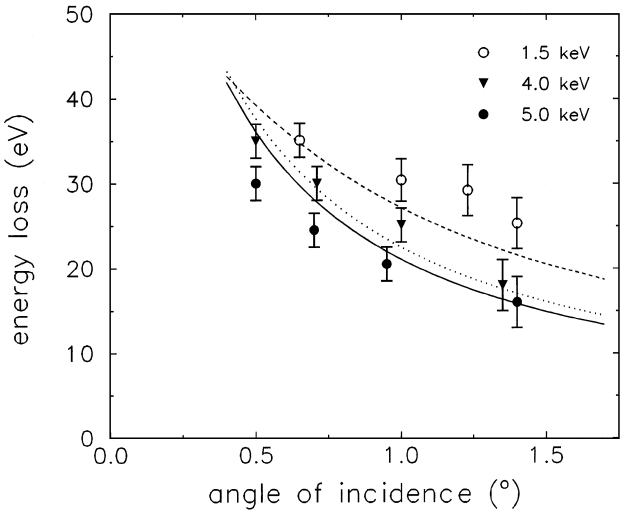

FIG. 2. Energy loss as a function of angle of incidence for 1.5, 4, and 5 keV Ne^+ ions scattered from LiF. The solid (5 keV), dotted (4 keV), and dashed (1.5 keV) curves represent results from our calculations (see text).

$[\varepsilon(\omega) - 1]/[\varepsilon(\omega) + 1]$ with the dielectric constant $\varepsilon(\omega)$ deduced from optical data for LiF [15], i.e., we neglect a spatial dispersion $\varepsilon(\vec{k}, \omega)$. Neglect of the spatial dispersion of the dielectric constant and use of optical data implies that only large wavelength components λ of the projectile field will contribute to the surface response; i.e., $\lambda > a$, where $a = 7.6$ a.u. is the lattice constant of LiF. From surface response theory [14], one estimates a critical distance below 2–3 a.u., where a dispersion of the dielectric constant might be important. At the higher end of scattering angles and collision energies in our studies, the turning points of projectile trajectories are close to this limit, and theory used here has to be considered with some care.

Within the surface response formalism one finds for the position dependent stopping power for a particle moving with charge Q and velocity v in front of the surface (atomic units) [6,11]

$$S(z) = \frac{2Q^2}{\pi v^2} \int_0^\infty d\omega\, \omega K_0\left(\frac{2\omega z}{v}\right) \mathrm{Im}\left(\frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1}\right), \quad (1)$$

where K_0 is the modified Bessel function of order 0. The imaginary part of the surface response function describes possible excitations in the target, which are concentrated for LiF to two frequency (energy) domains. For $\hbar\omega \geq 12$ eV optical absorption corresponds to electronic excitations from valence band to conduction band states or to excitons. At low frequencies, $\hbar\omega \approx 40$ meV, one has excitations of the optical phonon band, equivalent to an energy transfer into oscillations of ions at crystal lattice sites. We note that the stopping force acting on a projectile is oriented parallel to the surface. In grazing scattering the slow motion normal to the surface proceeds adiabatically without energy dissipation. Thus energy losses are not accompanied by an additional angular deflection of scattered projectiles.

For the range of distances and velocities of our studies with Ne^+ projectiles ($z \geq 2$ a.u. and $v \leq 0.1$ a.u.), the projectile motion will not couple to electronic excitations [K_0 in Eq. (1) is too small]. At variance, the projectile can dissipate a fraction of its energy via excitations of the optically active phonon band [6]. The energy loss of scattered projectiles is obtained from integrations over trajectories

$$\Delta E = \int_{\text{trajectory}} S(z)\, dx\,, \quad (2)$$

with the coordinate x chosen parallel to the surface. The trajectory is obtained from collective binary interaction potentials derived from quantum chemistry calculations [16] under incorporation of an image charge potential deduced also from the surface response formalism. For distances and velocities of relevance here, this image potential is well approximated by the simple classical expression $V_{\text{im}} = -[(\varepsilon_\infty - 1)/(\varepsilon_\infty + 1)][Q^2/4z]$ with $\varepsilon_\infty = 1.98$ for LiF [15]. By making use of other types of atom-surface interaction potentials, as, e.g., Ziegler-Biersack-Littmark potential [1]—the calculated energy losses differ by 1% to 15% depending on the energy for the normal motion. This is primarily caused by modified distances of closest approach and trajectories for the projectiles.

A comparison of our calculations with the experimental data is presented in Fig. 2. The overall agreement is good, in particular, specific features of the experiments as the dependence of ΔE with angle and projectile energy are correctly described by theory. In view of the approximations in the theoretical approach as well as the experimental sources for uncertainties mentioned above, slight deviations on a quantitative level, especially for the 1.5 keV data, should not be overestimated. We conclude from the data displayed in Fig. 2 first evidence for the dominant role of energy dissipation into excitation of (optical) phonons in an ion-solid scattering experiment.

In Fig. 3 we show the energy loss of Ne^+ ions as a function of projectile energy for a constant angle of incidence $\Phi_{\text{in}} = 1°$. The full circles [curve (a)] represent data for scattered Ne^+ ions which agree fairly well with theory (solid curve) outlined above. Note that the energy loss decreases with projectile energy. The open circles [curve (b)] in Fig. 3 represent data for Ne^0 atoms neutralized in the surface collision, presumably by an Auger neutralization process [10]. These energy losses are clearly smaller, as we have already shown in the spectra presented in Fig. 1.

From the following argument we conclude that this finding is consistent with our interpretation of data. Since the majority of incoming Ne^+ ions survives from Auger neutralization, Auger transition rates should be sufficiently

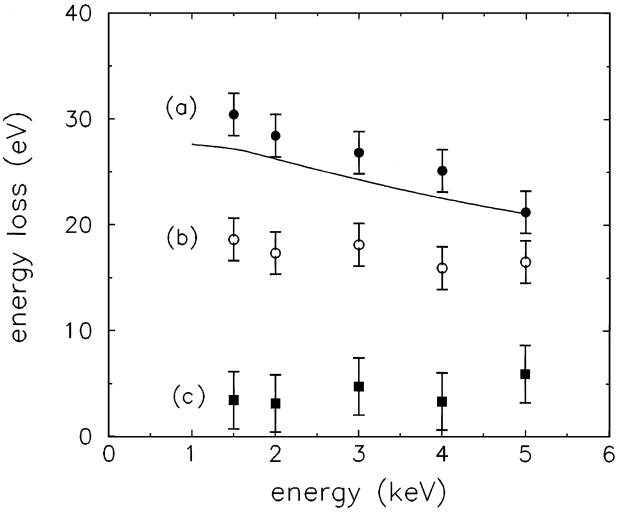

FIG. 3. Energy loss as a function of projectile energy for Ne^+ ions scattered from LiF under $\Phi_{\text{in}} = 1°$. Full circles (a): ΔE^+ for emerging Ne^+ ions; open circles (b): ΔE^0 for emerging Ne^0 atoms; full squares (c): energy difference $\Delta E^0 - \Delta E^+/2$. The solid curve represents results from our calculations (see text).

low, so that the neutralization proceeds around the closest distances of approach at the apex of trajectories; i.e., neutralized projectiles are singly charged on the first half of their trajectory and neutral on the second half. Since $S(z)$ and ΔE in Eqs. (1) and (2) scale with projectile charge, one expects then for the energy loss of neutralized Ne^+ ions $\Delta E^0 \approx \Delta E^+/2$ or $\Delta E^0 - \Delta E^+/2 \approx 0$. Inspection of data displayed in Fig. 3 reveals, however, that this difference is systematically larger by about 3 to 5 eV from zero [full squares, labeled (c)].

This difference can be understood by the energy difference of 9.6 eV between the top of the valence band (12 eV) and the Ne ground state (21.6 eV). Then an energy defect of at least 2.4 or 4 eV is present for Auger neutralization with excitation to vacuum or conduction band states, respectively. This energy defect has to be compensated by the kinetic energy of the projectiles. The effect observed in our studies supports this interpretation. One of the possible mechanisms of such an Auger process is a binary type quasimolecular or "Diabatic II" Auger transition [17]. Electronic states involved in this transition correspond to the molecular orbitals of the Ne^+/F^- system which are strongly splitted by the interaction [18]. In this respect, we note that energy loss spectra provide important additional information on the charge transfer process in comparison to a sheer analysis of charge states. This kind of "translational spectroscopy" [19] applied to ion-surface interactions has been demonstrated recently for the scattering of H^+ from a LiF surface [20,21].

In conclusion, grazing scattering of slow Ne^+ ions from a LiF(001) surface provides favorable conditions for the observation of a projectile energy loss owing to the excitation of optical phonons. Contributions from well-established mechanisms for energy loss of slow and swift ions interacting with solids are found on a negligible level for the specific system studied here. On the basis of linear response theory we succeed to describe the experiments on a quantitative level and to obtain substantial support for our interpretation. The observed effect of the energy loss on the outgoing charge state of scattered projectiles can be consistently explained by our approach.

The assistance of K. Maas, T. Bernhard, S. Lederer, R. A. Noack, and A. Laws in the preparation and running of the experiments and valuable discussions with Professor P. M. Echenique, Dr. A. Arnau (San Sebastian), and Professor J. P. Gauyacq (Orsay) are gratefully acknowledged. This work is supported by the Deutsche Forschungsgemeinschaft under Contract No. Wi 1336 and by the Franco-German PROCOPE-programme of DAAD/APAPE.

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