

Observation of photon-stimulated desorption following valence-band excitation of alkali halides

P. H. Bunton,* R. F. Haglund, Jr., D. Liu, and N. H. Tolk

Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235

(Received 25 April 1991; revised manuscript received 7 October 1991)

We report observations of photon-stimulated desorption of excited alkali-metal atoms following valence-band excitation of alkali halide crystals by tunable ultraviolet light. Excitation functions of excited Li and K atoms desorbed from LiF and KCl surfaces were measured in the photon-energy range 10–28 eV using a synchrotron light source. Simultaneous measurements of the secondary-electron yield demonstrate that excess metal on the surface is required for this process to occur; however, the temperature, time, and dose dependence of excited-atom and secondary-electron yields are uncorrelated. Possible models for the process of desorption stimulated by valence-band transitions are briefly considered.

INTRODUCTION

Photon-stimulated desorption (PSD) of excited alkali-metal atoms from alkali halides following core-level excitation was observed a decade ago.¹ Our recent detailed study of PSD following core-level transitions² showed that emission of excited atoms is correlated with the excitonic response of alkali halides to absorbed photons. While the detailed dynamics of excited alkali-metal-atom desorption remains a subject of active investigation, it is reasonable to assume that, for core-level excitation, it is connected to the interatomic Auger decay process which initiates the Knotek-Feibelman desorption mechanism.³ PSD following *valence-band* excitation of alkali halides, on the other hand, has hardly been studied at all and should be of particular interest because the interatomic Auger processes typical of core-level excitation can not occur, and hence the holes created on the halogen ions would be poorly screened, in contrast to core holes created by Auger processes.

In this paper we report observations of efficient photon-stimulated desorption of excited alkali-metal atoms from surfaces of LiF and KCl at photon energies *below* the lowest core-level excitation. Secondary-electron-emission measurements implicate excess metal on the surface in the desorption process. However, the temperature and time dependence of the excited-atom and secondary-electron yields are uncorrelated, suggesting that secondary-electron excitation of desorbed ground-state neutral atoms may not be the dominant mechanism in valence-band PSD. PSD of excited atoms by photons with such low energies is not consistent with any currently accepted mechanism for desorption induced by an electronic transition. We suggest that valence-band PSD of excited alkali-metal atoms may be due to vibrational and electronic relaxation of a highly excited state of the crystal localized near a self-trapped valence-band hole or an excited *F* center. Such a picture is plausible in the light of recent calculations of defects and localized excitations in alkali halides, but remains to be verified experimentally.

APPARATUS AND MEASUREMENTS

Our measurements of PSD following valence-band excitation were performed at the Aladdin Synchrotron Ra-

diation Center (SRC) at the University of Wisconsin. Bending-magnet radiation from an 800-MeV electron storage ring was dispersed either by a Seya-Namioka (SN) Rowland-type monochromator or by a toroidal-grating monochromator (TGM) and focused onto a sample at normal incidence in an ultrahigh-vacuum chamber with a base pressure generally $\sim 10^{-10}$ Torr. Useful photon flux from the monochromator was obtainable over the energy range 8–28 eV. Fluorescence from desorbing excited alkali-metal atoms in a small volume in front of the sample surface was focused by $f/5.6$ collection optics onto the entrance slit of a 0.3-m Czerny-Turner monochromator (MacPherson 218) equipped with a Thorn EMI 9659QB photomultiplier operated in photon-counting mode. Amplified photomultiplier-tube (PMT) pulses which exceeded the threshold of a discriminator were counted and stored in an Apple Macintosh SE computer, as described elsewhere.²

As described in earlier publications in detail,⁴ the desorbing alkali-metal atoms were identified from the free-atom-like emission spectrum typical of gas-phase fluorescence. For each point in an excitation function, the fluorescence yield was measured at the peak of the first resonance line of the desorbing excited atoms (“on resonance”) and then measured again at wavelengths “off resonance” on either side of the atomic emission line for background subtraction. For each run the storage ring current and the current recorded on a nickel mesh positioned to monitor the flux reflected from the grating were recorded for normalization. These two current readings were then used to normalize the data to counts per incident photon, except at photon energies where, as noted below, the Ni mesh response is poorly known.

The current of secondary electrons collected on a biased stainless-steel collector plate positioned a few centimeters from the sample was measured by a Keithley picoammeter. The bias voltage on the collector plate ranged from 9 to 90 V depending on the optimum scale for the electrometer; hence higher-energy electrons were not always detected. However, electrons with energies greater than, say, 10 eV probably represent only a tiny fraction of the measured current. Secondary-electron-energy distributions from $AlK\alpha$ (1487 eV) excitation of KCl and NaCl peak at about 1 eV with most of the electrons having energies under 6 eV.⁵ Secondary-electron

emission from LiF peaks near 2 eV, but has a range up to about 15 eV.⁵ Energy distributions of photoelectrons from KCl irradiated by 12–23 eV photons show that the bulk of secondary electrons have energies less than about 10 eV.⁶ Therefore, we assume that most of the secondary electrons in the present measurements were emitted with low enough energies to permit collection of a representative sample.

The collector plate was not shielded from either the reflected primary light or ultraviolet fluorescence from the sample; this might have caused some losses in electron current as a result of photoelectron emission from the collector. The background photoelectron current due to photoemission from the collector initiated by ultraviolet light reflected from the alkali halide target is estimated to be ~ 10 pA, for an unbiased collector, a photoelectron yield of 1, 50% reflectivity (90% specular), and a collector solid angle of 0.01 sr. With the assumption that the electronic excitations of the irradiated crystal relax by Auger decay at least 90% of the time, the electron yield from the collector because of sample fluorescence is at most of the same order of magnitude as that due to reflection, and more likely an order of magnitude smaller.

Samples used in this experiment were alkali halide single crystals, mostly obtained from Harshaw Chemical Company; some of the measurements on LiF were made on samples from Optovac. The samples were mounted on a copper target holder attached to a Huntington micromanipulator and were usually under vacuum within about an hour after being cleaved in air. Following installation of the samples in the UHV chamber, the vacuum system was then baked at 200°C for several hours, and the samples were subsequently cleaned by heating a few hours at 300–400°C. The composition of the alkali halide surface following the cleaving process has been studied for many years. The differing formation energies for cation and ion vacancies in lithium fluoride are known to produce a LiF surface which is metal rich upon cleaving.⁷ However, a secondary-ion-mass-spectroscopy (SIMS) study has shown that cleaving in air followed by immediate (~ 30 min) insertion into an unbaked vacuum system leaves surfaces of LiF, NaF, and NaCl with submonolayer contamination and without hydroxide or water layers.⁸ It is possible that baking of the chamber following sample insertion may have contaminated the surface. On the other hand, recent atomic-force microscopy studies of a NaCl surface, prepared by cleaving in air and baking in UHV at 150°C for a few hours, revealed the characteristic (1 \times 1) pattern of the perfect surface,⁹ suggesting that our experimental protocol should likewise produce a stoichiometric surface prior to irradiation.

EXPERIMENTAL RESULTS

Figure 1 shows two fluorescence spectra observed during uv-photon irradiation of LiF at photon energies of 13.5 and 21.5 eV in the Seya monochromator. The first resonance line (671 nm) of excited neutral lithium atoms is clearly evident. Since no filters were used for these measurements, the Li* yield at an incident photon energy of 13.5 eV could conceivably have contributions from

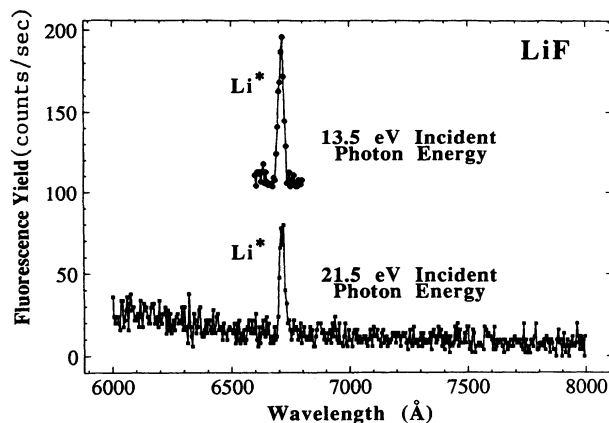


FIG. 1. Fluorescence scan from PSD of LiF at 13.5 and 22.5 eV, showing the optical signal from the $2p \rightarrow 2s$ transition (first resonance line) of the Li atom.

second-order light. (Because of its normal-incidence grating, the Seya will not transmit light in *any* order above about 30 eV.) However, the similarity of the excitation function for Li* desorption from LiF to the absorption spectrum of LiF, shown below, indicates that the desorption is indeed related to valence-band excitation. The Seya also transmits some visible light in first order; again, this might produce some desorption, but there is no reason why the excitation function should, in that case, mimic the structure of the absorption curve. Measurements on a toroidal-grating monochromator using a Sn filter and 22.5 eV incident first-order light confirmed that the valence-band desorption occurs in the absence of visible light. Since transitions to the conduction band from the first core band in LiF, the $F^- (2s)$ band, should not occur until nearly 38.5 eV,¹⁰ this is clear evidence that the desorption is produced by valence-band excitation.

An excitation function of desorbed excited lithium from LiF is shown in Fig. 2(a). These data were obtained using a sample cleaved from a single crystal of LiF supplied by Harshaw. The sample was yellow when delivered, indicating the existence of color centers; this sample produced the highest yields of excited atoms for low incident photon energies. However, the existence of the color centers is not required for valence-band PSD to occur: Small yields of Li* at photon energies near 20 eV—again, below the lowest core-level excitation—were also observed for samples from Optovac which showed no visible evidence of color centers. The data have been normalized to the Ni mesh current and to the response of Ni. The curve plotted through the experimental points was obtained by smoothing the data. The uv reflectance spectrum of Milgram and Givens¹¹ (MG) and the absorption data of Roessler and Walker¹² (RW) show similar structure, which is generally interpreted in terms either of exciton formation or of band-to-band transitions. The desorption yield resembles the RW single-crystal absorption spectrum more closely than it resembles the MG data, which were acquired on thin films. RW and MG both conclude that the peak at 12.85 eV is excitonic,

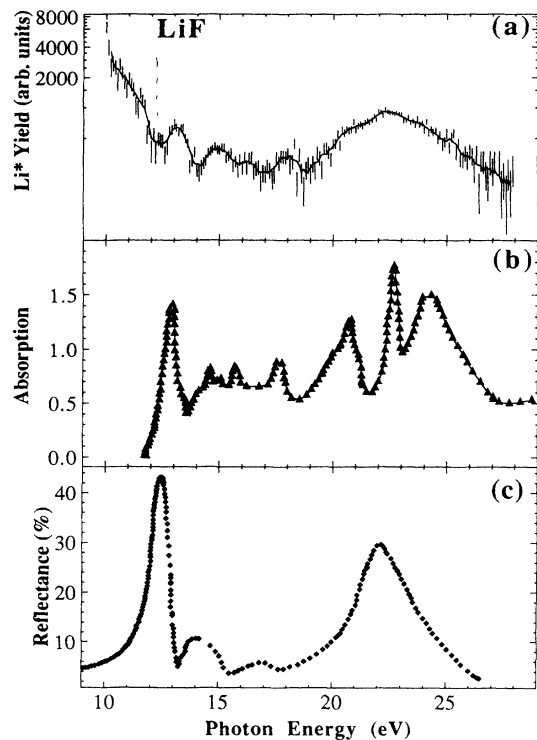


FIG. 2. (a) Excitation function of Li^* from LiF over the incident photon-energy range 8–28 eV. (b) Absorption spectrum of LiF measured in a single crystal, digitized from the original data in Ref. 12. (c) Reflectance spectrum from a thin film of LiF, digitized from Ref. 13.

while RW suggest that the peaks observed at 14.3, 17.4, and 23 eV are due to transitions from the valence band to the conduction band. This interpretation is consistent with that of Pantelides,¹⁰ who reports the threshold for interband transitions from the $\text{F}^- (2s)$ band to be 38.5 eV. The correspondence between the Li desorption yields and the features of the absorption and reflectance spectra are not always overwhelming. These characteristic peaks in the spectra are, however, at least circumstantial evidence that excited alkali-atom desorption is correlated with valence-band excitation and optical absorption.

That valence-band PSD of excited alkali-metal atoms occurs in alkali halides other than LiF—well known as something of an anomaly among alkali halides—is shown by experimental results on PSD of K^* from KCl. Figure 3(a) is an excitation function for the production of excited potassium under photon irradiation of KCl. Figure 3(c) is a scan across the exciton near 9.5 eV. The flux from the monochromator was too low to search for structure in the desorption curve at lower energies. The data have been normalized to the Ni mesh current. Because of the lack of data for the Ni mesh response below 10 eV, the data have not been normalized by the Ni mesh response. Shown for comparison in Figs. 3(b) and 3(d) are the absorption spectra of KCl obtained by digitizing the experimental curves published earlier by Blechschmidt *et al.*¹³ and Eby, Teggarden, and Dutton.¹⁴ Structure in the desorption yield near the position of the valence-band ex-

citon at approximately 9.5 eV is evidence that desorption due to valence-band excitation in KCl is occurring. The sloping background underneath the exciton and continuing to about 16 eV may be due to contributions from higher-order light. Some small features are observed in the desorption yield at approximately 13.5 and 14.5 eV;

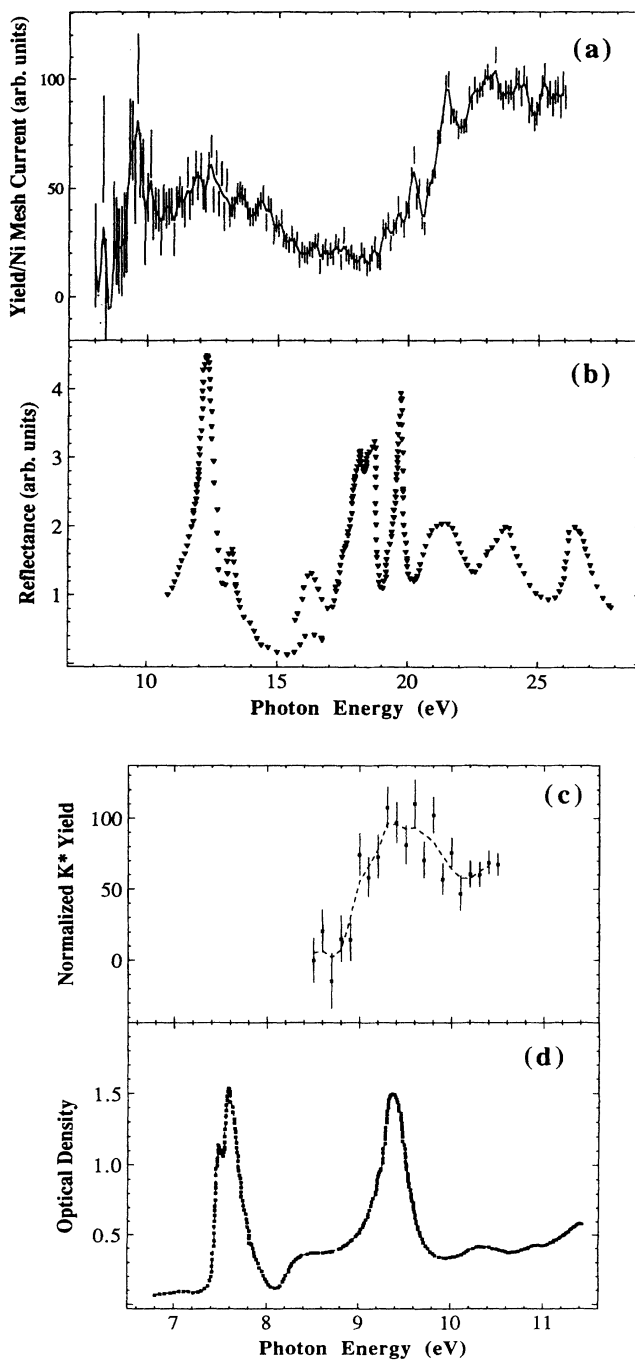


FIG. 3. (a) Excitation function of K^* (767-nm $4p \rightarrow 4s$ transition) from KCl. (b) Absorption data from KCl, from Ref. 14. (c) Excitation spectrum of K^* from KCl for photons near the surface exciton peak. (d) Reflectance spectrum from KCl near the surface exciton peak, adapted from Ref. 15.

they may be related to the peaks at 12.9 and 14.0 eV in the data of Blechschmidt *et al.*

Figure 4 shows the dependence of the Li* yields and total electron yields from LiF on total time of irradiation for an incident photon energy of 22.5 eV at nominal sample temperatures of 20, 60, 100, and 150 °C. The sample was annealed by baking above 400 °C for 2 h between each successive scan; the total time between scans was sometimes more than 2 h, however. Of particular note is the variation both in the time to reach peak yield and the slope of the yield-versus-time curve as the temperature is changed. In Fig. 5 the same data are replotted to reflect the variation with total absorbed photon dose. The initial rate of increase (with dose or time) of the Li* yield is faster at 60 and 100 °C than at room temperature; the maximum yield reached is higher at 60 °C and 100 °C than at room temperature, but then decreases dramatically by 150 °C. The Li* yield is immeasurably small by 200 °C.

The experimentally observed yields of excited desorbed atoms, whether plotted as a function of dose or time, rise rapidly with dose or time to a maximum and then exhibit a relatively gradual decay. The slope of the rapidly varying component is somewhat sensitive to temperature, while the negative slope of the slowly varying component seems to change rather less with temperature. The two room-temperature scans—which are separated by scans at higher temperatures—appear the same if plotted as a function of time (Fig. 4), but reach their maxima at different doses (Fig. 5). Thus time of irradiation, sample temperature, and total absorbed photon dose all play a role in the desorption kinetics.

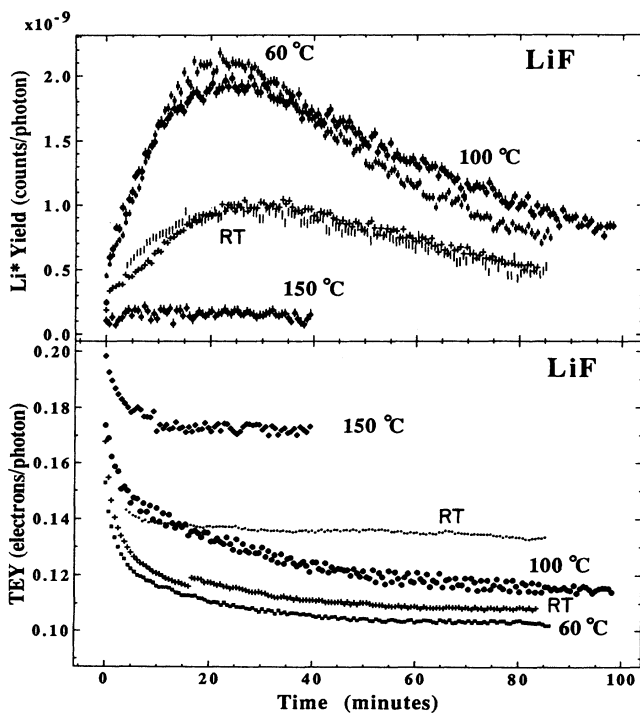


FIG. 4. Time dependence of the total electron and Li* yields from LiF under valence-band excitation (photon energy 21.5 eV), shown for several different temperatures as indicated.

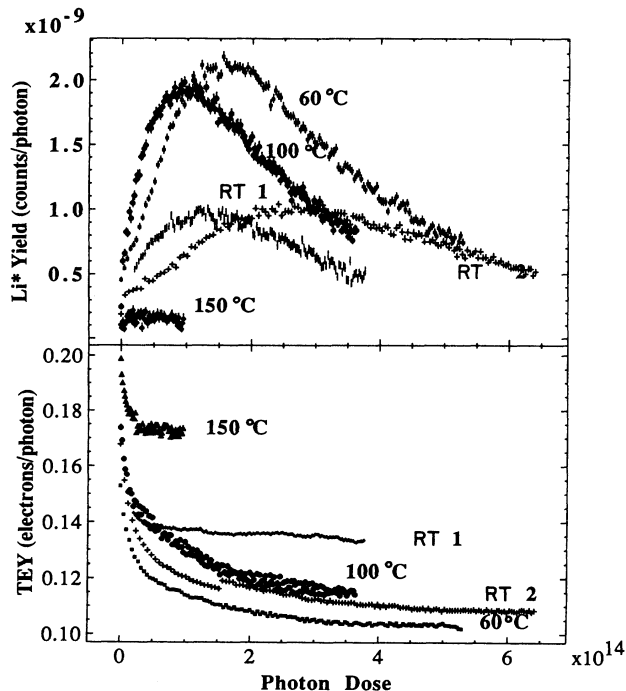


FIG. 5. Dose dependence of the total electron and Li* yields from LiF under valence-band excitation (photon energy 21.5 eV), shown for several different temperatures as indicated.

The electron yields in Figs. 4 and 5 do not resemble the Li* dependences on time, dose, or temperature. The cause of the initial decrease in electron yield with time or dose is unknown. It may be related to the charging of the sample during the irradiation, although it is not clear how charging would cause such an effect. More likely it is due to transient initial metallization of the surface, since secondary-electron emission from LiF is more than an order of magnitude more efficient than from a metallic Li surface.¹⁵ After that initial transient, the surface metallization apparently saturates, reaching a quasi-steady-state characteristic of the surface temperature; subsequent changes in desorption yield must be related to other factors, such as defect diffusion out of the near-surface region.

The formation of a metal-rich surface is well known to be the result of halogen emission and has been observed during photo irradiation from a synchrotron source in a fluorescence emission study of LiF.¹⁶ During Auger electron spectroscopy (AES) of LiF, excess surface metal was found to increase with temperature until approximately 270 °C and then to decrease rapidly to zero at higher temperatures,¹⁷ rather like the temperature dependence of the maximum Li* yield in Figs. 4 and 5. An electron-energy-loss-spectroscopy (EELS) study of LiF under electron irradiation indicated that excess metal is formed first in thin patches and eventually in three-dimensional islands, rather than in a uniform layer.¹⁸ Since the electron yield from Li metal is expected to be smaller than the electron yield from LiF,¹⁵ the electron yield would perhaps change more slowly with dose than the desorption yield if significant portions of the surface remain as

stoichiometric LiF. The vapor pressure of a metal depends on the droplet size, as does the work function.¹⁸ For example, at 200 °C the vapor pressure of a 5-Å-radius particle of Li is an order of magnitude higher than the vapor pressure of a 10-Å-radius particle. This change in vapor pressure with particle size could possibly explain why the Li* yield disappears at a lower temperature than did the metal in the AES study mentioned above.

DISCUSSION

Our experiments show that excited-alkali-metal-atom desorption can be initiated at photon energies below the lowest core-level-to-conduction-band transitions and also below band-to-band transitions originating in core levels. Moreover, even where higher-order light may be present, the structure of the excitation functions is generally correlated with excitonic features of vacuum ultraviolet reflectance and absorption spectra. Hence it is clear that the desorbed, excited alkali-metal atoms are produced by valence-band transitions. The mechanism for valence-band PSD, however, is not easily identified. The Menzel-Gomer-Redhead model¹⁹ of desorption offers little guidance in this case, since it is based on a diatomic model of the surface binding which is inappropriate to the long-range Coulomb forces characteristic of alkali halides. The Knotek-Feibelman⁵ (KF) or Auger-stimulated desorption (ASD) mechanisms²⁰ are based on interatomic Auger decay into the core holes created by the absorption of an ultraviolet photon. In the photon-energy range of our experiments, no core hole is formed, so that this mechanism does not apply either.

The dominant photon-stimulated desorption process from alkali halide surfaces is well known to be desorption of neutral atoms.²¹ Core-level PSD of ground-state alkali-metal atoms is initiated by self-trapping of a core hole to create a V_K center. The capture of an electron by the V_K center leads to the creation of a self-trapped exciton (STE). In its turn, the relaxation of the STE produces a mobile F - H -center pair of significantly different mobilities, the F center being an electron in a halogen vacancy and the H center, an X_2^- molecular ion. Rapid diffusion of the H center to the surface leads to the ejection of halogen atoms; slowly diffusing F centers, as they reach the surface, produce neutral metal atoms which desorb thermally. However, this model cannot, by itself, explain valence-band PSD of excited alkali-metal atoms since it fails to account for the internal state of the desorbing atom.

It has been suggested,²² extrapolating from electron-stimulated desorption experiments on NaCl, that PSD of excited alkali-metal atoms could arise from secondary-electron excitation of desorbed ground-state alkali-metal atoms could arise from secondary-electron excitation of desorbed ground-state alkali-metal atoms. The spectral features in our PSD experiments do not *ipso facto* rule out the production of excited atoms by this mechanism, since these features—and the secondary-electron yields—necessarily reflect the excitonic character of the optical absorption. However, secondary-electron excitation of desorbed ground-state atoms cannot be the only

source of the present observations, since secondary-electron yields plotted as a function of irradiation time, photon dose, or sample temperature are uncorrelated with the excited-atom yields. Moreover, the yields of ground-state alkali-metal atoms generally increase with temperature above the vaporization point of the alkali metal, which the excited-atom yields measured in recent PSD experiments *decrease* with temperature.²³ Indeed, at the temperatures in our experiments, the ground-state yield is below the threshold for detection by laser-induced fluorescence. There is no reason to expect electron yields to decrease with temperature, and the ground-state alkali-atom yield increases as the vapor pressure of the metal increases. Therefore, one would expect the excited-alkali-atom yield to increase with temperature, if secondary-electron excitation of desorbed ground-state atoms were the primary source of the excitation—contrary to our experimental observations.

We suggest, instead, that the excited alkali-metal atoms may be emitted from vibrationally and electronically excited complexes adjoining metal-ion sites on the surface. Nuclear motion of an alkali ion at one of these surface sites is initiated by enhanced vibrational excitation following creation either of a V_K center or an excited F center; the excited alkali atom is formed when an excited F center—not necessarily the one which initiates nuclear motion—neutralizes the moving ion. Valence-band photons are certainly energetic enough to form self-trapped holes and F centers; F centers may be excited by scattering of secondary electrons or fluorescence. Neutral alkali-atom desorption has been observed from RbBr samples containing F centers (albeit without measurement of the electronic state of the atom) during irradiation with F -band light.²⁴

Such a mechanism is also consistent with recent computer simulations of the vibrational and electronic effects of defect creation in alkali halides. Strong lattice distortion extending to the next-nearest neighbors of V_K centers in LiF has been demonstrated in recent simulations using Hartree-Fock molecular clusters.²⁵ It has also been shown that localized, highly anharmonic vibrational modes of a particle can be generated in a diatomic lattice given sufficient deformation energy.²⁶ The energy required to create this kind of deformation in LiF is approximately that available from the formation of an excited F center. Interestingly, these calculations also show that localization is enhanced in two dimensions vis à vis three dimensions. Finally, this picture is consistent with calculated electron distributions for excited F centers, which show significant charge density on the metal ions adjoining the anion vacancy where the F center resides.²⁷

This model for excited-alkali-metal-atom desorption also explains several features of the experiments reported here. The initial steep rise in excited-alkali-atom PSD yield (Figs. 4 and 5) could be due to the absorption of hot holes at excited surface-defect complexes; hot-hole absorption is believed to increase sharply as the surface is metallized.²⁸ Absorbed holes can self-trap, in turn, forming V_K centers which decay through the STE into F centers (which may be in excited states), H centers, and vibrationally excited quasimolecular complexes at or near

the surface. Excited-alkali-atom yield decreases with increasing temperature because the lifetime (i.e., survival probability) of excited F centers likewise decreases with increasing temperature.²⁹ The effect of the excited F centers can, in principle, be tested experimentally. However, there are no data at present from which to draw any definitive conclusions.

CONCLUSIONS

We have described observations of photon-stimulated desorption of excited alkali-metal atoms from alkali halide crystal surfaces following valence-band excitation. The structure in excitation functions of excited-atom yields is reasonably well correlated with excitonic structure observed in previous reflectance and absorption measurements. Our measurements of the secondary-electron yield as a function both of temperature and of dose show that the excited-atom yields are related to metallization of the irradiated surface. Nuclear motion leading to desorption of excited alkali-metal atoms may result from

the creation of highly excited vibrational modes of the lattice due to the generation of an excited F center at the surface, followed by neutralization of the metal ion into an excited state by capture of the F center.

ACKNOWLEDGMENTS

We are grateful to the staff of the Synchrotron Radiation Center (SRC) for their expert handling of the Aladdin storage ring. We thank R. A. Rosenberg of the SRC, R. T. Williams of Wake Forest University, J. Tellinghuisen and C. Ewig of Vanderbilt University, and N. Itoh, University of Nagoya, for stimulating discussions. One of us (P.H.B.) was supported by the National Aeronautics and Space Administration under Grant No. NGT-50126. This research was sponsored in part by the University Research Initiative of the Air Force Office of Scientific Research (AFOSR) under Contract No. F49620-86-C-0125, and by the AFOSR under Grant No. AFOSR-90-0030. The SRC is supported by the National Science Foundation.

*Present address: Department of Physics, Austin Peay State University, Box 4608, Clarksville, TN 37044.

¹N. H. Tolk, M. M. Traum, J. S. Kraus, T. R. Pian, W. E. Collins, N. G. Stoffel, and G. Margaritondo, *Phys. Rev. Lett.* **49**, 812 (1982).

²P. H. Bunton, R. F. Haglund, Jr., D. Liu, and N. H. Tolk, *Surf. Sci.* **243**, 227 (1991).

³M. L. Knotek and P. J. Feibelman, *Phys. Rev. Lett.* **40**, 964 (1978); also P. J. Feibelman and M. L. Knotek, *Phys. Rev. B* **18**, 6531 (1978).

⁴See Ref. 1, and also N. H. Tolk, R. F. Haglund, Jr., M. H. Mendenhall, and E. Taglauer, in *Desorption Induced by Electronic Transitions DIET II*, edited by W. Brenig and D. Menzel (Springer-Verlag, Berlin, 1985), pp. 152–157.

⁵B. L. Henke, J. Liesegang, and S. D. Smith, *Phys. Rev. B* **19**, 3004 (1979).

⁶W. Pong and J. A. Smith, *Phys. Rev. B* **9**, 2674 (1974).

⁷P. Wurz and C. H. Becker, *Surf. Sci.* **224**, 559 (1989).

⁸J. Estel, H. Hoinkes, H. Kaarmann, H. Nahr, and H. Wilsch, *Surf. Sci.* **54**, 393 (1976).

⁹G. Meyer and N. M. Amer, *Appl. Phys. Lett.* **56**, 2100 (1990).

¹⁰S. T. Pantelides, *Phys. Rev. B* **11**, 2391 (1975).

¹¹A. Milgram and M. P. Givens, *Phys. Rev.* **125**, 1506 (1962).

¹²D. M. Roessler and W. C. Walker, *J. Phys. Chem. Solids* **28**, 1507 (1967).

¹³D. Blechschmidt, R. Haensel, E. E. Koch, U. Nielsen, and M. Skibowski, *Phys. Status Solidi* **44**, 787 (1971).

¹⁴J. E. Eby, K. J. Teegarden, and D. B. Dutton, *Phys. Rev.* **116**, 1099 (1959).

¹⁵*CRC Handbook of Chemistry and Physics*, edited by R. C. Weast (CRC, Boca Raton, FL, 1988), p. E-376.

¹⁶K. L. Tsang, C. H. Zhang, T. A. Callcott, E. T. Arakawa, and D. L. Ederer, *Phys. Rev. B* **35**, 8374 (1987). See also R. F. Haglund, Jr., M. H. Mendenhall, N. H. Tolk, G. Betz, and W. Husinsky, *Nucl. Instrum. Meth. Phys. Res. B* **32**, 321 (1988).

¹⁷D. G. Lord and T. E. Gallon, *Surf. Sci.* **36**, 606 (1973).

¹⁸G. Singh and T. E. Gallon, *Solid State Commun.* **51**, 281 (1984).

¹⁹D. Menzel and R. Gomer, *J. Chem. Phys.* **41**, 3311 (1964); P. A. Redhead, *Can. J. Phys.* **42**, 886 (1964).

²⁰C. C. Parks, D. A. Shirley, and G. Loubriel, *Phys. Rev. B* **29**, 4709 (1984).

²¹N. G. Stoffel, R. Riedel, E. Colavita, G. Margaritondo, R. F. Haglund, Jr., E. Taglauer, and N. H. Tolk, *Phys. Rev. B* **32**, 6805 (1985).

²²R. E. Walkup, Ph. Avouris, and A. P. Ghosh, *Phys. Rev. Lett.* **57**, 2227 (1986).

²³W. Husinsky, P. Wurz, K. Mader, E. Wolfrum, B. Strehl, G. Betz, R. F. Haglund, Jr., A. V. Barnes, and N. H. Tolk, *Nucl. Instrum. Meth. Phys. Res. B* **33**, 824 (1988).

²⁴H. Kanzaki and T. Mori, *Phys. Rev. B* **29**, 3573 (1984).

²⁵R. Pandey and A. B. Kunz, *Phys. Rev. B* **38**, 10 150 (1988).

²⁶S. R. Bickham and A. J. Sievers, *Phys. Rev. B* **43**, 2339 (1991).

²⁷C. S. Ewig, J. Tellinghuisen, and M. H. Mendenhall (unpublished); *Chem. Phys. Lett.* (to be published).

²⁸T. A. Green, G. M. Loubriel, P. M. Richards, L. T. Hudson, P. M. Savundararaj, R. G. Albridge, A. V. Barnes, and N. H. Tolk, in *Desorption Induced by Electronic Transitions, DIET IV*, edited by G. Betz and P. Varga (Springer-Verlag, Berlin, 1990), p. 281.

²⁹D. Fröhlich and H. Mahr, *Phys. Rev.* **141**, 692 (1966).