Near-Surface Generation of F Centers by Synchrotron Radiation

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The formation of F centers by monochromatic soft x-ray radiation was studied in the range of photon energies 50 to 1500 eV by use of a sensitive laser-induced luminescence technique. Production efficiencies of the order of 1 keV/(F center) are obtained throughout the upper end of the above energy range in KCl and KBr at 77 K. Saturation densities of about 10^{18} cm^{-3} occur, with the total number of centers depending upon the depth of penetration of the radiation. Reduced efficiency is noted at the lowest energies and highest absorption coefficients, and is possibly related to the observed photodesorption of neutral and ion species from the surface.

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Unlike most covalent compounds, ionic crystals are readily damaged by ionizing radiation such as x rays or band-gap light. One of the principal products of damage is the F center, a negative-ion vacancy with a trapped electron. The use of short pulses of penetrating electrons and of near ultraviolet radiation has shown that F and H centers (interstitial halogen atoms) are efficiently produced within 10 ps, even when the crystal is at liquid-helium temperature.[1] It is now known that the primary process for F-center generation by x rays involves nonradiative recombination of electrons and holes through an excited state of the self-trapped exciton.[2]

Most of the work carried out so far on the production of point defects by x rays has involved polychromatic radiation and the volume generation of defects. On the other hand, little is known about the production of F centers by monochromatic soft x-ray radiation with photon energies from 50 up to about 1500 eV. Photons in this energy range are strongly absorbed (10^{-4} to 10^{-5} cm) near the surface of the crystal, and experiments at such energies are essential in order to complete our understanding of the general mechanisms involved in defect production.

F-center production near the surface is almost certainly involved in the photoyield of neutral atoms from the surface, a topic of considerable recent interest.[3] From a practical point of view, the control of defect formation by radiation near the surface of insulating crystals is important to the understanding of photoemission,[4] the remarkable dynamic range of the new photochromic area detectors for x rays and synchrotron radiation,[5] as well as the initial stages of radiation damage to windows and coated mirrors currently used in vacuum-ultraviolet laser systems.

In this Letter, we outline the results of radiolysis experiments carried out with the new 1-GeV electron storage ring at the University of Wisconsin Synchrotron Radiation Center, Stoughton, Wisconsin. Single crystals of nominally pure (Harshaw) KCl and KBr were cleaved in ultrahigh vacuum (1×10^{-9} Torr) and cooled to 77 K. The cleaved surfaces were then exposed to highly monochromatic beams of soft x-ray radiation in the energy range 50 to 1500 eV. A sensitive laser-induced luminescence technique[6] was used in order to follow directly the formation of a relatively small number of point defects in the beginning of the linear rise with exposure to the final saturated densities.

In all cases studied, the initial efficiency to produce one F center was of the order of one to a few kiloelectronvolts, in agreement with earlier studies[7] in the 50–150-eV range. The absorption coefficient for soft x rays in the sample was found to control the final saturation level of coloration more or less independently of incident x-ray intensity. The saturation curves were in reasonable agreement with current models[8,9] of stable volume color-center formation at low temperatures. In general, color-center formation in the energy range studied is consistent with electron-hole production followed by recombination of self-trapped excitons.

An outline of the sensitive method for detecting F centers as used at the synchrotron source is shown in Fig. 1. Four alkali-halide crystals, each about $1\times1\times0.2$ cm^3, were secured by low-vapor-pressure epoxy to the cold finger of a micromanipulator in an ultrahigh-vacuum chamber where they could be cleaved by a movable blade. They were then cooled to 77 K and accurately positioned in the highly focused spot of radiation (2.0 mm$\times$1.5 mm) from the University of Illinois extended-

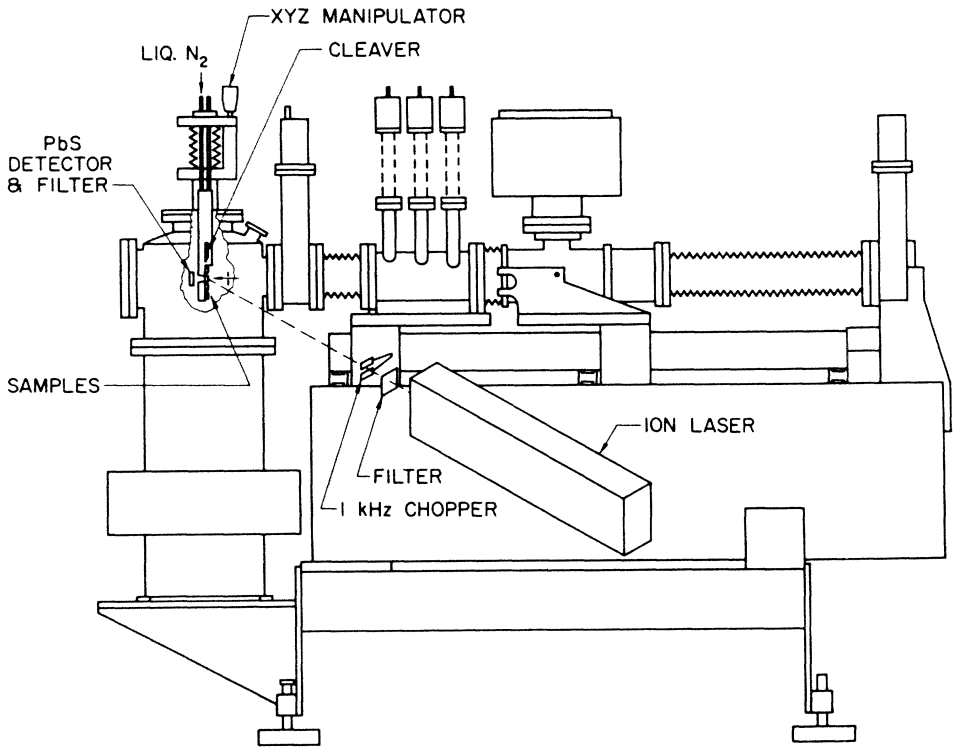

FIG. 1. An outline of the extended-range "grasshopper" or ERG monochromator (Refs. 10 and 11) installed on bending magnet No. 2 of the new 1-GeV storage ring at the Stoughton Synchrotron Radiation Center. X-ray radiation from a collecting mirror (with horizontal focusing) enters from the right, and is dispersed and focused at the exit slits just before the cleaved samples in an ultrahigh-vacuum chamber on the left. An intense beam of F-band light from a laser is incident through a window and luminescence from the point defects is detected (after a cutoff filter) by a lead-sulfide detector in vacuum.

range monochromator[10] on the new 1-GeV electron storage ring at Stoughton, Wisconsin. Simultaneously, the crystal was illuminated with an intense beam of F-band light by use of a narrow-pass filter and the appropriate line of a krypton-ion laser (532 nm for KCl, 647 nm for KBr). The laser beam was chopped at a frequency of 1 kHz by an electromechanical oscillator so that the Stokes-shifted near-infrared emission emitted by F centers could be detected by a PbS cell with use of a tuned preamplifier and lock-in detector. A low-pass filter ($\lambda > 750$ mm) before the detector effected almost complete separation of stray laser radiation.

The sample holder containing the cleaved crystals could be moved vertically so that unexposed areas of a crystal could be positioned in sequence. Thus, several coloration curves at different wavelengths could be obtained on each crystal. The spectral dependence of the incident x-ray flux was determined with use of the known photoyield of gold (and also a National Bureau of Standards photodiode). X-ray flux in the range of 10^{11} to 10^{12} photons/sec was usually employed.

The laser-induced luminescence method was calibrated by insertion of a crystal in the sample holder which was previously colored by the penetration of x rays to a known F-center density (about 10^{15} cm^{-3}, as determined by observation of optical density and application of Smakula's formula). This crystal was kept in the dark until it was cooled to liquid-nitrogen temperature, the laser light applied, and the lock-in signal observed. With inclusion of a correction for the illuminated volume, the sensitivity of the method was found to be 4.1×10^{12} (F centers)/μV in KBr and 1.1×10^{12} (F centers)/μV in KCl. Although these numbers are not highly accurate, they allow an estimate of the generation efficiencies in the soft-x-ray experiment. It is clear that a very small number of centers ($\sim10^{10}$) could be detected within the tiny cross-sectional area of the focused synchrotron radiation beam near the surface of the cleaved crystals.

In general, very little laser-induced luminescence signal (<0.02 μV) was observed for an unexposed area on a cleaved and cooled sample surface. The signal increased very rapidly, however, upon the opening of the shutter to the monochromator and storage ring as a result of F-center production. Initially, a linear rise in signal occurred in the so-called stage-I region of coloration. Within a minute or so, the signal would begin to level off or saturate corresponding to the so-called stage II of coloration. Figure 2 of Ref. 6 shows the growth curve of laser-induced luminescence for a nominally pure KBr crystal at 77 K exposed to penetrating x rays from a

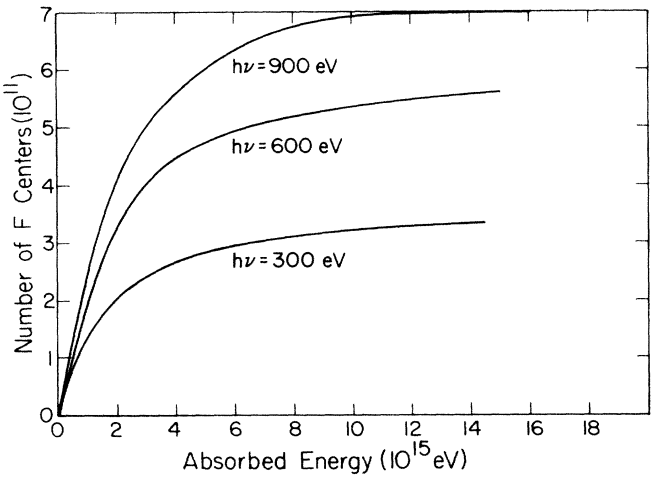

FIG. 2. *F*-center production near the surface of a KCl crystal as a function of adsorbed energy at x-ray photon energies of 300, 600, and 900 eV. The *F* centers are produced within an absorption depth (10^{-4}–10^{-5} cm) very close to the surface and in an irradiated area of about 2.0 mm × 1.5 mm.

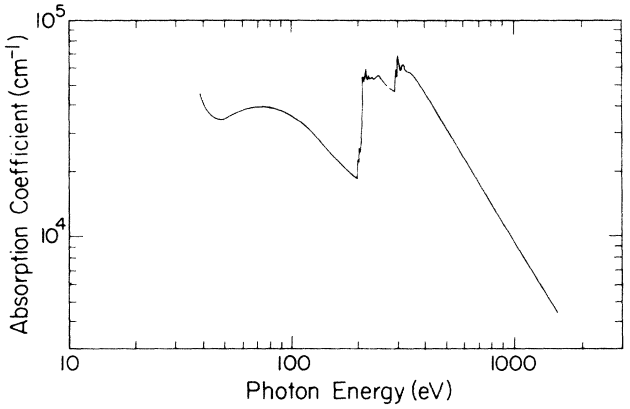

FIG. 3. Absorption coefficient of KCl as a function of photon energy. Data are from thin-film transmission measurements.

100-keV x-ray tube. Curves obtained in the synchrotron experiment were similar, except that the initial rise was more rapid, and the final saturation level depended strongly upon photon energy.

Results can be understood by the plotting of growth curves as a function of absorbed energy, after division by the number of incident photons per second and the photon energy. Such a plot for KCl is shown in Fig. 2 at soft x-ray energies of 300, 600, and 900 eV. The spectral bandwidth in each case was very narrow—of the order of 1.0 eV, corresponding to the 50-μm slit width in the monochromator.[10] The different saturation levels of these curves can be understood by consideration of the absorption depth of the incident x-ray radiation.

The absorption coefficient μ (inverse centimeters) of KCl is shown as a function of photon energy on a log-log scale in Fig. 3. These data were obtained in recent and in earlier experiments[12] by observation of the transmission of thin evaporated films. The chlorine $L_{2,3}$ edge can be seen at 200 eV and the potassium $L_{2,3}$ edge at 300 eV. Notice that at 600 eV the absorption coefficient for KCl decreases to less than half its value at 300 eV. It decreases by another factor of one-half in going from a photon energy of 600 to 900 eV. Clearly, the *F* centers in Fig. 2 are formed very close to the surface (10^{-5} to 10^{-4} cm), but a larger volume of coloration results at the higher photon energies, giving increased saturation levels and a larger total number of centers as the soft x rays penetrate more deeply into the crystal. At a given photon energy these saturation levels are more or less independent of x-ray intensity in agreement with, for example, the electron-bombardment experiments of Sonder.[13] Here the volume excitation rate is comparable to, or greater than, that employed in electron-bombardment studies.[13] Also the incident x-ray flux was varied over more than an order of magnitude without a noticeable effect on the saturation level at a given photon energy. In general, the stage-II behavior and saturation at volume densities of coloration approaching 10^{18} cm^{-3} can be understood in terms of well-known models.[8,9] The model of Comins and Carragher,[8] for example, assumes that stable color-center density is favored by the trapping of halogen at impurity-vacancy complexes.

We now turn to a discussion of the efficiency for *F*-center generation as a function of photon energy. Notice that the initial slopes of the three different coloration curves shown in Fig. 2 for KCl are approximately the same over the energy range (300–900 eV). A determination of the initial slope of these curves at the various photon energies for both KCl and KBr allows one to estimate the absorbed energy per *F* center. Values of these *F*-center creation energies are given in Table I. They roughly agree with the earlier preliminary work of Elango, Gähwiller, and Brown,[7] using broad-band synchrotron radiation but with an entirely different method for observation of the point defects.

TABLE I. Formation energy ε [keV/(*F* center)].

$h\nu$ (eV)	ε_{KCl}	ε_{KBr}
45	8.0[a]	10.8[a]
60	3.7	5.6
70	3.4[a]	2.9[a]
90	1.6	2.8
130	0.73[a]	1.2[a]
300	1.4	2.2
900	1.1	1.6
1200	1.3	1.8

[a]From Elango, Gähwiller, and Brown, Ref. 7.

The data of Table I show approximately constant formation energy as a function of photon energy, except at the lowest energy where an increase begins to take place. This increase occurs at the highest absorption coefficients and may be due to competing effects resulting in a reduced yield of F centers at the surface. The competing process could well be the important photodesorption of neutral sodium at the surface. For example, Haglund *et al.*[3] suggest that F-center and H-center formation, through the recombination of self-trapped excitons, is a precursor to photon-induced alkali-metal atom desorption from the free surface.[3] In this case, F centers created close to or diffusing to the surface provide the electrons for neutralization of uncoordinated alkali-metal ions which desorb thermally.

Exposures in KCl just above and just below the chlorine $L_{2,3}$ edge at 200 eV (refer to Fig. 3) give the same formation energy within $\pm 20\%$. This is in contrast to the increased efficiency observed above the Br K edge in KBr as discussed in Ref. 6. There, at a photon energy of 13.4 keV, the increased yield above the edge was explained in terms of electron-hole recombination and the vacancy-cascade mechanism.[14] The difference in the present case is not surprising, considering that the average ion charge resulting from sudden formation of a hole in the bromine K shell is 7 to 8, whereas a hole in the chlorine L shell at 200 eV is likely to leave the ion doubly charged at most. Moreover, such estimates of the vacancy cascade are for atoms. Condensed-matter effects may well be involved, especially in the efficiency for electron-hole pair formation following core excitation.

We suggest that the most important result of this work is to demonstrate that, under intense vacuum-ultraviolet radiation, point defects are generated near the surface of crystals such as KCl and KBr very rapidly and with extremely high density. The saturation color density level in Fig. 2 at 300 eV corresponds to $\sim 3\times 10^{17}$ cm^{-3}. Such densities very near the surface should be taken into account when interpreting photoemission measurements and also in the case of bombardment-induced yield experiments. For example, the F centers may be a source of electron yield especially at low photon energies where even partially occupied conduction-band states can be seen as reported by Himpsel and Steinmann.[4]

The efficiency of near-surface generation of point defects can be understood in terms of well-known electron-hole or self-trapped–exciton recombination processes widely applied to bulk alkali halides at much lower excitation rates. This result helps to explain the very wide dynamic range of area detectors which rely upon color-center storage and which, although developed for medical x rays, have been successfully applied to much higher fluxes at a synchrotron radiation source.[5]

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