Optical Radiation from Electron-Stimulated Desorption of Excited Particles

N. H. Tolk, L. C. Feldman, J. S. Kraus, R. J. Morris,[a] M. M. Traum, and J. C. Tully
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 12 September 1980)

Electron-surface collisions have been observed to result in the emission of optical radiation from desorbed atoms and molecules. The first resonance lines of Na and Li from alkali-halide targets, the Balmer lines of hydrogen, and OH molecular radiation are among the optical lines detected. These are the first observations of discrete line and molecular radiation originating from adsorbed particles ejected from the surface due to electron-stimulated desorption.

PACS numbers: 79.20.Kz

In this Letter we report on a newly observed phenomenon, the production of atomic and molecular radiation resulting from electron-stimulated desorption of excited particles. We have observed this effect when electrons with energy of 100–1000 eV are incident on selected alkali-halide and metal surfaces. Three general classes of emitted radiation are found: (a) discrete line radiation from desorbed surface species, such as the hydrogen Balmer lines, and from ejected bulk particles, such as the first resonance lines of sodium and lithium; (b) relatively broadband molecular radiation from free molecules, for example OH radiation emitted in front of the surface; and (c) broadband optical radiation arising from the solid which is known generally to occur when electrons bombard solid surfaces. In these experiments we were principally interested in radiation of types (a) and (b) so that the experimental geometry was chosen to maximize these radiations and to minimize the bulk radiation, type (c).

Considerable experimental and theoretical effort has been devoted to electron-stimulated desorption (ESD) studies of ground-state ions and neutrals[1] for a wide variety of target materials including alkali halides.[2] Relatively few studies have been concerned with particles emitted in excited states; these have dealt primarily with electron-induced production of long-lived metastable neutrals.[3] In one case involving electron-bombardment fluorescence of ice, tentative identification has been made of molecular radiation from OH.[4] The measurements reported here include (1) the first definitive work on radiation from electron-bombardment–induced emission of excited free substrate particles,[5] and (2) the first observations of characteristic radiation from desorbed free atoms and molecules which previously had been absorbates.

The apparatus for these experiments included an electron gun (100 eV to 1 keV), an ion source (100 eV to 10 keV) and a target chamber maintained at ultrahigh vacuum (2×10^{-10} Torr). A ~10-μA electron beam with a current density of ~1 mA/cm^2 was incident at 45° to the surface normal. Single-photon signals were observed at approximately 90° to the surface normal allowing measurements to be made in front of the surface as well as from the surface itself. Large count rates as high as 6×10^4 counts per second were observed from discrete atomic lines. The surface target materials used in these studies include NaCl cleaved just prior to introduction into the system, LiF, NaF, and stainless steel. The Na and Li resonance radiation increased with bombardment dose to a saturation level. The radiation was observed at an electron energy of 1 keV with use of a 0.3-m spectrometer with a resolution of 2.4 nm and spectral range of 250–800 nm. This range enabled us to observe the first resonance lines of Li and Na but not the resonance lines of F, Cl, or their ions, or hydrogen Lyman α.

When measurements were taken with the target tilted in such a way that the field of view included both the bulk and the near surface vacuum region, radiation from desorbed free atoms and molecules as well as bulk luminescence was observed, as shown in Fig. 1. In addition to the continuum, only the first resonance lines of sodium and lithium are descernible.

Discrete radiation could be emphaszed by tilting and translating the target so that only the region immediately in front of the target was observed (Fig. 2). The radiation observed in the NaCl case consists of the prominent Na *D* doublet at 589.0–589.6 nm, "molecularlike" structure in the 240–310-nm region as yet unidentified, and the first Balmer line of hydrogen H_α at 656.3 nm

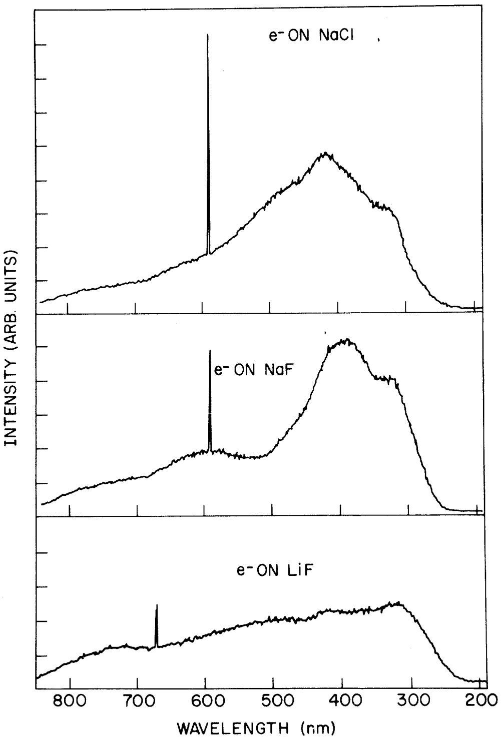

FIG. 1. Spectra of radiation produced by 1-keV e^- impact on NaCl, NaF, and LiF. The radiation was observed at 45° to the target surface normal with a spectral resolution of 2.4 nm.

arising from a hydrogen-containing surface or bulk contaminant. The rate of production of electron-bombardment-induced Na *D* radiation integrated over 4π sr for the NaCl target was calculated from our measurements to be $(3.2 \pm 1.5) \times 10^{-5}$ photons per incident electron.

Electron bombardment of NaF produced only the Na *D* doublet line. In the case of LiF bombardment, in addition to both the first resonance line of lithium (670.7 nm) and the H_α line at 656.3 nm, we observe faint lines in the vicinity of 690.0 nm. These arise from higher excited states of fluorine.

Our conclusion that the line and molecularlike radiation originates in front of the surface from ESD-excited free atoms and molecules is supported by the following points:

(a) The optical lines and bands are observed not to be shifted or broadened as they would be if the radiation originated from the surface.

(b) Tilting and translating the target effectively separates the radiation arising from the vacuum in front of the surface from that emitted from the surface itself.

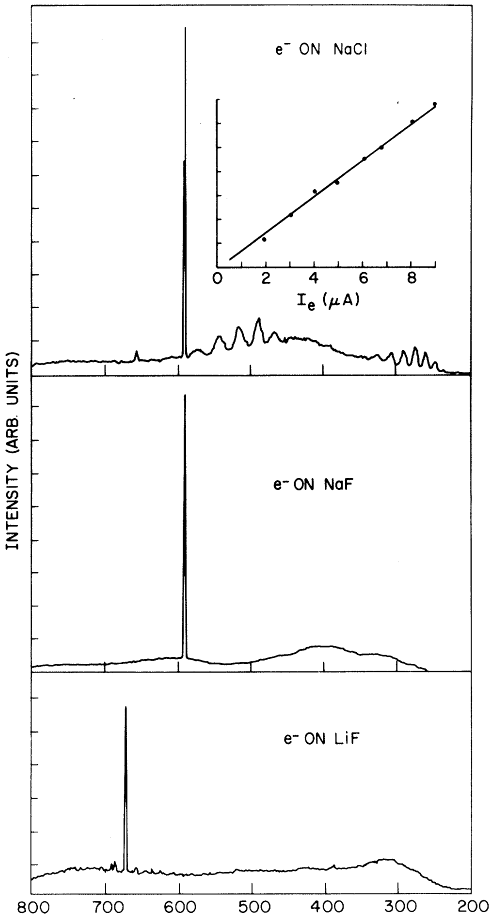

FIG. 2. Spectra of radiation produced by 1-keV e^- impact on NaCl, NaF, and LiF, obtained at approximately 90° to the surface normal. The inset shows the intensity of the Na *D* line as a function of incident-electron-beam current. A straight line has been drawn through the data points.

(c) As shown in the inset to Fig. 2, the Na *D* photon signal was found to be linear with the electron current, indicating that the creation of a free excited atom or molecule is an isolated event and, in particular, does not arise either from the subsequent gas-phase excitation of particles desorbed from the surface or from the thermal evolution of excited particles.

In marked contrast to ion bombardment,[6] the only sodium and lithium radiation detected in the ESD experiment are the first resonance lines (589.0–589.6 nm for Na and 670.7 nm for Li; see Fig. 2). This indicates that there exists a strong excited-state selection process associated with the ESD mechanism of an as yet undetermined nature.

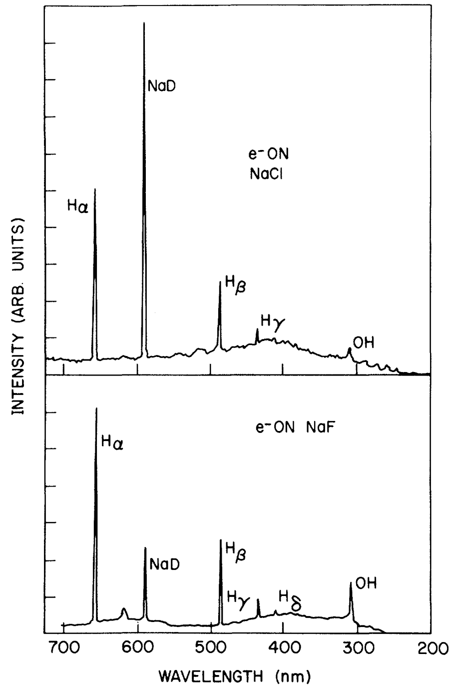

FIG. 3. Spectra of radiation produced by 1-keV e^- impact on NaCl and NaF, obtained as in Fig. 2, at 90° to the surface normal. The data is taken with a partial pressure of 2×10^{-6} Torr of H_2 in the target chamber.

In order to enhance ESD of excited hydrogen atoms, we introduced a small partial pressure of H_2 gas into the target chamber. Figure 3 shows the electron-bombardment spectra arising from NaCl and NaF targets in the presence of 2×10^{-6} Torr partial pressure of H_2. In each case, the Na and Li resonance lines were somewhat reduced in intensity. The most striking feature of the spectra, however, is the greatly increased intensity of the hydrogen Balmer lines; at least four of the series are readily observed. The first Balmer line, H_α, was observed under these same conditions as a result of bombardment of stainless steel. In addition, a new feature is observed: radiation from the gas-phase emission of the hydroxyl radical OH at 306 nm (0-0, $\tilde{A}^2\Sigma^+ \rightarrow \tilde{X}^2\Pi$). When the target was removed from the field of view, the radiation signals disappeared, indicating no contribution to the signal from electron-gas collisions.

In the attempt to understand the electron-sputtering process of alkali halides, two mechanisms are generally invoked.[7,8] An H center, produced by the radiationless decay of an electron-bombardment–induced exciton, may diffuse to the surface by means of a focused-collision-replacement sequence causing the directional ejection of a halogen with kinetic energy above 1 eV, resulting in "nonthermal" sputtering. In addition, electron impact may give rise to the creation of a V_k center which upon diffusion to the surface can result in the emission of a halogen atom at thermal energies, i.e., "thermal" sputtering. The nonstoichiometry caused by the halogen sputtering processes is presumed to lead to excess metal on the surface.

In addition to the physical mechanisms described above, atomic particles absorbed on the surface may be desorbed by electron bombardment (such as the excited hydrogen which we have observed) due either to the Menzel-Gomer-Redhead outer-shell[9,10] or the Knotek-Feibelman inner-shell[11] electronic excitation processes. Further experiments are required to determine how these processes or other processes give rise to excited neutrals. Careful energy-dependent, optical line-radiation measurements may contribute to a resolution of this question. The sensitive detection of excited hydrogen from the surface through the measurement of Balmer radiation reported here is noteworthy also because of the paucity of techniques for detecting surface hydrogen. The high intensity of the first resonance lines observed for the alkalis suggests that a spectrometer sensitive in the vacuum ultraviolet would detect intense Lyman-α emission as well as the first resonance lines of the halogens.

Studies of optical radiation from particles ejected in excited states by electron bombardment promise to be important in the understanding of the interaction of excited free atoms with various surfaces. This new class of experiments, from which one may obtain final states, will also contribute to an increased understanding of the electron-stimulated–desorption and photon-stimulated–desorption phenomena, in addition to providing new and powerful techniques for surface analysis which will complement existing methods.

We are grateful to H. J. Guggenheim for providing us with excellent alkali-halide crystals.

---

[a] Present address: Columbia University, New York, N. Y. 10027.

[1] See, for example, D. Menzel, Surf. Sci. 47, 370 (1975); T. E. Madey and J. T. Yates, Jr., Surf. Sci. 63, 203 (1977); P. J. Feibelman and M. L. Knotek, Phys. Rev. B 18, 6531 (1978); D. P. Woodruff, M. M. Traum, H. H. Farrell, N. V. Smith, P. D. Johnson,

D. A. King, R. L. Benbow, and Z. Hurych, Phys. Rev. B 21, 5642 (1980).

[2] N. Itoh, Nucl. Instrum. Methods 132, 201 (1976); Y. Al Jammal and P. D. Townsend, J. Phys. C 6, 955 (1973); P. W. Palmberg and T. N. Rhodin, J. Phys. Chem. Solids 29, 1917 (1968); P. D. Townsend and D. J. Elliott, Phys. Lett. 28A, 8, 587 (1969).

[3] I. G. Newsham and D. R. Sandstrom, J. Vac. Sci. Technol. 10, 39 (1973).

[4] R. H. Prince, G. N. Sears, and F. J. Morgan, J. Chem. Phys. 64, 3978 (1976).

[5] In the course of their studies of electron-bombardment–induced exciton luminescence from NaCl, Townsend *et al.* reported, in passing, observations of sodium *D* lines emitted from neutral excited sodium atoms which had evolved from the surface bulk: P. D. Townsend, A. Mahjoobi, A. J. Michael, and M. Saidoh, J. Phys. C 9, 4203 (1976).

[6] N. H. Tolk, I. S. T. Tsong, and C. W. White, Anal. Chem. 49, 16 (1977), and references therein.

[7] P. D. Townsend *et al.*, Radiat. Eff. 30, 55 (1976).

[8] H. Overeijnder, M. Szymonski, A. Haring, and A. E. deVries, Radiat. Eff. 36, 63 (1978).

[9] D. Menzel and R. Gomer, J. Chem. Phys. 41, 3311 (1964).

[10] P. A. Redhead, Can. J. Phys. 42, 886 (1964).

[11] M. L. Knotek and P. J. Feibelman, Phys. Rev. Lett. 40, 964 (1978).

Metal-Insulator Transition in Granular Aluminum

R. C. Dynes and J. P. Garno
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 30 October 1980)

The metal-insulator transition in granular aluminum has been observed. The resistivity has been varied over six orders of magnitude from metallic to a material where the conduction is via variable-range hopping. As the transition is approached from the metallic side, tunneling measurements have shown a $V^{1/2}$ dependence of the density of states, in agreement with recent theories.

PACS numbers: 71.30.+h, 72.15.Cz

The metal-insulator transition has been a subject of study for decades.[1] Recently, the nature of this transition and the concept of minimum metallic conductivity has come under scrutiny as the concepts of localization[2] and electron correlation[3] evolve. Recent results[4] on two-dimensional (2D) systems illustrate the importance of these effects. We report here tunneling measurements into granular 3D Al films in the vicinity of this transition. We find that Coulomb effects[3] are dominant approaching the transition and that large square-root singularities in the electronic density of states correlate with electron diffusivity. The details of the density of states are found to be in agreement with the theory of Altshuler and Aronov[5] and with the recent theory of the metal-insulator transition of McMillan.[6]

The measurements reported here are for samples with resistivities at 4.2 K ranging from $\sim 10^{-7}$ to 1 Ω cm. The samples consist of "granular aluminum" films, i.e., Al films prepared in an oxygen atmosphere. There is substantial literature on the preparation and properties of these films.[7,8] Our films were prepared by evaporation from resistively heated filaments in an oxygen partial pressure ranging from $\sim 5\times 10^{-7}$ to 2×10^{-4} Torr. In addition to maintaining constant pressure during evaporation it was also imperative that the evaporation rate be kept constant, as a small variation in rate here resulted in inhomogeneities in the film. The samples reported here were evaporated at a rate of ~20 Å/sec and had thicknesses ranging from 100 to 5000 Å. All samples consisted of a bottom film of clean Al, subsequently oxidized to form the tunnel barrier, and a cross stripe of the granular Al. With suitable lead configurations the film resistance and the junction resistance could both be measured using four terminal probes.

The dependence of the superconducting transition temperature T_c with resistivity $\rho(4.2\ \mathrm{K})$ is shown in Fig. 1. These results are in agreement with previous investigations[7-10] of the superconductivity of granular Al. With increasing resistivity, the T_c is observed to rise to 2.2 K, at which point it saturates. With increasing ρ, T_c remains relatively constant and then begins to broaden substantially and decrease. The tunneling measurements reported here indicate that correlated with this decrease in T_c is a decrease in the density of states $N(E)$ at E_{F}. The metal-insulator transition occurs when $N(E_{\mathrm{F}})$ goes to zero (and superconductivity disappears). From Fig. 1 this apparently occurs at a resistivity $\rho \gtrsim 10^{-1}$ Ω cm