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Spectral dependence of point defect production by x rays in RbBr

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F-center formation by monochromatic x rays has been studied above and below the bromine and rubidium *K*-absorption edges in crystals of RbBr. The x-ray beam from a double silicon crystal monochromator on an undulator at the Advanced Photon Source was used to produce these point defects, which were detected by a sensitive laser-induced luminescence method. Experiments were carried out over a wide range of monochromatic x-ray intensity, with emphasis on the nearly linear initial slope of defect formation with exposure. No significant increase in *F*-center formation efficiency was found upon crossing the bromine *K* edge, which indicates that additional Auger-cascade mechanisms do not appreciably add to the usual multiple ionization electron-hole recombination processes known to generate point defects. [S0163-1829(99)14733-7]

I. INTRODUCTION

A good deal is known about the detailed mechanism of radiation damage in insulating ionic crystals such as the alkali halides. For example, it is known that ionizing radiation produces *F* centers (electrons trapped at negative ion vacancies) and *H* centers (interstitial halogen atoms) through nonradiative recombination of electron hole pairs.[1,2] In the case of vacuum ultraviolet radiation,[3] and also for x rays,[4] the coloration efficiency (initial stage) within the volume of an alkali halide crystal turns out to be of the order of one keV per *F* center, and this efficiency varies slowly, if at all, with x-ray energy. A possible exception to this statement might be the occurance of mechanisms, other than outer level ionization followed by electron hole recombination across the valence band. One such process might be core level excitation above an inner level absorption edge followed by an Auger cascade and the formation of multiple electron hole pairs, which could then combine nonradiatively forming *F* centers by the usual process. Other possible core level processes for forming *F* centers are the Varley mechanism[5] and the recombination of a self-trapped core exciton as suggested by Kotani and Toyozawa.[6] On the other hand, it is hard to see how these last two mechanisms would result in a large increase in defect formation efficiency (more than one *F* center per absorbed x-ray photon).

On the experimental side, early reports have appeared in the literature concerning a possible increase in *F*-center production efficiency for x rays, above the Br *K* shell threshold in KBr,[7] and also above the Cl *K* edge in KCl.[8] In 1989 a theoretical study appeared by Green *et al.*[9] on Auger induced valence processes in the alkali halides. Among other issues, these authors considered the difficulty in explaining a large increase in efficiency for formation of *F* centers at the bromine *K* edge. They pointed out that increased production of electron-hole pairs due to the Auger cascade should be more or less insignificant compared to the number of electron-hole pairs already existing at energies below the edge.

More recently, considering the importance of the edge issue, Kondo and co-workers[10] undertook a study of the effects of core-level excitation on *F*-center formation efficiency at liquid helium temperature in KBr and KCl. These workers used intense synchrotron radiation and optical measurements of the resulting *F*-band absorption. Little or no discernible increase in *F*-center formation efficiency was found upon tuning above either the Br *K* edge in KBr or the Cl *K* edge in KCl. Subsequently, Yanagihara *et al.*[11] extended the work on KBr to liquid nitrogen temperature, where only a very small, if any, increase in *F*-center formation efficiency was found at liquid nitrogen temperature upon tuning above the bromine inner level threshold. This result on KBr was recently confirmed[12] using tunable synchrotron radiation along with the sensitive laser-induced luminescence method[7] to detect the generated *F* centers.

The present paper extends the work referenced above on the spectral response of defect formation above the bromine *K* edge in KBr to the Rb and Br edges in RbBr. As pointed out by Kondo *et al.*,[13] KBr and RbBr may be the most favorable materials for observing a possible *K*-edge effect. *F* centers form readily in these alkali bromides due to favorable ion size, the so called Rabin-Klick criterion.[14]

In the work reported here synchrotron radiation was used for the x-ray exposure, but a very wide range of intensity was employed by detuning the undulator with respect to the monochromator setting. Moreover, the laser-induced luminescence[7] method was used to detect the *F* centers, as

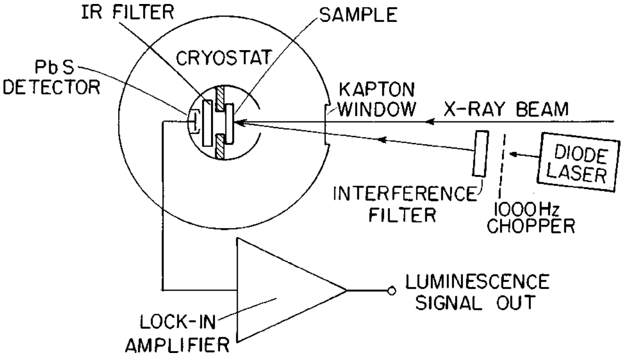

FIG. 1. Schematic of the laser-induced luminescence method as used here for detecting *F* centers produced by a normally incident monochromatic x-ray beam. Notice that the laser beam enters the front face of the sample at a small angle with the incident x-ray beam.

this technique is capable of a very wide dynamic range. The experimental methods are described in the next section, followed by a section on experimental results and Sec. IV on results and conclusions.

II. EXPERIMENTAL METHOD

The experiments were carried out using highly monochromatic x rays from the Pacific Northwest Consortium PNC-CAT insertion device beamline at the Advanced Photon Source (APS).[15] X rays from the sector 20 undulator pass through a double-crystal monochromator, a gas ionization chamber for monitoring purposes and finally on to the alkali halide sample within a cryostat in the experimental hutch.

A small optical cryostat[16] was modified so that the laser-induced luminescence measurements[7] could be carried out on an optical table in the x-ray beam. Figure 1 shows how the x-ray beam enters the vacuum region of the cryostat through a thin Kapton window. Samples of high purity RbBr, $7\,\mathrm{mm}\times 10\,\mathrm{mm}\times 2\,\mathrm{mm}$, were cleaved from crystals kindly supplied by Professor Fritz Luty at the University of Utah. A crystal of unknown purity grown by Semielements Inc. was also tested. The cleaved samples were mounted on the tail of the cryostat in vacuum in such a way that a laser beam of 670 nm radiation could be focused onto the crystal in the region of x-ray exposure. This beam, whose wavelength is close to the center of the *F*-absorption band in RbBr, was produced by a laboratory diode laser (Imatronic LDL175, Edmund Part No. F39569). Provision was made so that the cryostat with sample could be precisely moved in the vertical direction by microstepping. Because the x-ray beam was apertured to only 1 mm wide by 0.2 mm high, this small beam size allowed for exposure at eight separate positions on each crystal. The laser beam could be focused to a spot as small as 50 microns in diameter within the area exposed to x rays.

Following excitation and lattice relaxation, the *F* center in the alkali halides decays by emission in the near infrared, at about one micron wavelength. This laser-induced luminescence was detected by means of a PbS detector (Hamamatsu P397) within the cryostat close to the back face of the sample. This small detector was heat sunk to the outer dewar of the cryostat near room temperature, whereas the inner dewar was used to cool the sample to 77 K. The incoming laser beam, chopped at 1000 cycles per second, was filtered by a 670 nm narrow bandpass interference filter. An infrared cutoff filter (Corning No. 2540) was placed between the sample and the PbS detector. This arrangement allowed for good separation between the light inducing the luminescence and the Stoke-shifted infrared *F*-center emission. The luminescence signal was detected by an EG and G, Princeton Applied Research, Model 5204 lock-in amplifier referenced to the 1 kHz chopper.

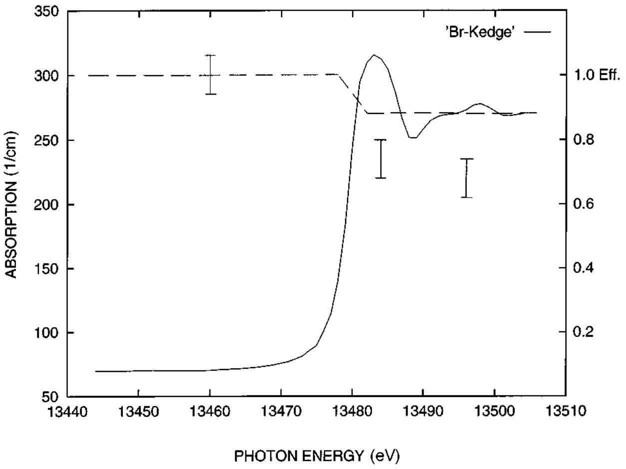

FIG. 2. The solid line shows the bromine *K*-absorption edge in RbBr as measured on a thin powder sample at room temperature. The vertical error bars show the values of observed *F*-center formation efficiency (referred to 13 460 eV, below the edge) and plotted using the scale Eff. given on the right. The dashed line is the estimated efficiency taking into account the escape of fluorescent radiation from the front face of the crystal, as discussed in Sec. IV.

The output of the lock-in amplifier, after digitizing, was brought out of the experimental hutch at the beamline by means of coaxial cables along with information on the cryostat position, incoming x-ray intensity and monochromator position. Data collection software based upon EPICS was used as developed by the Experimental Facilities Division of the APS. It was possible to extract multiple data files which could be tranmitted over the Internet for processing at the University of Washington.

A key feature of the experiment was the possibility of exposing the sample to x rays over a very wide range of intensity. Although the x-ray monochromator had very good energy resolution (about 2.5 eV bandwidth at 13 keV), the total flux in the submillimeter size beam at the peak of the first harmonic from undulator A was of the order of 10^{10} photons per second. On the other hand, the intensity could be changed over several orders of magnitude by simply adjusting the undulator gap so that the first harmonic energy moved above or below the setting of the x-ray monochromator. In this way the exposing x-ray flux could be varied from below 10^7 to over 10^{10} photons per second.

III. EXPERIMENTAL RESULTS

A few high resolution x-ray absorption measurements were made on RbBr in order to precisely locate the atomic inner level absorption edges. The solid line in Fig. 2 shows a plot of the *K*-shell absorption edge for bromine in RbBr. A

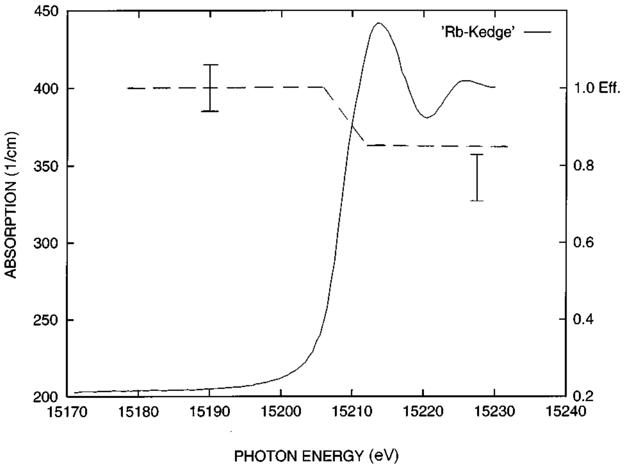

FIG. 3. The solid line shows the rubidium *K*-absorption edge in RbBr as measured on a thin powder sample at room temperature. The vertical error bars show the values of observed *F*-center formation efficiency (referred to 15 190 eV, below the edge) and plotted using the scale eff given on the right. The dashed line is the estimated efficiency taking into account the escape of fluorescent radiation from the front face of the crystal, as discussed in Sec. IV.

similar scan of the rubidium *K* edge is given in Fig. 3. This data was obtained on the PNC-CAT beamline by observing the transmission of thin polycrystalline samples at room temperature, and then determining the absorption coefficient from $\ln(I_0/I)$. The results were normalized to the well known x-ray absorption coefficients above and below the x-ray absorption edges.[17] Care was taken to prepare and measure the samples free from moisture. Measurements show that the absorption constant of RbBr varies from approximately 40 cm^{-1} below the bromine edge to about 300 cm^{-1} above the edge.

Notice the prominent peak or ''white line'' at 13482 eV in the case of the bromine edge, Fig. 2, and at 15213 eV in the case of the rubidium edge, Fig. 3. These absorption edge features might properly be ascribed to the formation of core excitons. They closely resemble the band gap exciton peaks showing up in recent *ab initio* absorption edge calculations taking electron-hole interaction into account.[18] These white lines also frequently appear in x-ray absorption near edge structure (XANES), where interaction between excited electron and core hole appears. They appear in RbBr potassium mixed salts[19] and in many other cases. A good comparison between experiment and multiple scattering theory, including the core hole, has recently been obtained for the boron *K* edge in cubic BN and the XANES structure of other compounds.[20]

In the radiation damage experiments, we compare the rate of formation of *F* centers above the bromine *K* edge, at say 13 496 eV, with the rate of formation below the edge at 13 460 eV. Data was taken sequentially in pairs so that the rate of formation above and below the *K* edge could be determined from the initial linear slope of the observed *F*-center luminescence signal, recorded during x-ray exposure as a function of time.

Figure 4 shows an example of the laser-induced *F*-center luminescence signal for a RbBr crystal at 77 K during exposure to monochromatic x rays at 13 460 eV. In this example a moderately high x-ray flux was used, of the order of 10^9 photons per second. The laser beam was incident upon the front face of the crystal along with the incident x rays. Notice the initial very rapid rise, as soon as the x rays were turned on at about 5 sec, followed by evidence of eventual saturation. In the model of Comins and Carragher,[21] this so-called stage I of *F*-center growth is a dynamic intensity-dependent process. Here this could be readily seen by taking scans at different x-ray intensity.

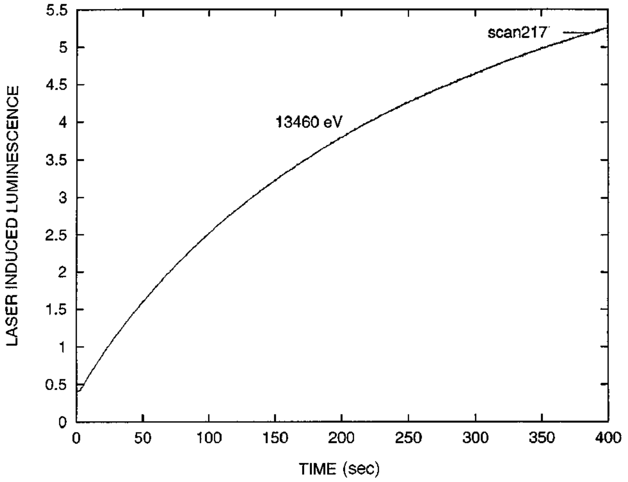

FIG. 4. Showing laser-induced luminescence due to *F* centers produced in a RbBr crystal under exposure to an intense monochromatic x-ray beam below the bomine *K* edge at a photon energy of 13 460 eV. The luminescence signal is plotted as a function of time during exposure, and data points were taken every 0.2 sec. The I_0 monitor signal was 2270, corresponding to about 3×10^9 photons/second within an $1\,\mathrm{mm}\times0.2\,\mathrm{mm}$ exposed area on the face of the crystal.

The primary process in stage I is the formation of *F* and *H* centers as a result of the radiationless decay of self-trapped excitons formed from electron-hole pairs produced by ionizing radiation.[1] The *H* center is the antimorph of the *F* center, essentially an interstitial halogen atom. Stable *F*-center formation requires that the *H* centers be trapped at defects, probably at substitutional divalent impurities such as calcium with associated vacancies (an impurity-vacancy dipole). Trapping at aggregates of impurity-vacancy dipoles also play a role depending upon temperature.

In our experiment at 77 K, the initial laser-induced luminescence signal rises more or less steeply depending upon the x-ray intensity. Let us concentrate upon the initial slope and compare the data for short scans taken at different photon energies. For this purpose, we normalize the data in each scan by dividing by the the incident x-ray flux, as measured by the I_0 reference signal. Several exposures were then taken on the same crystal as described in the next paragraph.

First, the uncolored crystal of RbBr was cooled to 77 K, then it was irradiated by x rays in a localized unexposed part of the crystal so as to produce a visible colored spot on the crystal. Then the laser beam was moved to this spot and carefully adjusted so as to maximize the laser-induced luminescence signal. The cryostat with crystal and detector was then microstepped to a fresh unexposed position so that a new coloration curve could be taken. Figure 5 shows the first 20 sec of exposure at 13 460 eV, below the bromine *K* edge

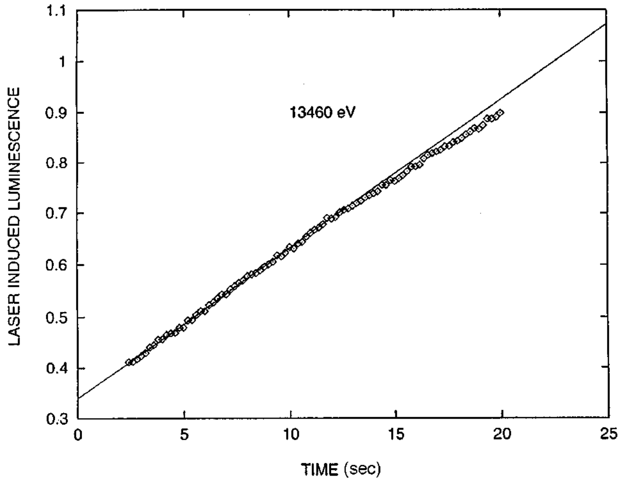

FIG. 5. Showing the initial linear portion of the laser-induced luminescence signal shortly after the x-ray beam was turned on at 2.4 sec. The x-ray photon energy was 13 460 eV, and the I_0 monitor signal was 2270, as in Fig. 4.

in RbBr. Notice the quality of the data and that a good linear initial slope can be obtained.

After data of the type shown in Fig. 5 was taken below the x-ray absorption edge, the crystal and cryostat was then moved to a new unexposed spot on the sample where the laser-induced luminescence was observed as a function of time for x-rays above the edge in the peak of the white line at 13 494 eV and a little farther into the continuum at 13 496 eV. The initial slopes above the edge could then be normalized to the initial slope at 13 460 eV below the edge. The ratio of these slopes (above/below) are shown with vertical error bars in Fig. 2, where the the ratio is read on the scale at the right. The ratio is likewise given for two energies near the rubidium edge, 15 190 and 15 228 eV in Fig. 3 and listed along with the data for the bromine edge in Table I.

In all scans a well defined initial linear rise was observed, and this could be used to determine the efficiency for *F*-center production with reasonable accuracy. A calibration run could also be taken measuring the optical density in the *F* band after exposure. The number of *F* centers per unit volume could then be determined from the optical density using Smakula's equation. Such a procedure yields a generation efficiency of the order of magnitude of 1 keV per *F* center. Further discussion of the results is given in the next section.

TABLE I. Initial slopes of laser-induced-luminescence signal versus time after the beginning of exposure for pairs of scans at the two energies shown. The ratio of slope above to below the given edge appears in the last column for each pair of scans.

Scan No.	Energy (eV)	Normalized slope (arb. units)	Ratio (above/below)
217*br*	13 460 below	0.0293	
218*br*	13 496 above	0.0196	0.669 ± 0.05
222*br*	13 460 below	0.0272	
219*br*	13 484 above	0.0196	0.720 ± 0.05
220*rb*	15 190 below	0.0337	
221*rb*	15 228 above	0.0255	0.756 ± 0.05

IV. DISCUSSION AND CONCLUSIONS

Early experiments[7] on KBr using the laser induced luminescence method suggested that a sizable increase in *F*-center formation efficiency occurred upon tuning the x-ray energy just above the bromine *K* edge. On the other hand, recent observations by Kondo and associates[11] on KBr at both liquid nitrogen and liquid helium temperatures give a slight decrease upon crossing the inner shell absorption edge. This has recently been confirmed in the case of KBr using synchrotron radiation and the sensitive laser induce luminescence method for detecting point defects. The present work confirms the small decrease above both the rubidium and the bromine *K* edges in RbBr.

The early laboratory experiments on KBr reporting a strong increase[7] involved long exposures to a very weak x-ray source, consequently a great deal of uncertainty was reported for each data point. Another important difference between the work reported here and the early experiments is that here the luminescence-exciting laser beam was incident through the front face of the crystal at a small angle with the x-ray beam. In the early experiments the laser beam was incident upon the side of the crystal. This geometry was also explored in the present experiments, with scans taken at very low x-ray intensity as well as high x-ray intensity. Frequently, with side geometry, the initial rise of the luminescence signal was found to curve upwards from the onset of exposure. In other words, the initial slope for side geometry was not linear. When both the incoming x rays and the laser beam were incident upon the front face of the crystal, the initial rise of the *F*-center luminescence signal was linear over a reasonable range of exposure. This was true for highly focused and also for defocused laser beams. The difference between the two geometries may be associated with the exponential penetration of x rays into the volume of the crystal and with the greatly different absorption depth above, as compared to below, the innershell threshold. Thus, with the laser beam incident upon the front face of the crystal, possible artifacts occur due to changes in the x-ray absorption depth are eliminated.

The size of the decrease in *F*-center formation efficiency above the *K* edge reported in Table I and Figs. 2 and 3 suggests that one should correct for the actual energy deposited within the crystal. The observed decrease may well be due to the loss of x-ray fluorescence energy through the face of the crystal. Likewise in the case of a well focused laser beam, any escape of fluorescent x-ray energy out of the sampled volume would result in a reduction of signal above the *K* edge. Let us estimate the first of these two losses, the escape of x-ray fluorescence energy through the front face of the crystal. Our derivation is similar to that given in Ref. 11 except that the fluorescent x-ray flux escaping in the normal direction was not directly measured. We therefore use the well known quantum efficiency for *K*-shell fluorescence efficiency[22] and allow for all backward angles of escaping x-ray fluorescence radiation through the face of the crystal. A thick crystal is assumed, in fact it is semi-infinite in the sense that the incident x-ray radiation is absorbed close to the front face of the crystal, and even though the fluorescence radiation is absorbed less strongly, it does not escape the back face of the thick crystal.

Let N_0 equal the number of photons/second incident normally upon the RbBr crystal at an energy $E_1 = 13\,496$ eV, which is above the bromine absorption threshold, where the absorption coefficient $k_1 = 275\ \mathrm{cm}^{-1}$. Just below the edge, at an energy $E_2 = 13\,460$ eV the absorption coefficient is $k_2 = 70\ \mathrm{cm}^{-1}$ for RbBr. K-shell fluorescence occurs at about $E_3 = 11\,900$ eV, where the absorption coefficient is $k_3 = 110\ \mathrm{cm}^{-1}$. Given N_0 and k_1, the number of photons absorbed in a thickness dx at a depth x is $dN = k_1 N_0 e^{-k_1 x} dx$. The fraction of these used for K-shell ionization is simply obtained by multiplying by $(k_1 - k_2)/k_1$. Therefore, the number of photons absorbed in dx and remitted as fluorescence radiation, is given by

$$dN_L = \eta (k_1 - k_2) N_0 e^{-k_1 x} dx, \tag{1}$$

where the K-shell fluorescence quantum efficiency is given by η. The L-shell emission efficiency is quite small, but the K-shell emission is as high as $\eta = 0.62$ for bromine and 0.68 for rubidium.[22] Assuming isotropic emission within the volume of the crystal, the number of photons which escape the front surface of the crystal can be estimated by integrating over solid angle $\Delta\Omega = 2\pi \sin\theta \Delta\theta$. It is necessary to take into account the absorption of emitted radiation along the path $l = x/\cos\theta$ where the x axis is perpendicular to the surface of the crystal. The total number of photons escaping in the back direction from the face of the crystal is thus an integral of the form

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

Now integrating over x, N_L becomes

$$N_L = N_0 \eta \frac{(k_1 - k_2)}{2k_3} \int_0^{\pi/2} \frac{\sin\theta \cos\theta d\theta}{1 + b\cos\theta}. \tag{3}$$

The integral in Eq. (3) can be evaluated with the result that

$$N_L = N_0 \eta \frac{(k_1 - k_2)}{2k_3} \left[\frac{b - \ln(1+b)}{b^2} \right], \tag{4}$$

where we have defined b as $b = k_1/k_3$.

Neglecting small energy differences, the energy efficiency above, as compared to below, the edge is given by

$$E_{ff} = \frac{N_0 E_1 - N_L E_3}{N_0 E_1}. \tag{5}$$

This last result can be evaluated using Eq. (4) and the numbers for E_1, E_3, k_1, k_2, and k_3. The result is $E_{ff} = 0.898$ for the bromine edge and $E_{ff} = 0.849$ for the rubidium edge. These estimates were used to draw the dashed lines in Figs. 2 and 3, which show how one expects the efficiency (plotted using the right scale) to vary due to fluorescent radiation escaping the front face of the crystal. In both cases the observed F-center formation efficiency above the K edge, shown by the error bars, lies somewhat below the dashed line. This is very likely due to escape of fluorescence x-ray radiation from the region of focused laser excitation, not taken into account by the above calculation. The absorption depth for x-ray fluorescent photons is of the order of 200–300 microns, therefore some additional loss is to be expected.

A general conclusion of the present work is that a large increase in F-center formation efficiency does not occur as the x-ray energy is tuned through the K-absorption edges in RbBr. This is in agreement with recent results[12] on KBr using synchrotron radiation and the laser-induced-luminescence method of detecting point defects. It also agrees with the results of Kondo[13] and co-workers[11] on KBr at both liquid helium and liquid nitrogen temperatures. Apparently for x-rays just above inner level thresholds, most F centers are produced by the usual recombination of electron-hole pairs, and the additional pairs produced by the Auger cascade are of small importance, as suggested by Green *et al.*[9]

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[1] N. Itoh and K. Tanimura, J. Phys. Chem. Solids **51**, 717 (1990).

[2] E. Sonder and W. A. Sibley, in *Point Defects in Solids*, edited by J. H. Crawford and L. M. Slifkin (Plenum, New York, 1972), p. 201.

[3] M. Elango, C. Gahwiller, and F. C. Brown, Solid State Commun. **8**, 893 (1970).

[4] F. C. Brown, B. R. Sever, and J. P. Stott, Phys. Rev. Lett. **18**, 2279 (1986).

[5] J. H. O. Varley, J. Phys. Chem. Solids **23**, 985 (1962).

[6] A. Kotani and Y. Toyozawa, in *Synchrotron Radiation*, edited by C. Kunz (Springer, Berlin, 1978), p. 169.

[7] B. R. Sever, N. Kristianpoller, and F. C. Brown, Phys. Rev. B **34**, 1257 (1986).

[8] J. Sharma and R. Smoluchowski, Phys. Rev. **137**, A259 (1965).

[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] Y. Kondo, S. Hoshina, S. Hirota, I. Goto, Y. Kondo, M. Yanagihara, H. Kimura, and T. Hanyuu, Phys. Rev. Lett. **70**, 810 (1993).

[11] M. Yanagihara, S. Hirota, and Y. Kondo, Phys. Rev. B **53**, 13 386 (1996).

[12] F. C. Brown, S. M. Heald, D. L. Brewe, and De-Tong Jiang,

Nuovo Cimento D **20**, 853 (1998).

[13] Y. Kondo, Y. Suzuki, K. Shimoyama, and M. Yanagihara, Mater. Sci. Forum **239-241**, 587 (1997).

[14] H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

[15] S. M. Heald, E. A. Stern, F. C. Brown, K. H. Kim, B. Barg, and E. D. Crozier, Rev. Sci. Instrum. **67**, 3373 (1996), SRI95 CDROM version; see also S. M. Heald, D. L. Brewe, E. A. Stern, K. H. Kim, F. C. Brown, DeTong Jiang, and E. D. Crozier, J. Synchrotron Radiat. **6**, 347 (1999).

[16] R. Z. Bachrach, Solid State Commun. **7**, 1093 (1969).

[17] J. M. Auerbach and G. Tirsell (unpublished).

[18] S. Albrecht, L. Reining, R. Del Sole, and G. Onida, Phys. Rev. Lett. **80**, 4510 (1998); see also L. X. Benedict, E. L. Shirley, and R. B. Bohn, *ibid.* **80**, 4514 (1998).

[19] A. Frenkel, E. A. Stern, A. Voronel, M. Qian, and M. Newville, Phys. Rev. B **49**, 11 662 (1994).

[20] A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson, Phys. Rev. B **58**, 7565 (1998).

[21] J. D. Comins and B. O. Carragher, Phys. Rev. B **24**, 283 (1981).

[22] M. O. Krause, J. Phys. Chem. Ref. Data **8**, 307 (1979).