PHYSICAL REVIEW B VOLUME 53, NUMBER 20 15 MAY 1996-II

F-center formation by Br K-hole Auger decay in KBr

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(Received 24 April 1995; revised manuscript received 14 December 1995)

Spectral dependence of the F-center formation efficiency has been measured for KBr single crystals at liquid-helium and nitrogen temperatures in the vicinity of the K edge of bromine at 13.47 keV. The F-center formation efficiency was evaluated by the optical absorption measurement under irradiation with monochromatized synchrotron x rays. The efficiency was normalized to the deposited x-ray energy estimated by a sensitive photocalorimetric measurement. It has been found that the F-center formation efficiency shows an ~24% stepwise increase above the core threshold at liquid-helium temperature. This result suggests that the multiple ionization mechanism, following the core-hole Auger cascade, might participate actively in the F-center formation process. [S0163-1829(96)07320-1]

I. INTRODUCTION

The effect of core-hole excitation on the efficiency of the photochemical processes in solids such as surface desorption and defect formation has attracted much interest from the aspect of the core-hole decay mechanism. Knotek and Feibelman[1] observed thresholds for electron-stimulated desorption of positive ions from certain d-band metal oxides. They have concluded that the enhancement comes from the core-hole Auger decay. From the analogy we can expect that the similar mechanism plays an important role for the defect formation in bulk materials. The production of F and H centers by ionizing radiation is a well-known phenomenon in alkali halide crystals. The F center is a halogen ion vacancy trapping an electron, and the H center is the complementary interstitial atom. It is well understood that from the electron-hole pairs (e-h pairs) generated by ionizing radiation self-trapped excitons (STE's) are produced accompanied with lattice distortion. During e-h recombination the STE also passes through states that provide entry to the F and H center pair (F-H pair) production channel.[2] For the deep core excitation with x rays, an F-center formation model based on a multiple ionization mechanism was proposed by Varley[3,4] in 1954, more than two decades prior to the work of Knotek and Feibelman. According to his model a hole excited with an x-ray photon in a deep core state of a halogen ion results in several valence holes on the same halogen ion by the Auger cascade. If these holes stay on the halogen ion for a sufficiently long time, this multiply charged anion will be ejected from its initial lattice site owing to the Coulombic repulsion. The concept of the multiple ionization model is based on the Auger cascade. The photochemical process of the Varley model is fairly consistent with that of the surface desorption observed by Knotek and Feibelman.

Sever, Kristianpoller, and Brown[5] reported a definite increase in the F-center formation efficiency at the K edge of bromine in KBr. By using a traditional x-ray source and a sensitive luminescence detection method, they evaluated the efficiency to be 3.0 F centers per absorbed x-ray photon above the core threshold in KBr at liquid-nitrogen temperature (LNT), contrasting to 0.4 F centers just below the core threshold. They explained this increment of 2.6 in the efficiency above the core-edge threshold in terms of additional e-h pairs produced by the Auger cascade rather than the multiple ionization mechanism. On the contrary, Green *et al.*[6] showed that the number of e-h pairs does not increase above the core threshold on the basis of the following discussion. The dominant process of the e-h pair production is not the Auger cascade but inelastic scattering of the high-energy electrons excited by primary x-ray photons or by the subsequent Auger transitions. Based on the empirical rule proposed by Alig and Bloom[7] that the energy of about 3 times the band-gap energy is consumed to make an e-h pair by inelastic scattering, about 600 e-h pairs are generated in a KBr crystal on absorption of one x-ray photon of 13.5 keV. On the other hand, several additional holes are generated by the Auger cascade, being overwhelmed by the 600 e-h pairs. That is, the e-h pair production efficiency would not increase stepwise at the core-edge threshold. Therefore, it seems hard to expect that the number of e-h pairs multiplies by a factor of 8 above the K edge of bromine. Most of the F-H pairs generated by the e-h recombination are unstable and recombine with each other.[2,8] Thus, they needed to implicitly assume extra stability for the F-H pairs generated from the additional e-h pairs above the K edge.

The luminescence detection method of Sever, Kristianpoller, and Brown is very sensitive, and they would possibly observe extrinsic F centers in the surface region as is described later. On the other hand, the traditional absorption method enables us to observe intrinsic F centers in a bulk. However, the latter measurement requires a sufficient number of F centers. In order to produce F centers with monochromatic x rays in the absorption method, we need an intense x-ray source, and therefore have to wait for synchrotron x-ray sources to appear.

By means of the optical absorption method we have recently measured the spectral dependence of the F-center formation efficiency in KCl and KBr in the photon energy range of the *K* edge of chlorine and bromine, respectively, at liquid-helium temperature (LHeT).[9] We obtained growth curves of the *F* bands by measuring the intensity of the transmitted probe light tuned to the respective *F* bands, while irradiating the crystals with monochromatic synchrotron x rays. In contrast with Sever, Kristianpoller, and Brown,[5] we observed no discernible increase in the *F*-center formation efficiency at the thresholds in KCl and KBr within experimental error. Although scattering of the data was roughly 10%, the increment was less than 8. However, we should compare the results carefully because the experimental procedures are quite different.

Because of the scattering of the data we have not drawn a definite conclusion as to whether the multiple ionization mechanism works effectively or not in the *F*-center formation process. The constant efficiency per absorbed energy in the *F*-center formation suggests that the net efficiency would increase to some extent at the core threshold owing to the energy loss due to secondary processes such as x-ray fluorescence. In order to discuss this problem exactly the *F*-center formation efficiency should be measured with regard to the deposited x-ray energy, where the energy outgoing from the bulk by the x-ray fluorescence is excepted. Hereafter we will distinguish the deposited energy from the absorbed energy.

In this study we measure carefully the *F*-center formation efficiency using an improved procedure for KBr single crystals at low temperatures. In order to estimate the rate of the energy deposition for the incident x rays, we measure the spectral dependence of the efficiency of thermal conversion using photocalorimetric spectroscopy.[10] We also measure the bromine *K* fluorescence efficiency to discuss quantitatively the rate of the energy loss due to the radiative process. Studies for the *e*-*h* pair production efficiency are also essential to examine the conclusion proposed by Sever, Kristianpoller, and Brown. The STE luminescence yield is, though its contribution to the energy loss is absolutely low, proportional to the *e*-*h* pair production efficiency. In KBr two luminescence bands, which are called σ and π luminescences, are observed at 4.4 and 2.3 eV, respectively, as the STE luminescence at low temperatures.[11,12] We measure excitation spectra for the STE luminescence as a measure of the *e*-*h* pair production efficiency.

For studies using photocalorimetric spectroscopy and STE luminescence, LHeT is indispensable. LHeT can provide several advantages for the study of the *F*-formation efficiency. The *F* and *H* centers are not able to move at LHeT, which allows one to disregard the *F*-center bleaching due to the recombination with a well-separated *H* center. Thus the *F*-center formation efficiency does not depend on its concentration, and the concentration of the *F* center increases in proportion to the irradiation time.[13–15] Besides, the *F*-center formation efficiency is insensitive to the impurities at LHeT.[13] On the other hand, it is known that the α center, the ionized *F* center, is several times higher than the *F* center in the concentration at LHeT.[16,17] We need to know the relationship between these anion-vacancy centers to understand the defect formation. Srinivasan and Compton[14] showed that the concentration ratio of the α center to *F* center was almost constant over the x-ray irradiation time. Therefore, we will regard the *F* center to be representative of the anion-vacancy centers. In the following sections we describe the experimental details and the results, putting emphasis on the difference from our previous work and those of Sever, Kristianpoller, and Brown.[5]

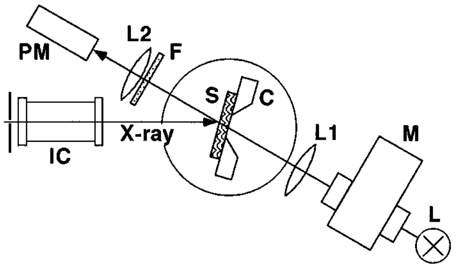

FIG. 1. A schematic for the measurement of the *F*-center formation efficiency: IC is ionization chamber, *L* iodine lamp, *M* monochromator, *L*1 and *L*2 lenses, *S* sample crystal, *C* cold finger, *F* filter, and PM photomultiplier tube.

II. EXPERIMENTAL DETAILS

The details of the experimental procedures for the spectral efficiencies of *F*-center formation, thermal conversion, x-ray fluorescence, and STE luminescence in KBr are described in sequence in the following sections.

A. *F*-center formation efficiency

The *F* centers were produced using synchrotron radiation from a normal bending magnet of the 2.5-GeV Photon Factory ring at Tsukuba, Japan. A schematic for the measurement of *F*-center formation efficiency is illustrated in Fig. 1. The synchrotron x rays were monochromatized with a silicon double-crystal monochromator, which provided about 10^{10} x-ray photons/sec with a beam size of 4 mm (horizontal) by 2 mm (vertical) over 13–15 keV for the beam current of 300 mA with an energy resolution of about 2.7 eV. The emergent x-ray beam passed through a small aperture and an ionization chamber and then came to the sample crystal mounted in a cryostat. The output of the ionization chamber was used as an intensity monitor for the incident beam, and was used for normalization of the measured quantities.

Cross-sectional uniformity of the incident x-ray beam is essential to estimate accurately the *F*-center density. Otherwise it would depend on the position measured with the probe light. Unfortunately, the incident beam showed spatial nonuniformity in the intensity. However, it was found that the intensity profile was quite stable and independent of the x-ray energy studied. In this study the *F*-center growth curves were measured at four x-ray energies for one sample. The energy-independent intensity profile made such a measurement quite sound.

Several KBr crystals of about 1 mm in thickness cleaved from a single crystal obtained from University of Utah (grown in inert gas) were attached to the cold finger of the cryostat with silicon grease. The x-ray beam was incident on the front surface of a sample crystal at an angle of 15°. The probe light of 600 nm for the *F* band of KBr was generated from an iodine lamp using a monochromator. It was incident from the back face of the sample through a small opening of the sample holder at an incidence angle of 15°. The probe

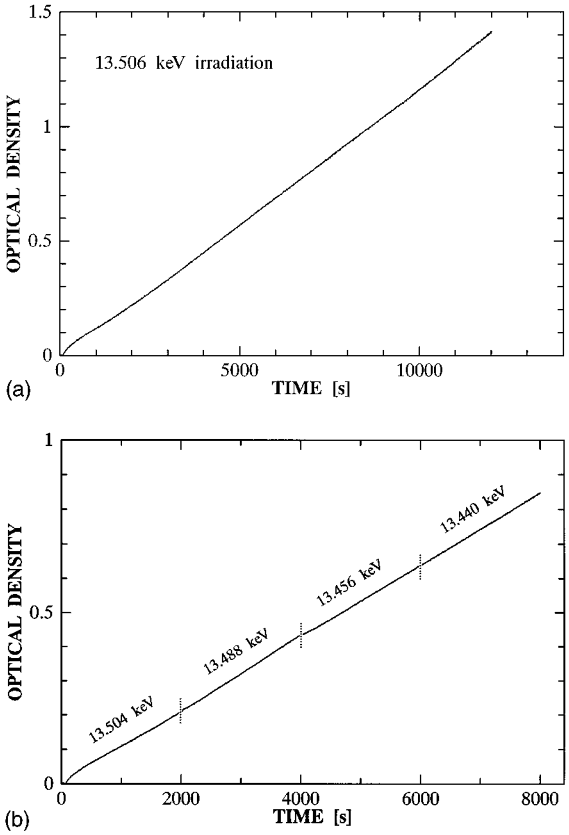

FIG. 2. (a) A growth curve of the F band in KBr induced by x-ray irradiation at 13.506 keV at LHeT. (b) A growth curve of the F band in KBr measured for the four x-ray energies denoted along the curve.

light was focused less than 1×1 mm^2 on the sample to observe exactly the same position inside the area exposed to the primary x-ray beam. The transmitted probe light was then refocused on a photomultiplier tube through a low-pass filter, which rejects the unwanted π and σ emission components. The attenuation rate of the probe light due to the increase in the F-center density and thus the optical density was measured as a function of the x-ray irradiation time t. The rate of the increment in the optical density provides the F-center formation efficiency. The intensity of the probe light was optimized so that the bleaching effect for the created F centers may be negligibly small.

Figure 2(a) shows a growth curve of the F band induced by x-ray irradiation at 13.506 keV at LHeT. The growth curve shows a rapid increase with exponential saturation in the early stage, $t<1000$ sec, and a linear increase at a steady rate in the latter stage, 1000 sec$<t$. The saturation in the F-center growth comes from filling the preexisting vacancies with the conduction electrons generated under the irradiation. In fact, we have observed that the STE luminescence is suppressed in the early stage.[18] After filling the preexisting vacancies the growth curve shows an almost linear increase. The steady slope of the growth curve in the latter stage provides the F-center formation efficiency. Judging from the result, 2000 sec was enough for irradiation to estimate the F-center formation efficiency at an x-ray energy.

From the slope of the growth curve the F-center formation efficiency was estimated. For example, from Fig. 2(a) the number of F centers per unit area, N_F, is expressed as a function of t (sec) as $N_F=2\times10^{11}t/\mathrm{cm}^2$. Unfortunately the absolute x-ray flux provided at the beamline 6B was not measured in this experiment. Using the nominal photon number of the beamline 6B, about 10^{10} photons/sec for the cross section of 2×4 mm^2, the F-center formation efficiency at 13.506 keV was roughly estimated to be about two F centers per absorbed x-ray photon. In other words, the energy required to produce an F center at LHeT is about 7 keV/(F center), which agrees roughly with the value of 3.3 keV/(F center) reported by Ritz.[15,19]

Contrary to the previous study,[9] where an F-center growth curve at an x-ray energy was measured for one sample, we measured at four x-ray energies for one sample in this study. Each sample was subjected to irradiation for 2000 sec at an x-ray energy, i.e., for 8000 sec in total. Of the four irradiation energies the lowest and the highest energies were always fixed to 13.440 and 13.504 keV, below and above the K edge of bromine at 13.472 keV, to examine the reproducibility of the efficiency as well as to cancel the dependence on the sample configuration. Of the remaining two energies, one was chosen between 13.440 keV and the core threshold, and the other was chosen between the core threshold and 13.504 keV. Each sample was irradiated with x rays in due order of the energy, i.e., from 13.504 to 13.440 keV. Figure 2(b) shows an example of the growth curve, which was obtained from serial measurements for energies of 13.504, 13.488, 13.456, and 13.440 keV. At the onset of x-ray irradiation for each energy the growth curve showed kink, especially at $t=0$ (onset of the x-ray irradiation) and $t=4000$ sec (the x-ray energy crossing the K edge of bromine). The growth curve was analyzed to a sum of exponential and linear growth. When the x-ray energy changes from above to below the K edge of bromine, the penetration depth of the x ray increases by about 8 times. The formation of additional F centers in the deep crystal region and the bleaching of the already formed F centers should be taken into account. However, the sum of two exponential functions, for growth and bleaching effects, and a linear function are applicable. The slope of the linear growth region gives the F-center formation efficiency. As is noticed in Fig. 2(b), the linearity of the growth curve for 13.440 keV was better than that for 13.504 keV. Actually the slope of the 13.440 keV growth curve fluctuated from sample to sample within 2%. Therefore, the slope for 13.440 keV was employed to normalize the slopes for the other energies for each sample.

B. Thermal conversion efficiency

Under x-ray irradiation various defects including F centers are produced in alkali halide crystals, but a mere fraction of the incident energy was consumed for their creation. Most of the incident energy would finally change into thermal energy. Therefore, the thermal conversion efficiency would correspond exactly to the rate of deposition for the incident x-ray energy. The thermal conversion efficiency in various crystals can be studied by means of photocalorimetric method.[10] Figure 3 shows a schematic for the photocalorimetric measurement used in this study. A sample of 5×5 mm^2 by 1 mm in thickness was suspended with thin quartz

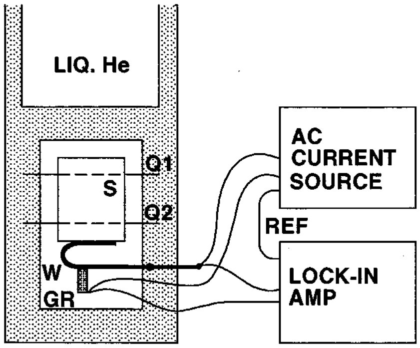

FIG. 3. A schematic for the photocalorimetric measurement in this study: *S* is sample crystal, *Q*1 and *Q*2 thin quartz wires, *W* thin gold wire, GR Ge resistor thermometer.

wires and thermally linked to a copper heat sink of a temperature about 5 K with a gold wire of 0.1 mm diameter. To this wire was also thermally linked a germanium temperature sensor (Cryocal E-500). Another germanium sensor with almost the same characteristics as the former was attached to the copper heat sink to compensate the effect of thermal drift (not shown in the figure). The heat dissipated in the sample causes change in the resistance of the former germanium sensor. The resistance change was measured with a sensitive ac bridge. With this system we were able to detect the power dissipation as low as 10^{-8} W. Since the incident x-ray flux was 10^{10} photons/sec, i.e., 10^{-5} W, this method is useful to estimate accurately the thermal conversion efficiency.

C. X-ray fluorescence efficiency

The quantum efficiency of the bromine *K* fluorescence in a KBr crystal was measured at room temperature in the following manner. A cleaved KBr crystal was positioned perpendicular to the incident x-ray beam. A Schottky-barrier type photodiode[20] with a sensitive area of 98 mm^2 (Hamamatsu Photonics G-2119-01) was positioned about 50 mm in front of the sample to measure the x-ray fluorescence intensity. All were arranged in atmosphere. An excitation spectrum for the bromine *K* fluorescence was measured from 13.3 to 13.7 keV by scanning the energy of the incident x rays. The intensity of the incident x rays was measured over the same energy range with the same photodiode positioned at the sample. The sensitivity of the photodiode was calibrated to the ionization chamber. The fluorescence efficiency was estimated on the assumption that the x-ray fluorescence is isotropically emitted. The emitted x rays will be reabsorbed while passing through to the surface. Using the absorption coefficients, the fluorescence quantum yield of the bromine *K* shell was estimated from the measured efficiency. Detail of the formulation is described in Appendix. Although the sample temperature and the incidence angle of the x ray were not equivalent with those in the *F*-center formation measurement, they are not essential for the present study.

D. STE luminescence efficiency

In KBr σ and π emissions are observed at 4.4 and 2.3 eV, respectively, at low temperatures. The luminescence spectra were measured at LHeT using the same setup for the *F*-center growth measurement except for the iodine lamp, which was replaced with the photomultiplier tube (see Fig. 1). In this measurement the luminescence light emerging backward was focused with the lens onto the exit slit of the monochromator. Excitation spectra for the two STE luminescence bands were measured using the secondary monochromator at the respective peak energies by normal dc measurement.

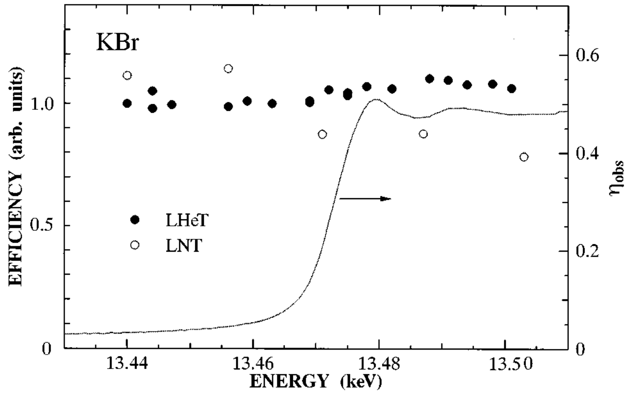

FIG. 4. Spectral dependence of the *F*-center formation efficiency around the *K* edge of bromine measured for KBr at LHeT (solid circles) and LNT (open circles). The excitation spectrum for the bromine $K\alpha$ fluorescence efficiency η_{obs} is also illustrated with a thin solid curve.

III. RESULTS

The *F*-center formation efficiency per absorbed x-ray energy at LHeT obtained in this study is shown in Fig. 4 with solid circles. For reference, the excitation spectrum for the bromine *K* fluorescence measured in this study is also illustrated with a thin solid curve. The scattering in the *F*-center formation efficiency is 3%, a fair amount smaller than that of our previous study. As is seen, the formation efficiency per absorbed energy increases stepwise by about 8% at the core-edge threshold. The definite increase implies a net increase in the efficiency per deposited energy. However, similar to our previous work,[9] it would not increase stepwise by a factor of 8 times observed by Sever, Kristianpoller, and Brown. The *F*-center formation efficiency was also measured at LNT at eleven energies between 13.38 and 13.54 keV using the same method as in the previous study.[9] Some of them are shown in Fig. 4 with open circles. The efficiency seems to decrease at the core-edge threshold. However, because of the low reliability of the previous method and the data fluctuation, it is difficult to draw the above conclusion. Anyway, it is essential that the efficiency does not show a stepwise increase as large as reported by Sever, Kristianpoller, and Brown.[5]

The thermal conversion efficiency measured using the photocalorimetric method is shown in Fig. 5 with a dotted curve. It shows small structures, which correlate inversely with the structures in the efficiency of the bromine *K* fluorescence shown in Fig. 4. The thermal conversion efficiency is normalized to one below the core threshold. The relative efficiency drops stepwise by about 13% at the core threshold.

As mentioned above, the excitation spectrum for the bro-

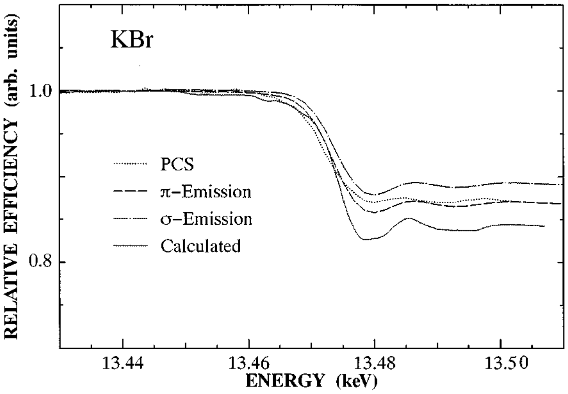

FIG. 5. Spectral dependence of the thermal conversion efficiency (dotted curve) and σ (dashed-dotted curve) and π (dashed curve) luminescences measured for KBr single crystals at LHeT. Spectral dependence of the term of $1-0.34\eta_{\mathrm{obs}}$ (thin solid curve) is also plotted for comparison.

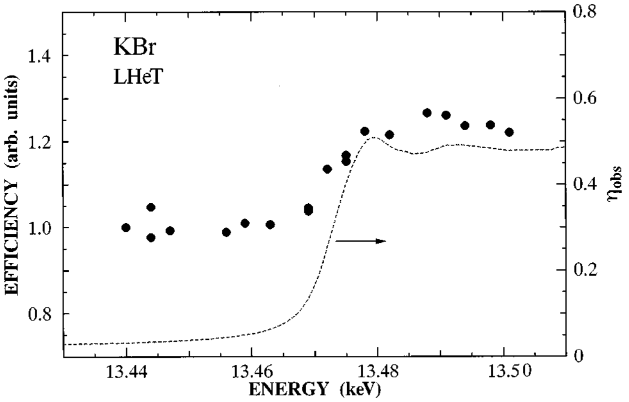

FIG. 6. Spectral dependence of the F-center formation efficiency in KBr at LHeT normalized to the thermal conversion efficiency (see Fig. 5). The excitation spectrum for the bromine $K\alpha$ fluorescence efficiency η_{obs} is also illustrated with a thin solid curve.

mine K fluorescence is illustrated in Fig. 4 with a thin solid curve. A stepwise increase appears at the bromine K edge, suggesting that the x-ray fluorescence originates from the bromine K-hole relaxation. The bromine K fluorescence is composed of $K\alpha_1$ (11.92 keV) and $K\alpha_2$ (11.88 keV) and partly of $K\beta_1$ (13.29 keV), which is negligible in this study. From the geometry of the measurement with the photodiode the K fluorescence efficiency was estimated. We first calculated the apparent quantum efficiency η_{obs} using Eq. (A11), where the quantum efficiencies of the photodiode measured at $E_1=13.5$ keV (above the bromine K edge) and $E_3=11.9$ keV (the bromine $K\alpha$) were used. The right-hand ordinate on Fig. 4 stands for η_{obs} thus estimated. The efficiency was about 51% above the core threshold. From Eq. (A8) we estimated the fluorescence quantum efficiency of the bromine K hole to be about 68%, where we used the absorption coefficients $k_1=300$, $k_2=40$, and $k_3=54$ cm^{-1} (Ref. 5) for E_1, $E_2=13.4$ keV (just below the K edge), and E_3, respectively. The estimated value agrees fairly well with the atomic data, ~62%.[21]

The excitation spectra for the σ and π luminescences are shown in Fig. 5 with the dashed-dotted curve and dashed curves, respectively. They show small structures correlating inversely with the x-ray fluorescence. The decrement in the σ-luminescence yield above the core threshold was slightly smaller than that of the π-luminescence yield, which has not yet been resolved. The luminescence efficiency per absorbed x-ray energy averaged over the two luminescence bands decreases by about 13% above the bromine K edge. The decrement agrees fairly well with the drop in the thermal conversion efficiency shown above.

IV. DISCUSSION

A KBr crystal reemits a fraction of the absorbed energy as the bromine K fluorescence with the efficiency η under exposure to x rays above the K edge of bromine. Since the crystal is thick in comparison with the penetration depth of the incident x rays, the fluorescence x rays reemitted forward are completely reabsorbed by the crystal, while some portion of those reemitted backward can escape from the surface of the crystal. The energy dissipated in the crystal above the K edge is calculated using Eq. (A14). As is noticed, the right-hand side of Eq. (A14) is a function of k_1, i.e., E_1. However, we assume that k_1 and E_1 are constant to make the discussion simple. Using $k_1=300$, $k_2=40$, and $k_3=54$ cm^{-1}, and $E_1=13.48$ and $E_3=11.9$ keV the deposited energy relative to that below the K edge is reduced to $1-0.34\eta_{\mathrm{obs}}$. The spectral dependence of the term $1-0.34\eta_{\mathrm{obs}}$ is shown in Fig. 5 with a thin solid curve. Since most of the e-h pairs are generated by inelastic scattering of high-energy photoelectrons and Auger electrons, the efficiency of the e-h pair formation is linearly proportional to the energy deposited in the crystal. This energy dependence can be confirmed by measuring the spectral efficiencies of the thermal conversion and the STE luminescence. Figure 5 compares the term $1-0.34\eta_{\mathrm{obs}}$ with the thermal conversion efficiency and the STE luminescence yield. Their agreement is quite good. This result suggests strongly that the dominant energy-loss process is the secondary x-ray emission under x-ray exposure above the K edge.

Based upon the results we calculate the F-center formation efficiency per deposited x-ray energy. As for the deposited energy we employ the thermal conversion efficiency. The F-center formation efficiency per deposited energy at LHeT is plotted in Fig. 6 with solid circles. The stepwise increase is ~24% and an increment in the efficiency is definitely ascertained. Similar to Fig. 4, the excitation spectrum for the bromine K fluorescence is also shown in the figure.

The result of this study is clearly incompatible with that of Sever, Kristianpoller, and Brown. They studied the F-center formation under the F-center concentration of 10^{11}/cm^3, which is considerably lower than that of this study, i.e., 10^{15} to 10^{17} F centers/cm^3. The F-center growth measured by Sever, Kristianpoller, and Brown would correspond to the early stage of the growth curve shown in Fig. 2(a). The F-center formation in the early stage may be mainly due to extrinsic processes; for example, filling of the preexisting vacancies with generated electrons and the vacancy formations in the surface region. The increment of a factor of 8 at the bromine K edge coincides with the increase in the absorption coefficient of KBr at the K edge, i.e., 40–300 cm^{-1}. The surface effect plays a significant role in the F-center formation. In the surface region, some of the generated core holes by x rays may result in desorption of Br^0 and Br_2^-. Since most of the F centers formed by the x-ray irradiation recombine with the H centers to restore the normal lattice points, desorption of Br^0 or Br_2^- may lead to the efficient formation of stable F centers near the surface.

As mentioned in Sec. I, Srinivasan and Compton[14] showed that the concentration ratio of the α to F center kept constant up to the F-center concentration of $7\times10^{16}/\mathrm{cm}^3$ at LHeT, which is roughly the same with that in this study. On the contrary, Ritz[15] reported that they largely depended on the temperature as well as their concentration. The inconsistency would come from the difference in the sample quality. Srinivasan and Compton prepared their samples by zone-refining method, while Ritz obtained crystals from Harshaw Chemical Company. The single crystal used in this study was grown in inert gas. With regard to the impurities our sample would be very close to that of Srinivasan and Compton. Thus we may expect that the α to F center ratio is almost constant over the F-center concentration studied.

The deposited energy in a unit volume increases by about 8 times when the excitation energy crosses the bromine K edge, because the absorption coefficient increases stepwise from $k_2=40\ \mathrm{cm}^{-1}$ to $k_1=300\ \mathrm{cm}^{-1}$. Thus the excitation-intensity dependence of the F-formation efficiency should be taken into account. However, for the following reasons, the efficiency obtained in this study seems to be independent of the excitation intensity. Most of the F-H pairs generated by the e-h recombination are unstable and recombine with each other.[2,8] Only the well-separated F and H centers are stable. Since the bleaching effect due to the F-H recombination is the second-order reaction, the F-formation efficiency would depend on the concentration of the stable F center. However, the concentration of the generated F center was rather low, i.e., at most 10^{17} (F centers)/cm^3 in this study. Besides, F and H centers are immobile at LHeT. Thus the bleaching effect due to the F-H recombination is negligible.

In the previous study for KCl, we did not observe core-excitation effects on the F-formation efficiency at the K edge of chlorine, while we have observed a discernible increase at the K edge of bromine in KBr. Since core holes in a deeper core level would generate more holes around the excited ion site, the effect of the Coulombic repulsion would be more remarkable. If the observed increase in the F-formation efficiency originates from the multiple ionization mechanism, we may expect a clearer effect on the F formation at the K edge of iodine in KI or RbI crystals.

V. SUMMARY

Spectral F-center formation efficiency has been measured for KBr single crystals at liquid-helium and nitrogen temperatures in the vicinity of the K edge of bromine by using the traditional F-absorption method. The samples were irradiated with monochromatized synchrotron x rays. The F-center formation efficiency was normalized to the deposited x-ray energy estimated from the sensitive photocalorimetric measurement. It has been found that the F-center formation efficiency shows a stepwise increase of ~24%. It has been also found from the excitation spectra for the STE luminescence that the e-h pair production efficiency does not increase above the core threshold. Our result disagrees with that of Sever, Kristianpoller, and Brown. This result suggests that it is not the multiplication of e-h pairs, but the multiple ionization, following the core-hole Auger cascade, that might participate actively in the F-center formation process.

ACKNOWLEDGMENTS

The authors appreciate the support of the staff of the Photon Factory. This work has been performed under the approval of the Photon Factory Program Advisory Committee (Proposals No. 89–114 and No. 91–200).

APPENDIX

Consider first a crystal that emits K x-ray photons of energy E_3, when excited with x-ray photons of energy E_1 above the K edge threshold. It has absorption coefficients k_1 and k_3 at E_1 and E_3, respectively. Besides, we assume an absorption coefficient k_2 at E_2 just below the K edge. It represents the background for the K-shell absorption above the K edge. Let N_0 x-ray photons of energy E_1 be perpendicularly incident on the crystal in a unit time. The absorbed photons in the volume of thickness Δx at a depth x below the irradiated surface is given by

$$\Delta N = k_1 N_0 e^{-k_1 x}\Delta x. \tag{A1}$$

The number of photons used for the K-shell ionization is

$$\frac{k_1-k_2}{k_1}\,\Delta N = (k_1-k_2)N_0 e^{-k_1 x}\Delta x. \tag{A2}$$

Therefore, the number of photons, ΔN_L, reemitted inside the volume Δx is given by

$$\Delta N_L = \eta(k_1-k_2)N_0 e^{-k_1 x}\Delta x, \tag{A3}$$

where η is the quantum efficiency of the K-shell fluorescence. We assume now that the x-ray fluorescence is emitted isotropically. The photons emitted in the solid angle $\Delta\Omega = 2\pi\sin\theta\Delta\theta$, where θ is measured from the x axis, will be reabsorbed while proceeding along the path of $l = x/\cos\theta$. Therefore, the number of photons observed at the surface is

$$\Delta N_L(\theta) = \eta(k_1-k_2)N_0 e^{-k_1 x}\Delta x e^{-k_3 l}\,\frac{\Delta\Omega}{4\pi}. \tag{A4}$$

The total number of photons appearing outside the crystal surface is presented by the following integral form:

$$N_L = \frac{1}{4\pi}\int_0^\infty\int_0^{\pi/2} N_0\,\eta(k_1-k_2)e^{-(k_1+k_3/\cos\theta)x}d\Omega\ dx. \tag{A5}$$

When we substitute $\theta=0$, we can get the number of photons per solid angle observed in the direction normal to the crystal surface, that is,

$$N_L(0) = \frac{1}{4\pi}\int_0^\infty N_0\,\eta(k_1-k_2)e^{-(k_1+k_3)x}dx$$
$$= \frac{1}{4\pi}\,\frac{k_1-k_2}{k_1+k_3}\,N_0\,\eta. \tag{A6}$$

Thus, η is given by

$$\eta = 4\pi \frac{k_1 + k_3}{k_1 - k_2} \frac{N_L(0)}{N_0}. \tag{A7}$$

Here we define the apparent quantum efficiency, $\eta_{\mathrm{obs}} = 4\pi N_L(0)/N_0$. It is directly obtained from the measurement described below. Since $N_L(0)$ and N_0 are functions of E_1, η_{obs} is also a function of E_1. Using this, we obtain η by

$$\eta = \frac{k_1 + k_3}{k_1 - k_2} \eta_{\mathrm{obs}}. \tag{A8}$$

In practice, with use of a photodiode we measure the photocurrent for the incident and emitted x rays, I_0 and I_L. They can be represented using the quantum efficiency of the photodiode, $S(E)$, as

$$I_0 = eN_0 S(E_1), \tag{A9a}$$

$$I_L = eN_L(0)\Omega S(E_3). \tag{A9b}$$

where e is the electronic charge and Ω is the solid angle for the sensitive area of the photodiode. From these

$$\frac{I_L}{I_0} = \frac{N_L(0)\Omega S(E_3)}{N_0 S(E_1)} = \frac{\Omega}{4\pi} \frac{S(E_3)}{S(E_1)} \eta_{\mathrm{obs}}. \tag{A10}$$

Therefore, using the measured quantities we calculate η_{obs}, and thus η, by the following equation:

$$\eta_{\mathrm{obs}} = \frac{4\pi}{\Omega} \frac{I_L}{I_0} \frac{S(E_1)}{S(E_3)}. \tag{A11}$$

On the other hand, from Eq. (A5) the total number of photons emitted from the crystal surface is

$$N_L = \frac{k_1 - k_2}{2k_1} \left(1 - \frac{k_3}{k_1} \ln \frac{k_1 + k_3}{k_3} \right) N_0 \eta. \tag{A12}$$

Using Eq. (A8),

$$\frac{N_L}{N_0} = \frac{k_1 + k_3}{2k_1} \left(1 - \frac{k_3}{k_1} \ln \frac{k_1 + k_3}{k_3} \right) \eta_{\mathrm{obs}}. \tag{A13}$$

Thus the energetic deposition efficiency for the incident x rays, $(N_0 E_1 - N_L E_3)/N_0 E_1$, is given by

$$\frac{N_0 E_1 - N_L E_3}{N_0 E_1} = 1 - \frac{k_1 + k_3}{2k_1} \left(1 - \frac{k_3}{k_1} \ln \frac{k_1 + k_3}{k_3} \right) \frac{E_3}{E_1} \eta_{\mathrm{obs}}. \tag{A14}$$

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