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Electron-stimulated desorption of neutral lithium atoms from LiF due to excitation of surface excitons

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We have measured electron-stimulated desorption of neutral lithium atoms from LiF at energies near the band gap of the crystal. The significant contribution to the desorption yield of neutral alkali-metal atoms due to the creation of surface excitons is resolved. These measurements also prove the theoretically expected threshold for desorption at the energy of the bulk exciton.

I. INTRODUCTION

Electron-stimulated desorption (ESD) from alkali halides has been studied for more than 20 years. Although the mechanism leading to desorption of halogen atoms and consequent evaporation of the alkali-metal atoms is generally agreed on,[1-3] some questions remain of current interest.[4] We will briefly review the most important features of the model.

The interaction of electrons with an alkali halide lattice is restricted to the halogen sublattice. The first step in the desorption process of ground-state alkali-metal atoms is the excitation of a valence electron to a bound state in the band gap (exciton) or into the conduction band (hole), depending on the energy transferred by the primary electron. The exciton or the hole becomes self-trapped, the former forming a self-trapped exciton (STE) directly and the latter forming a self-trapped exciton after trapping an electron.[5] The band gap has a width of 14.2 eV in LiF,[6] whereas 12.6 eV suffices for the creation of an exciton.[7] The STE formed by this excitation may lead to production of a F-H–center pair. A F center is an electron on an anion (X^-) vacancy and an H center is comparable to an $X_2{}^-$ molecule on an anion lattice site. If an H center reaches the surface it will decay by emitting a neutral halogen atom and thus restore the lattice on the surface. Whereas H centers are responsible for halogen emission, F centers cause alkali desorption. F centers formed at the surface or having diffused to the surface will decay in neutralizing a surface alkali-metal ion. At sufficiently high temperatures alkali desorption occurs due to evaporation of the metal layer. In this paper a careful measurement of the desorption yield Li^0 versus electron energy is presented. The results show that desorption can occur at considerable lower energies than the bulk exciton. Comparison with recent electron-energy-loss spectroscopy (EELS) experiments and theoretical electronic structure calculations give evidence for desorption due to excitations of surface excitons or excitations across the reduced surface band gap.

II. EXPERIMENTAL SETUP

Single-crystal (100) surfaces of LiF held at a temperature of 400 °C were irradiated with 5- to 20-eV electrons. The beam current was 10 μA at 20 eV (measured on the crystal) and decreased to 1 μA at 5 eV. The irradiated area had an approximate size of 4 mm^2. The crystal was covered with a molybdenum mesh of 85% transmissivity to prevent sample charging. The electron gun is described in detail in Ref. 8. The work function of the cathode was measured to be $\Phi_c = 1.9$ eV. The voltages for the focus electrode and the anode were optimized to maximum beam current, which corresponds to maximum desorption rate. Floating the cathode with respect to the target by U_{ct} determined the beam energy. The angle of incidence of the electron beam was 45° with respect to the crystal surface normal. We have measured neutral alkali-metal atoms with a quadrupole mass spectrometer viewing the surface perpendicularly. The pulses from the secondary electron multiplier were processed digitally in pulse counting mode. The data points in Fig. 1 reflect an integration time of 100 s each. Careful background determination and subtraction were performed. The UHV system maintained a base pressure of less than 3×10^{-10} mbar during the measurements. Crystals of optical quality have been cleaved in air and cleaned in the vacuum system by prolonged heating at 400 °C, which has been proven to give satisfactory surface cleanness.[9]

During the measurement the crystal temperature was held constant at 400 °C based on the following considerations. This temperature allows for maximum alkali-metal desorption without sublimating the crystal.[10] High temperatures increase ionic mobility, thereby reducing sam-

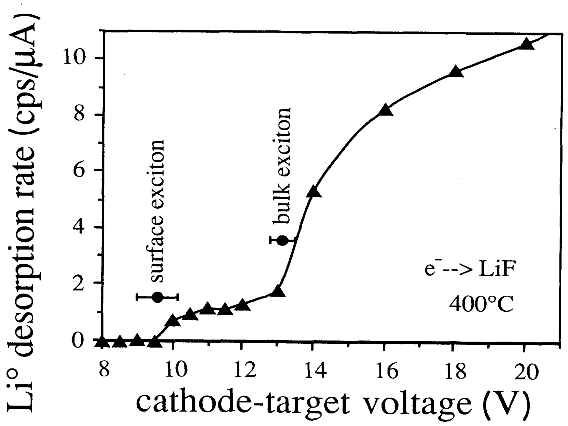

FIG. 1. Li^0 desorption rate as a function of electron energy. A threshold can be seen at the surface exciton energy (9.6±0.6 V) and an edge at the bulk exciton energy (13.1±0.4 V). The energy scale is not corrected for the work functions of the target and the cathode of the electron gun.

ple charging and facilitating surface reconstruction. Consequently, the surface is only moderately damaged, in spite of the high primary current density used.

The actual kinetic energy E_{kin} of the electrons is determined by the potential difference between the vacuum levels of cathode and target. U_{ct} however lies between the two Fermi levels, so that the work functions of cathode Φ_c and target Φ_t have to be accounted for,

$$E_{\text{kin}} = qU_{ct} - \Phi_c + \Phi_t \tag{1}$$

with q the electron charge. The work function of the cathode Φ_c was determined to be 1.9 eV. The determination of the work function of the crystal Φ_t will be discussed in a later section of the paper.

III. EXPERIMENTAL RESULTS

We measured the desorption rate of neutral lithium atoms (Li^0) as function of energy of the incident electron beam given by the voltage U_{ct} between the cathode of the electron gun and the target.

Two important features can be seen in the energy dependence of the Li^0 yield shown in Fig. 1: (i) The Li^0 yield drops sharply towards 13.1±0.4 V; (ii) desorption continues at a small rate down to 9.6±0.6 V. The desorption yield is corrected for the decrease in beam current with decreasing electron energy. The error bars result from six independent series of measurements.

IV. DISCUSSION

We interpret the edge seen at $U_{ct} = 13.1 \pm 0.4$ V in Fig. 1 as the threshold for defect generation in the bulk via bulk excitons. The creation of a bulk exciton requires a minimum energy transfer of 12.6 eV (Ref. 7) to a valence electron. Using Eq. (1) we find $\Phi_t = 1.4$ eV. This is caused by the existence of surface states and will be explained later in this section. The surface states reduce the width of the band gap at the surface.

The desorption below 13.1±0.4 V down to a threshold at $U_{ct} = 9.6 \pm 0.6$ V is attributed to the creation of surface excitons. Using Eq. (1) and $\Phi_t = 1.4$ eV and $\Phi_c = 1.9$ eV, we find the actual energy of the threshold approximately at 9.1±0.6 eV. In a recent high-resolution EELS (HREELS) study,[11] the surface exciton in LiF was found at 10.7 eV. The corresponding exciton edge, which represents the minimum excitation energy, lies at 9.7 eV. The reasonable agreement with Ref. 11 supports our assumption, that the creation of surface excitons is responsible for Li^0 desorption below the energy of the bulk exciton.

Further support for the proposed picture is provided by electronic structure calculations. The calculations are performed using a method recently developed for ionic solids.[12] The method is based on the charge self-consistent extended Hückel theory and qualitatively describes the effects of the Madelung potential on the electronic energy levels. The LiF crystal is modeled using the cluster depicted in Fig. 2. This cluster is sufficiently large to allow a reasonable description of the Madelung potential. This is important since the surface states are strongly influenced by the changes in the Madelung potential at the surface of an ionic solid.[13]

The cluster is also large enough to allow a consistent definition of surface and bulk atoms. The bulk atoms are defined as the atoms closest to the center of the cluster and the surface atoms are the atoms closest to the center of the surfaces of the cluster. The sensitivity of the calculated density of states (DOS) features to cluster size has been checked by application to 2×2×2 and 4×4×4 clusters. The general features of the calculated DOS for these smaller clusters remain the same as for the 6×6×6 cluster but a slight tendency for increasing band gap with cluster size was observed. This observation is analogous to the finding for NaCl clusters.[12] We do however feel confident that Fig. 2 qualitatively represents both the surface and the bulk properties of LiF. The parameters that are required for the modeling of the atomic orbitals as well as the procedure used in the calculation of the density of states are described in Ref. 12.

The results for the total density of states (TDOS) and the local density of states (LDOS) projected onto different sites are presented in the remaining graphs of Fig. 2. The bulk LDOS for Li and F [Li(b) and F(b)] indicates a bulk band gap of around 13 V. This value is slightly smaller than the value 14 eV found for the perfect crystal.[6] The discrepancy is not significant and most likely caused by the present use of a finite cluster. On the surface the occurrence of surface states starting at −5 eV below the vacuum level reduces the band gap to approximately 9 eV. The various surface states result from the lowering of the Madelung potential at the surface. The calculation thus predicts a "surface band gap" of around 9 eV. The surface states will be filled up by continuous electron irradiation, which lowers the work function considerably. This finding is consistent with the appearance of lower excitation thresholds at surfaces.

The previous discussion is illustrated by the schematic

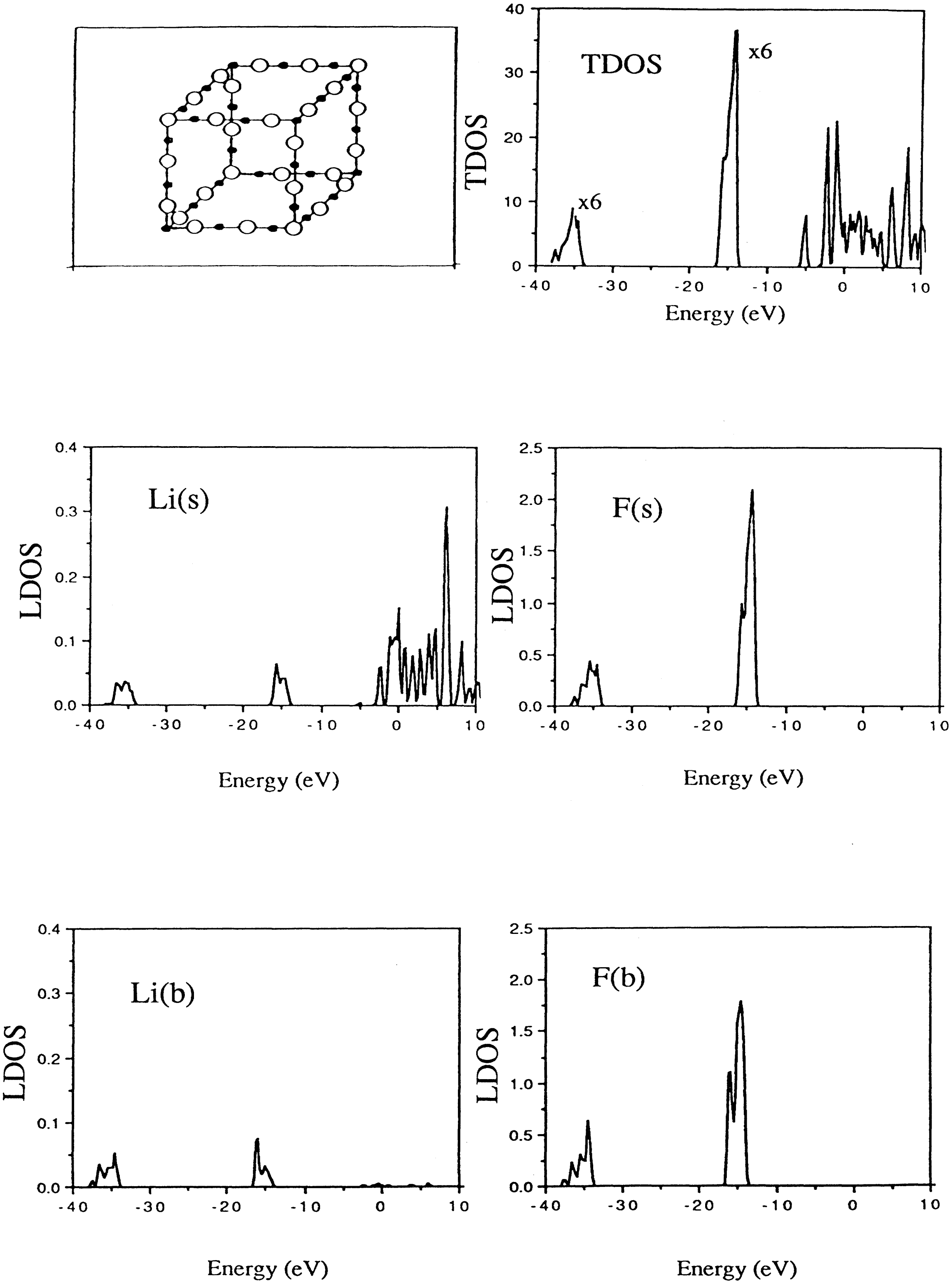

FIG. 2. Calculated TDOS and LDOS projected on a lithium surface atom Li(s), a fluorine surface atom F(s), a lithium bulk atom Li(b), and a fluorine bulk atom F(b), for the $6\times6\times6$ LiF cluster indicated in the upper left-hand corner. The horizontal axis is the energy in eV measured from the vacuum level. The vertical axis is in arbitrary units and different in the different situations. Note that the valence core peaks in the TDOS inset have been scaled down by a factor of 5.

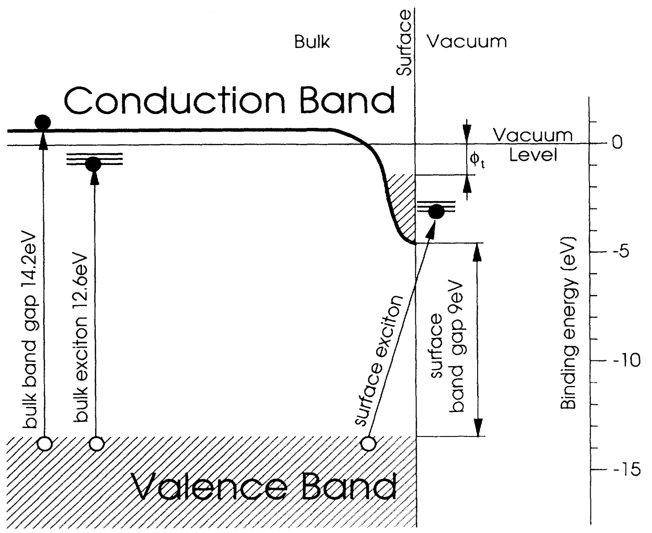

FIG. 3. Schematic drawing of the relevant energy levels in a LiF crystal and how the levels are shifted at the surface.

drawing of Fig. 3, which depicts all relevant energy levels. The energies for the bulk band gap and bulk exciton are taken from Refs. 6 and 7, respectively. The band gap on the surface reduces to 9 eV according to our calculation. The authors of Ref. 11 determined the energy level for the surface exciton and they proposed the final state of the excited electron to be located outside the surface. Electron irradiation fills the states on the surface up to an energy Φ_t below the vacuum level. In sum, the lowered excitation threshold at the surface permits electron-stimulated desorption for primary energies smaller than the bandgap of LiF, which is what we found experimentally.

V. CONCLUSIONS

We have presented measurements of the desorption yield as a function of electron energy from LiF. The experiment reveals a strong desorption threshold at 13.1±0.4 V corresponding to the creation of a bulk exciton. In addition, largely increased sensitivity allowed us to observe desorption by electrons below this threshold down to an energy of 9.1±0.6 eV. Using electronic structure calculations the nature of the lower threshold could be resolved and attributed to the surface-mediated shift in excitation thresholds. These findings are of potential importance for the understanding of the microscopic mechanisms for electron-stimulated desorption from a wide range of different alkali halides. The model proposed might analogously be applicable to photon-stimulated desorption.

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