Effects of Core-Level Excitation on the F-Center Formation in KCl and KBr at Liquid-Helium Temperature

Yasuhiro Kondo, Shuuji Hoshina, ^(a) Shouichi Hirota, Ikuma Goto, and Yoshiaki Kon'no Department of Applied Physics, Tohoku University, Aramaki, Aoba, Sendai 980, Japan

Mihiro Yanagihara and Hiroaki Kimura^(b)

Research Institute for Scientific Measurements, Tohoku University, Katahira, Aoba, Sendai 980, Japan

Takaaki Hanyuu

Department of Physics, Tokyo Metropolitan University, Minami-Ohsawa, Hachiohji, Tokyo 192-03, Japan (Received 19 August 1992)

The spectral dependence of the F-center formation efficiency in KCl and KBr was measured in the photon energy region of the Cl K and Br K edges at liquid-helium temperature. No discernible increase in the F-center formation efficiency was observed at either the Cl or Br K edge.

PACS numbers: 61.72.Ji, 61.80.Cb, 78.50.Ec, 78.70.Dm

The production of defects by ionizing radiation in alkali halides has been studied for several decades. Presently, it is known that the primary products of irradiation by x rays or band-gap lights are the F- and Hcenter pairs. The F center is a negative-ion vacancy trapping an electron, and the H center is an interstitial halogen atom. Most of the F and H centers are formed by the nonradiative recombination of electron-hole pairs (*e*-*h* pairs), which are generated by ionizing radiation [1].

However, in the early stage of the studies on the defect formation, the following mechanism characteristic of xray irradiation was proposed by Varley [2,3]. An x-ray photon creates a hole in the deep core state of a halogen ion. This deep core hole decays into several valence holes on the same halogen ion by the intra-atomic Auger cascade, forming a positively charged halogen ion. If the holes can remain on the halogen ion for a sufficiently long time, this positive halogen ion may be ejected from its lattice point due to Coulomb repulsion. After the proposal by Varley, several experimental works [4-7] to examine the core effect on the F-center formation efficiency have been reported. However, clear evidence has not been shown because of the experimental difficulties, such as using weak monochromatic x-ray beams or filtered x rays with broad spectral width.

Recently, Sever, Kristianpoller, and Brown [8] reported a definite increase in the *F*-center formation efficiency at the Br K edge in KBr. By using a monochromatic x-ray source and a sensitive luminescence detection method, they obtained the efficiency of three *F* centers per absorbed x-ray photon above the Br K edge in KBr at liquid-nitrogen temperature (LNT), contrasting to the 0.4 *F* centers just below the K edge. They explained this increment of 2.6 in the efficiency in terms of the additional production of *e*-*h* pairs above the edge due to the Auger cascade. On the other hand, Green *et al.* [9] showed that the number of *e*-*h* pairs does not increase above the K edge based on the following discussions: The

dominant process of the e-h pair production is not the Auger cascade but the inelastic scattering of the highenergy electrons produced by absorption of x-ray photons or by the Auger transition. If we use the empirical rule proposed by Alig and Bloom [10] that it takes about 2 times the band-gap energy to make an e-h pair by inelastic scattering, about 600 e-h pairs are generated in the KBr crystal by absorption of one x-ray photon of 13.4 keV. On the other hand, only several additional holes are estimated to be generated by the Auger cascade, being overwhelmed by the 600 e-h pairs [9]. Therefore, it seems hard to expect the *e*-*h* pairs to multiply by a factor of 8 above the Br K edge. This conclusion by Green et al. has been confirmed by our recent experimental results [11] that the number of *e*-*h* pairs produced by x-ray irradiation does not increase when the x-ray energy crosses the Cl K edge in KCl at liquid-helium temperature (LHeT) [11]. Therefore, to explain the factor of 8 change in the F-center formation efficiency, both Sever, Kristianpoller, and Brown and Green et al. had to assume extra stability for the F-H pairs produced by the recombination of electrons and holes generated by the Auger cascades.

Rabin and Klick [12] found that the *F*-center formation by ionizing radiation is a bulk property when the *F*center concentration is 10^{15} to 10^{16} /cm³ and when the temperature is as low as LHeT. On the other hand, Sever, Kristianpoller, and Brown [8] measured the efficiency at the *F*-center concentration of about 10^{11} /cm³ at LNT. It is, therefore, necessary to remeasure the *F*-center formation efficiency in a sufficient concentration at LHeT. In this Letter, we report the spectral dependence of the *F*-center formation efficiency in the Cl *K* and Br *K* edge regions in KCl and KBr at LHeT.

The monochromatic x rays were obtained from a 2.5 GeV positron storage ring at the Photon Factory, Tsukuba, coupled with double crystal x-ray monochromators. For measurements in the Cl K edge region, beam line

BL-11B was used where x-ray flux of about 10¹¹ photons/sec was provided between 2.6 and 3.0 keV at a stored beam current of 200 mA. For the Br K edge, beam line BL-6B which provided x-ray flux of about 10^{10} photons/sec between 13.0 and 15.0 keV at the beam current of 200 mA was used. The x-ray beam was incident at an angle of 22.5° (15°) on a cleaved surface of a KCl (KBr) crystal. A probe light, whose wavelength was tuned to the peak energies of the F bands in KCl (KBr), was incident at an angle of -22.5° (-15°) on the KCl (KBr) crystal. It was focused on the crystal in such a way that the probe light examined exactly the same region of the sample exposed to the x-ray beam. The beam size of the probe light was less than $1 \times 1 \text{ mm}^2$ at the sample surface and was sufficiently small compared to the x-ray beam size of $4 \times 4 \text{ mm}^2$ at BL-11B and 2×6 mm² at BL-6B. The attenuation of the probe light due to the F-center absorption was measured with a photomultiplier (Hamamatsu Photonics R928) and an electrometer as a function of the x-ray irradiation time. After the first 30 min of exposure to the x-ray beam, the absorption spectrum was measured. It was then confirmed that the absorption was solely due to the F centers. The number of F centers per unit area was estimated from the attenuation of the transmitted probe light and from Smakula's formula [13] using an oscillator strength of 0.8. By turning off the probe light, excitation spectra of the intrinsic luminescence were measured with the same detection system as for the probe light. The x-ray fluorescence, $K\alpha$ and $K\beta$, of a halogen ion was emitted backward, and was detected by a windowless Shottkeybarrier-type photodiode (Hamamatsu Photonics G-1127-04).

The sample crystals of KCl were cleaved from a block of single crystal obtained from Union Material Co., Ibaraki, Japan, while KBr samples were prepared from a block of the KBr crystal purchased from the Crystal Growth Laboratory, University of Utah. Each cleaved crystal ($6 \times 6 \times 1 \text{ mm}^3$ in size) was mounted on a copper cold block of a cryostat and cooled down to LHeT.

Figure 1 shows a typical growth curve of the F band induced by the x-ray irradiation at 13.62 keV in KBr at LHeT. As shown in Fig. 1, the growth curve consists of two stages: an early stage of rapid growth, in which the F-center formation saturates in a few minutes, and a latter stage of linear growth, in which the rate of the Fcenter formation is almost constant. The rapid nonlinear growth in the early stage has already been observed by Ritz [4] and was attributed to residual impurities or negative-ion vacancies in the crystal. Similar nonlinear growth was observed at the outset of the x-ray stimulated intrinsic luminescence [11]. The F-center formation by filling the negative-ion vacancies that exist originally in the crystal may be responsible for the nonlinear growth. The latter stage, where the F center is formed almost linearly as a function of exposure time, has been also ob-



FIG. 1. Growth curve of absorbance at 600 nm in KBr induced by irradiation of 13.62 keV x rays at LHeT.

served by Rabin and Klick [12], and by Ritz [14]. It has been attributed to an intrinsic process since the slope of the linear growth is not sensitive to impurities in the crystal [12,15]. In KCl, similar growth curves of the F band were also obtained for the irradiation of x rays between 2.81 and 2.84 keV.

From the slope of the growth curve in the latter stage the *F*-center formation efficiency can be estimated. For example, the number of *F* centers per unit area, N_F , in the latter stage, shown in Fig. 1 (13.62 keV irradiation), is expressed as a function of irradiation time, *t* (sec), by

$$N_F = 2.1 \times 10^{11} t / \text{cm}^2.$$
 (1)

Since the x-ray flux from the BL-6B was about 10^{10} photons/sec and its cross section was $2 \times 6 \text{ mm}^2$, the *F*-center formation efficiency at 13.62 keV is 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 6 keV/(*F* center), which is in rough agreement with the value of 3.3 keV/(*F* center) reported by Ritz [4,14].

Unfortunately, the absolute photon number of the xray beams could not be measured in the present experiments. Therefore relative F-center formation efficiencies were calculated in KCl and KBr and were plotted in Figs. 2 and 3, respectively, in their halogen K edge regions versus x-ray energy. The excitation spectra of K fluorescence of halogen ions are also shown in Figs. 2 and 3 in order to locate the corresponding halogen K edges. Although the scattering of the data is fairly large, Figs. 2 and 3 show that the F-center formation efficiencies in both KCl and KBr seem to be constant in the displayed energy range and that a step increase in the efficiencies is not observed at the corresponding halogen K edges.

Our results are clearly different from those of Sever, Kristianpoller, and Brown [8]; that is, a stepwise increase of a factor of 8 in the *F*-center formation efficiency at the Br *K* edge was reported. However, their experimental condition is different from ours: They studied the *F*center formation in an *F*-center concentration of 10^{11} / cm³ and the sample temperature was at LNT, while in



FIG. 2. Spectral dependence of the relative *F*-center formation efficiency around the Cl K edge in KCl at LHeT. Circles show the efficiency at each energy. The excitation spectrum of the Cl-K fluorescence is also shown by the curve.

the present experiment, we measured in the concentration of 10^{15} to 10^{17} (*F* centers)/cm³ at LHeT. Therefore, measurements at LNT in high *F*-center concentrations are required for further discussions.

When a crystal is subjected to x rays above the K edges of the constituent ions, a fraction of the absorbed x-ray energy is reemitted as the K fluorescence with the efficiency η_K . If the crystal is thick in comparison with the penetration depth of x rays in the energy region of Kfluorescence, only the x-ray fluorescence emitted backward can escape from the surface of the crystal, while the fluorescence emitted forward is reabsorbed by the crystal. Hence, approximately half of the reemitted energy is reabsorbed by the crystal. The energy dissipated in the crystal above the K edge is, therefore, reduced to $1 - \eta_K/2$ of that below the edge. Since most of the *e*-h pairs are generated by the inelastic scattering of high energy photoelectrons and Auger electrons, the efficiency of the *e*-*h* pair formation is linearly proportional to the energy dissipated in the crystal. This energy dependence can be confirmed by measuring the efficiency of exciton luminescence which is due to recombination of the e-hpairs. For example, Bianconi, Jackson, and Monahan [16] observed a decrease in luminescence efficiency due to the Ca K fluorescence in CaF_2 .

If most of the *F*-*H* pairs which can remain stable after x-ray irradiation are formed by the nonradiative recombination of the *e*-*h* pairs, both efficiencies, the *F*-center formation and the exciton luminescence, should show the same excitation energy dependence around the Cl *K* edge. In KCl, η_K is about 9% [17]. However, the expected 4.5% decrease in efficiency of the intrinsic luminescence is too small to observe, and no change in the efficiency has been observed for the excitation below and above the Cl *K* edge [11]. The *F*-center formation efficiency in this region is also almost constant as shown in Fig. 2, within the experimental error.

According to Krause [17], η_K is as high as 50% in KBr. In the present study, however, a decrease of about 15% in the intrinsic luminescence efficiency was observed above



FIG. 3. Spectral dependence of the relative F-center formation efficiency around the Br K edge in KBr at LHeT. Circles show the efficiency at each energy. The excitation spectra of the Br-K fluorescence and exciton luminescence are shown by solid and dotted curves, respectively.

the Br K edge in KBr, as shown in Fig. 3. The smaller decrease of 15% instead of the expected decrease of 25% may be due to the reabsorption of x-ray fluorescence. On the other hand, the F-center formation efficiency which is shown in Fig. 3 is almost constant in the energy region investigated. The constant F-center formation efficiency, therefore, indicates that the ratio of the efficiency of Fcenter formation to that of the e-h pair formation increases above the K edge, since the number of e-h pairs generated above the edge decreases by 15%. If this is the case, core effects such as Varley's mechanism must be taken into account. However, Fig. 3 shows that the experimental error of the F-center formation efficiency is comparable to the decrement of the exciton luminescence, 15%, and more precise measurements are required for further discussions about the Br K-core effects.

This work has been performed under the approval of the Photon Factory Program Advisory Committee (Proposals No. 89-114 and No. 91-200).

- ^(a)Present address: Asahi Chemical Industry Co., Ltd., Sodegaura, Kimitsu, Chiba 299, Japan.
- ^(b)Present address: Department of Synchrotron Radiation Science, Graduate University for Advanced Studies, PF, KEK, Oho, Tsukuba 305, Japan.
- N. Itoh and K. Tanimura, J. Phys. Chem. Solids 51, 717 (1990).
- [2] J. H. O. Varley, Nature (London) 174, 886 (1954).
- [3] J. H. O. Varley, J. Phys. Chem. Solids 23, 985 (1962).
- [4] V. H. Ritz, Phys. Rev. 133, A1452 (1964).
- [5] J. Sharma and R. Smoluchowski, Phys. Rev. 137, A259 (1965).
- [6] N. Itoh, J. Sharma, and R. Smoluchowski, in Proceedings of the International Symposium on Color Centers in Alkali Halides, 1965, Urbana, Illinois (unpublished), Abstract No. 95.
- [7] B. A. Cruz-Vidal and H. J. Gomberg, J. Phys. Chem. Solids 31, 1273 (1970).

- [8] B. R. Sever, N. Kristianpoller, and F. C. Brown, Phys. Rev. B 34, 1257 (1986).
- [9] T. A. Green, M. E. Riley, P. M. Richards, G. M. Loubriel, D. R. Jennison, and R. T. Williams, Phys. Rev. B 39, 5407 (1989).
- [10] R. C. Alig and S. Bloom, Phys. Rev. Lett. 35, 1522 (1975).
- [11] Y. Kondo, S. Hoshina, M. Yanagihara, H. Kimura, T. Hanyu, and S. Yamaguchi, Solid State Commun. 80, 431 (1991).
- [12] H. Rabin and C. C. Klick, Phys. Rev. 117, 1005 (1960).
- [13] J. J. Markham, F-Centers in Alkali Halides, Solid State Physics Supplement No. 8, edited by F. Seitz and D. Turnbull (Academic, New York, 1966).
- [14] V. Ritz, Phys. Rev. 142, 505 (1966).
- [15] T. M. Srinivasan and W. D. Compton, Phys. Rev. 137, A264 (1965).
- [16] A. Bianconi, D. Jackson, and K. Monahan, Phys. Rev. B 17, 2021 (1978).
- [17] M. O. Krause, J. Phys. Chem. Ref. Data 8, 307 (1988).