Optical-luminescence yield spectra produced by x-ray excitation

Shuichi Emura, Toshihiro Moriga,* and Jun Takizawa The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki 567, Japan

Masaharu Nomura and Karl Rudolf Bauchspiess Photon Factory, National Laboratory for High Energy Physics (KEK), Oho 1-1, Tsukuba 305, Japan

Takatoshi Murata and Katsuyuki Harada Department of Physics, Kyoto University of Education, Fukakusa, Fushimi, Kyoto 612, Japan

Hironobu Maeda

Department of Chemistry, Faculty of Science, Okayama University, Okayama 700, Japan (Received 9 September 1992)

A general formula for the optical-luminescence yield spectra arising from the core excitation is derived, making use of a simple phenomenological model. In this model, it is assumed that various excitations from core electron levels give rise to an identical luminescence in the individual yields. A smaller yield of the inner-core electron excitation than that of the outer-core electron excitation results in a variety of anomalous yield spectra such as those with a negative jump, a positive jump with an inverted oscillation part, and an overtone oscillation. Effective thickness is introduced to explain the opticalluminescence yield spectrum of an opaque powdered specimen. It is pointed out, within the framework of the present model, that for a certain physical condition of the specimens, the yield spectra are deformed and its oscillatory part lacks the precise structural information. The theory is examined by applying it to the yield spectra observed in CaF_2 , where the original spectra taken from the differently prepared forms—the powdered layers in different thicknesses, a pressed pellet, and a single crystal—at 30 and 90 K are presented. A switching of the edge jump is observed in the single crystal and the pressed pellet with increasing temperature. Experimental results are consistently explained by the proposed model and the observed yield spectra are well reproduced from the absorption spectrum.

I. INTRODUCTION

In optical-luminescence yield spectra produced by the deep-core-electron excitations, a totally complementary behavior with its absorption spectrum was reported.¹ This work again brought the focus of attention to the anomalies in the yield spectra as the secondary effects in the inner-core-electron excitations. Several further experimental and theoretical works were promoted after this work, and different anomalies were observed. When it dates back to the 1960s and 1970s, a definite complementarity with the absorption spectrum was indeed observed in the energy region from the fundamental absorption edge ($\sim 6 \text{ eV}$) up to the ultrasoft x ray (~ 250 eV). However, to our knowledge, no great attempt to elucidate these anomalies has been made. As presented below in detail, the anticorrelation behavior of the yield spectra to the absorption is universally observed in the intrinsic luminescences from a single-crystal, impurityinduced luminescence, liquid fluorescence, and in the photocurrent measurement on a single crystal and liquids over a wide energy range up to hard x ray. To aid in the understanding of present states of this problem, it is now appropriate to view the previous studies.

Bianconi, Jackson, and Monahan¹ observed the optical-luminescence yield spectrum from a single crystal of CaF_2 . Their measurements indicated that the observed

spectrum is completely inverted over a wide energy region above the Ca K edge in comparison with the absorption spectrum. They explained this inversion in terms of the branching ratio of the optical-luminescence yield to an x-ray fluorescence yield. They further presented the possibility of a detection method for extended x-rayabsorption fine-structure (EXAFS) spectra in the same category as those from other secondary phenomena created by x-ray excitation such as fluorescent x-ray detections² and total electron yield detections.³⁻⁵ Goulon *et al.*⁶ repeated the measurement on the same substance but in the powdered form, and found a predominant positive-edge jump and an in-phase oscillation in contrast with the spectrum from the single crystal.

Using this method, Goulon and co-workers,^{7,8} and subsequently Pettifer and Bourdillon,⁹ demonstrated the possibility of site selectivity with the thin mixed-powder specimens of ZnO-ZnTPP (zinc mesotetraphenylporphyrin) and ZnS-ZnSe, respectively. The observed spectra show the normal positive-edge jumps. Goulon *et al.* also discussed a criterion for the appearance of positive or negative jumps in the thick transparent specimens⁷ and later in the powdered specimens.^{6,8} Their formula for the simulation of the spectra does not entirely explain the observed comprehensive spectra. Extensive studies by Sham and co-workers^{10–16} have shown the x-ray induced conductivity spectra in liquid specimens as a function of

<u>47</u> 6918

the exciting x-ray photon energy. They performed simultaneous observations of the photoconductivity and the optical-luminescence yield spectra.^{14,15} The luminescence yield spectra were taken at a right angle to the exciting x-ray beam and surprisingly showed the same negative jumps as in the photoconductivity spectra. In a recent paper, Sham and Holroyd¹⁶ reported an interesting result which showed an inverted oscillation in the positive-jump spectrum, and suggested a criterion for positive or negative jumps by taking into account the solute concentration. Murata *et al.*¹⁷ argued that the EXAFS oscillation of a matrix can be observed by detecting the luminescence from impurity centers in an impurity-activated phosphor (NaBr:Cu⁺), which results in a negative-jump spectrum in a thick single crystal.

The negative jumps (usually called dips in the literature of ultraviolet regions) have also been observed in the exci-tation spectra of ionic crystals,^{18–28} molecular com-pounds,²⁹ and solid rare gas^{30,31} ranging from the fundamental absorption edge to the ultrasoft x-ray energy region. Complementary spectra for the absorption or reflection were found in some portion of the spectra. Furthermore, the symmetric excitation spectra for two distinguishable luminescences in an identical crystal were found.³² Surface^{29, 32, 33} and polariton^{34, 35} effects were employed to explain the anticorrelation behaviors of the excitation spectra to the absorption spectra. Almost all experiments were carried out on sufficiently thick crystals in relation to the photon penetration depth, that is, under the condition of total absorption. It should be stressed that the relative thickness is one of the physical quantities controlling the yield spectra. Yanagihara et al.³⁶ extended the observation of the excitation spectra in alkali halide crystals to the region of the deep-lying core excitation and found similar inverted spectra in the thick single crystals as were seen in CaF₂. Their diminutions reach a value of 35% at the K K edge in KBr, and 16% at the K K edge and 46% at the Cl K edge in KCl. These values are significantly larger than that in the case of the Ca Kedge in CaF_2 (about 6%). It is of interest that a remarkable discrepancy exists in the decrement of the opticalluminescence yield between the K K edge (16%) and the Cl K edge (46%) in KCl while only a small difference is found between the kind of emissions (σ and π emissions) in KBr. Recently, Kondo et al.³⁷ have attempted to explain the anticorrelation behavior of the intrinsicluminescence yield in the Cl 1s absorption region of KCl in terms of the nonradiative destruction of the electronhole pairs by the x-ray induced defect and shown a good agreement with experiment.

In the above-mentioned studies, various suggestions have been advanced concerning the physical origin of the anticorrelation behavior, and several criteria have been presented for the appearance of the normal and inverted jumps. However, to date there is no consistent explanation for the appearance of the dip spectra in the energy range from the vacuum-ultraviolet region up to the ultrasoft x-ray and the anomalous yield spectra in the hard x-ray energy region. These phenomena, as reported in the literature, seem to depend on the specimen preparation methods. Therefore, in order to understand more clearly the nature of these peculiar phenomena in the yield spectra, it is desirable to carry out the experiments in a systematic manner.

In the present paper, it will be shown, on the basis of a simple phenomenological model, that various opticalluminescence yield spectra observed in the hard x-ray energy region can be simulated and that other phenomena can also be predicted. It is described in detail that the anticorrelation behavior of the yield spectra to the absorption occurs when more than two excitation processes having different yields compete for a particular luminescence band. The key physical quantities are the sample thickness and the yield ratio of the optical luminescence. In the experiments conducted here, these are parameters adjustable through preparation of specimens and variation of temperature. A formula and simulation of the spectra are first performed for the substance made from a single element in Sec. II A. This formula is extended to complex systems in Sec. II B. Section II C describes how the various anomalous spectra appear. These formulas are applied to analyze the spectra from CaF₂ prepared in various forms and at two different temperatures in Sec. III, where the experimental methods and the original spectra are also presented. Section IV is devoted to a brief discussion on the yield as the phenomenological parameter in the present model. A summary is given in Sec. V.

II. THEORY

In the higher-energy electron excitation above the fundamental absorption region, there may be more than two processes in electron excitation for an opticalluminescence band. For such cases, it is reasonably accepted that each electron-excitation process gives rise to the same luminescence with the different yields because the relaxation processes in each excitation leading to the initial state of the luminescence take different channels. Taking this into view we propose a model which is schematically represented in Fig. 1 in which three kinds of excitation-luminescence cycle with the respective yields and relaxation events of an x-ray fluorescence, an Auger effect, inelastic multiscatterings of photoexcited electrons, and nonradiative decays by electron-phonon scattering are depicted.

A. Simulation of the yield spectra in the two-component case

In this section, we derive an expression for the opticalluminescence yield spectra due to x-ray excitations in the simplest case, which leads us to a general description of the problem. The substances transparent in the photon energy region of the optical luminescence received by the detector are considered here. The results obtained can be applied to other yield spectra due to core excitations via similar processes such as measurements of photoconductivity in x-ray excitation. First, we consider the absorption of x rays near the K-edge energy E_0 in a substance made of a single element of thickness t. The derived expression will be extended subsequently to a general form



FIG. 1. A schematic diagram of the excitation-luminescence cycles. Three different excitations—from a 1s state (absorption coefficient μ_1) to a continuum state, a 1s state (μ_2) to a bound state, and a 2s (μ_3) to a continuum state—give rise to a single luminescence with the respective luminescence yields η_1 , η_2 , and η_3 . The events of an x-ray fluorescence, a *KLL* Auger, electron multiscatterings, a nonradiative decay due to electron-phonon scattering, and radiative transitions are schematically depicted.

in the next section.

At a distance x from the front surface of the specimen, the x-ray photons are absorbed by an amount

$$dI = \{\mu(E) + \mu'(E)\}I(x)dx , \qquad (1)$$

where $I(x) = I_0 \exp[-\{\mu(E) + \mu'(E)\}x]$ is the intensity of the exciting x rays at a depth x (I_0 is the intensity of the incident x rays), and $\mu(E)$ and $\mu'(E)$ are the absorption coefficients for the L-shell and K-shell excitations, respectively. Here, $\mu'(E) = 0$ at $E < E_0$. The absorption intensity dI(x) in Eq. (1) is divided into the L-shell and the K-shell absorptions. Total yields of the optical luminescence due to the L-shell and the K-shell excitations are defined as $\eta(E)$ and $\eta'(E)$, respectively. Electrons (core holes) excited by x-ray photons occupy their relaxed excited states (RES, the initial state of the luminescence) after undergoing the complex relaxation processes (see Fig. 1). Little is known concerning the detailed physics of optical luminescences due to the x-ray excitations, and therefore, we will not explicate the cascade processes in detail but merely point out its general features. The yields defined above should be considered as phenomenological parameters in the present model. The intensities of the optical luminescences induced by the L-shell and K-shell excitations are given as

$$dP(x) = \mu \eta I(x) dx \tag{2}$$

and

$$dP'(x) = \mu' \eta' I(x) dx , \qquad (3)$$

respectively. Substituting I(x), expressed by the intensity I_0 of the incident x-ray photons into Eqs. (2) and (3), and integrating over the sample thickness t, lead to the intensities of the optical luminescence due to the L-shell and K-shell excitations as

$$P = \int_{0}^{t} dP = I_{0} \frac{\mu}{\mu + \mu'} \eta [1 - \exp\{-(\mu + \mu')t\}]$$
(4)

and

$$P' = \int_0^t dP' = I_0 \frac{\mu'}{\mu + \mu'} \eta' [1 - \exp\{-(\mu + \mu')t\}], \quad (5)$$

respectively. The total intensity is represented as P + P'. As $\mu'=0$ at $E < E_0$, the intensity of the optical luminescence in the energy region below the K edge is

$$P_0 = I_0 \{1 - \exp(-\mu t)\} \eta .$$
 (6)

It will be convenient for the following discussion to define the ratio R of the total intensity to P_0 as

$$R = \frac{P + P'}{P_0} = \frac{1 - \exp\{-(\mu + \mu')t\}}{1 - \exp(-\mu t)} \frac{\mu + \mu'B}{\mu + \mu'} , \qquad (7)$$

where $B \equiv \eta' / \eta > 0$. R < 1 means a negative jump in the spectrum. It is also useful to roughly examine the limiting values of R as a function of the parameters t and B such as

$$R_{t \to \infty} = \frac{\mu + \mu' B}{\mu + \mu'} , \qquad (8)$$

$$R_{t \to 0} = 1 + \frac{\mu'}{\mu} B > 1 , \qquad (9)$$

and

$$R_{B\to 0} = \frac{1 - \exp\{-(\mu + \mu')t\}}{1 - \exp(-\mu t)} \frac{\mu}{\mu + \mu'} .$$
 (10)

When B > 1, the yield spectrum will be a normal one for any arbitrary sample thickness. For a sufficiently thick and transparent specimen, a negative jump spectrum will be observed under the condition of B < 1 as is apparent from Eq. (8). On the other hand, a thinner specimen will also exhibit a normal spectrum [Eq. (9)]. In Eq. (10), $B \rightarrow 0 \ (\eta' \rightarrow 0)$ means that there is no contribution from the K-shell excitation to the optical luminescence and an inverted spectrum results for an arbitrary sample thickness. It can be easily seen from Eq. (9) and the above explanations that the factor $[1-\exp\{-(\mu+\mu')t\}]/$ $\{1 - \exp(-\mu t)\}$ contributes to a positive jump while the factor $(\mu + \mu'B)/(\mu + \mu')$ is associated with the negative jump under the condition B < 1. A balance between the two terms determines the nature of the spectrum, as will be demonstrated later.

A numerical calculation of R is made for various cases. The dependence of R on the sample thickness t for various yield ratios B is shown in Fig. 2. Figure 3 presents the dependence of R on the yield ratio for various thicknesses. Here, $\mu(E)$, $\mu'(E)$, $\eta(E)$, and $\eta'(E)$ are kept constant for a while. The constant absorption coefficients



FIG. 2. The intensity ratio R of the yield above and below the K edge as a function of the sample thickness. Normal and inverted jumps are observed above and below R = 1, respectively. Curves 1, 2, 3, and 4 correspond to the yield ratios of B = 1, 0.5, 0.2, and 0.1, respectively.

used here are 220 cm⁻¹ for μ and 660 cm⁻¹ for μ' . From these figures, the boundary (R = 1) for the negative- and the positive-edge jumps can be obtained for the condition B < 1. Generally, when a weak negative-jump spectrum is observed for thicker transparent specimens, a large positive jump will be found for the identical thinner specimens.

Figures 4 and 5 display plots of R as a function of the absorption coefficient μ' for the different yield ratios and the sample thicknesses, respectively. The yields (or its ratio B) and the absorption coefficient μ are inherently dependent on the photon energy. Although keeping these parameters constant, the general aspects of the spectra can be still verified. In both of the figures, the luminescence-intensity ratio depends on the absorption coefficient μ' in an identical manner. This implies that the edge jump spectrum can be controlled equally well by adjusting the sample thickness and/or the yield ratio. Maxima are found in the region where R > 1. For the certain thicknesses and the yield ratios, the boundary



FIG. 3. The intensity ratio R of the yield above and below the K edge as a function of the yield ratio B. Normal and inverted jumps are observed above and below R = 1, respectively. Lines 1, 2, 3, and 4 correspond to the sample thicknesses of t = 1, 2, 5, and 10×10^{-3} cm, respectively.



FIG. 4. The dependence of the luminescence intensity ratio R on the absorption coefficient (μ') for various sample thicknesses t. Curves 1 through 7 correspond to the sample thicknesses of 2, 3, 3.5, 4, 4.5, 5, and 6×10^{-3} cm, respectively. The remaining parameters in Eq. (7) are $\mu = 220$ cm⁻¹ and B = 0.5.

(R = 1) can also be detected. Three kinds of curves in the shape, a saturating form, a form having a maximum, and a monotonously decreasing form, can be recognized. The interesting features of the yield spectra are produced from the curves having a maximum and will be presented in Sec. II C.

Next, it will be demonstrated that the inverted and normal oscillatory behaviors can be plotted from Eq. (7) using the appropriate parameters. The energy-dependent absorption coefficient $\mu(E)$ is written as a function of the wave number k (= $[2m(E - E_0)]^{1/2}/\hbar$ with an electron mass *m* and the Planck's constant \hbar) of a photoelectron,

$$\mu'(k) = \mu'_0 \exp(-sk) \{ 1 + A \exp(-\sigma^2 k^2) \sin 2kr \} .$$
(11)

Here, r is the absorber-backscatterer distance, σ the Debye-Waller factor, and A corresponds to the backscattering amplitude which, for simplicity, is assigned a constant value. The term $\exp(-sk)$ is a state density function which is introduced to realistically display the spectrum. Substituting Eq. (11) into Eq. (7), both the normal and the inverted spectra can be simulated, as shown in Fig. 6. The parameters used to reproduce the spectra are listed in Table I. The inverted spectrum (b) is obtained with $t=1\times10^{-2}$ cm while the normal spectrum (a) results from $t=1\times10^{-3}$ cm. The complementary spectra (a) and (b) are entirely symmetric around R=1and were reproduced by adjusting only the sample thickness. Similarly, the complementary spectra can also be simulated by using suitable yield ratios with a fixed thickness.



FIG. 5. The dependence of the luminescence intensity ratio R on the absorption coefficient (μ') for various yield ratios B. Curves 1 through 8 correspond to the yield ratios of 1.0, 0.70, 0.60, 0.55, 0.50, 0.45, 0.40, and 0.25, respectively. The remaining parameters in Eq. (7) are $\mu = 220$ cm⁻¹ and $t = 4 \times 10^{-3}$ cm.



FIG. 6. Simulated yield spectra with only the sample thickness being altered for (a) $t=1\times10^{-3}$ cm and (b) $t=1\times10^{-2}$ cm. The other parameters are listed in Table I.

TABLE I. Relevant parameters used to simulate the yield spectra.

the second se		
μ	220 cm ^{-1}	
μ'	660 cm^{-1}	
S	0.06 Å	
A	0.1	
σ	0.08 Å	
r	2.34 Å	
В	0.33	
t	0.001 cm (a), 0.01 cm (b)	

B. Extension to the complex systems

Equation (7) can be easily extended to the case of three component parts with the absorption coefficients and the yields corresponding to a compound AX consisting of the atoms A and X. The absorption coefficients for the atom A, below and above the K edge of the X atom, are termed $\mu_a(E)$, $\mu_b(E)$, and $\mu_c(E)$, and the yields corresponding to each absorption coefficient $\eta_a(E)$, $\eta_b(E)$, and $\eta_c(E)$, respectively. Following the same procedure which leads to Eq. (7), an expression for the ratio R for the three components can be obtained as

$$R = \frac{1 - \exp(-qt)}{1 - \exp(-pt)} \frac{p}{q} \frac{\mu_a \eta_a + \mu_b \eta_b + \mu_c \eta_c}{\mu_a \eta_a + \mu_b \eta_b} , \qquad (12)$$

where $p = \mu_a + \mu_b$ and $q = \mu_a + \mu_b + \mu_c$. For $\eta_a = \eta_b$, Eq. (12) reduces to Eq. (7). Therefore, Eq. (7) can be extended to more complicated systems without any special considerations. No new behavior will be found due to this extension since the introduction of an effective absorption coefficient μ'_a reduced as

$$\mu_a' = (\eta_a / \eta_b) \mu_a , \qquad (13)$$

allows the yield ratio R to be represented in a similar form,

$$R = \frac{1 - \exp(-qt)}{1 - \exp(-pt)} \frac{p}{q} \frac{\mu'_a + \mu_b + \mu_c B'}{\mu'_a + \mu_b} , \qquad (14)$$

where $B' = \eta_c / \eta_b$. Obviously, when the conditions $\mu'_a \gg \mu_b$ and $\mu'_a \gg \mu_c$ are satisfied, R is nearly equal to unity and the edge jump is hardly recognized in the yield spectrum. Further extension to $n \ (\geq 4)$ component systems can be similarly achieved as

$$R = \frac{1 - \exp(-q_n t)}{1 - \exp(-p_n t)} \frac{p_n}{q_n} \frac{\sum_{i=1}^{n} \mu_i \eta_i}{\sum_{i=1}^{n-1} \mu_i \eta_i} , \qquad (15)$$

where

$$p_n = \sum_{i=1}^{n-1} \mu_i$$
 (16)

and

$$q_n = \sum_{i=1}^n \mu_i = p_n + \mu_n .$$
 (17)

C. Simulation of the anomalous spectra

The comprehensive behavior of the spectra is advanced from the curves having a maximum in Figs. 4 and 5. An appropriate curve ($t = 4 \times 10^{-3}$ cm, B = 0.5) from Fig. 4 is replotted in Fig. 7 with the spectra being presented for the two regions denoted by B and C, and for the region around the point marked by R_c . The absorption spectra used in calculating the yield spectra are also indicated in the lower left-hand corner. When the absorption coefficients are so low as to be in region $A [R(\mu') > 1]$, $dR(\mu')/d\mu' > 0$], the usual yield spectra reproducible to the absorption spectra are observed. Approaching the maximum value of $R(\mu')$, the amplitude of the EXAFS oscillation weakens. At the maximum R_c [$R(\mu') > 1$, $dR(\mu')/d\mu'=0$], the critical point, where the oscillatory part converts from a normal form to eventually exhibiting an inverted form, is reached. When the absorption coefficient of a specimen corresponds to the maximum point, the oscillatory part shows an overtone of the original oscillation as illustrated in the upper right-hand portion of Fig. 7 [spectrum (a)]. That is, the oscillation form of the absorption spectrum is not preserved in the optical-luminescence yield spectra. In the lower righthand portion, the ordinate R has been expanded around the point R_c to clearly display the overtone oscillation. A positive-jump spectrum having an inverted oscillatory part can be seen for region B [$R(\mu') > 1$, $dR(\mu')/d\mu' < 0$,



FIG. 7. Schematic illustration of three peculiar yield spectra. The intensity-ratio curve is replotted from Fig. 3 for $t=4\times10^{-3}$ cm and B=0.5 (curve 4). In the lower left-hand portion, the simulated absorption spectra as input from Eq. (11) with A=0.1, $\sigma=0.16$, and r=2.34 Å are given. The corresponding yield spectra are calculated at $\mu'_0=299.1$ (R_c), 600 (region B), and 1250 cm⁻¹ (region C), and are plotted as a function of wave number of a photoexcited electron in the right-hand portion of the figure. In the lower right-hand corner, the inset shows the expanded oscillatory part of the yield spectrum at R_c .

spectrum (b)], which is experimentally found in a photoconductivity-yield spectrum of a liquid specimen of medial concentration by Sham and Holroyd.¹⁶ In practice, the conversion of the inverted oscillation to the normal one may occur when μ' decreases across the point R_c with increasing photon energy. For region $C[R(\mu') < 1, dR(\mu')/d\mu' < 0]$, a positive hump will be observed at the rising part of the absorption edge jump followed by a sharp drop exhibiting a negative-jump spectrum with an inverted oscillatory part [spectrum (c)]. Furthermore, such curves 1 and 7 in Fig. 4 $[dR(\mu')/d\mu'=0]$ offer a singular spectrum in which the structures completely vanish. Structureless yield spectra have been reported for the intrinsic luminescence in the vacuum ultraviolet region of NaBr, AgCl, and AgBr.²⁸

In experiments, these peculiar spectra can be produced by adjusting the sample thickness and/or by a change in the yield ratio *B* at different temperatures, since the relaxation paths of the excited electrons and the core holes are sensitive to temperature. Therefore, the variation in temperature allows one to observe the comprehensive spectra with the use of a single specimen. An example is shown in Fig. 8 where the spectra were calculated by taking the sample thickness as 14.0×10^{-4} cm (a), 14.5×10^{-4} cm (b), and 15.0×10^{-4} cm (c). A small change in the thickness drastically changes the nature of the oscillatory part.

It should be noted that the amplitude of the EXAFS oscillation in the yield spectra must be rectified for an exact analysis of the coordination number. The oscillation amplitude in the absorption spectrum is modified in the corresponding yield spectrum owing to a nonlinear relation of $R(\mu')$ as shown in Figs. 4 and 5. Around the crit-



FIG. 8. Variation of the yield spectra as a function of wave number of a photoexcited electron around the critical point R_c for the different sample thicknesses of (a) 1.40×10^{-4} cm, (b) 14.5×10^{-4} cm, and (c) 15.0×10^{-4} cm. The constant parameter s in Eq. (11) is neglected to avoid confusion. The magnified oscillatory parts are shown in the inset. The drastic change of the oscillatory behavior from a normal phase to an inversion phase through an overtone oscillation can be seen with a change of only 1×10^{-4} cm in thickness.

III. APPLICATION TO THE OBSERVED SPECTRA

As was stated in Sec. I, CaF_2 shows contrary behaviors of the yield spectra depending on the method of the specimen preparation; a small negative jump for the single crystal¹ and a large positive jump for the powdered layer.⁶ In order to demonstrate the applicability of the theory, we performed systematic measurements—at two different temperatures and with four different treatments of the specimen—of the optical-luminescence yield spectra from CaF₂. The experimental methods and detailed original results are described first in this section.

A. Experimental procedure

The different forms of specimens, a cleaved single crystal $(10 \times 5 \times 1 \text{ mm}^3)$, powdered layers with the different thicknesses each heaped loosely on a membrane filter,³⁸ and a pressed powder $(4 \times 10^{-2} \text{ cm})$ by about 3.5 kb in the form of a pellet, were examined. The thickness of the thin powdered layers was estimated from the magnitude of the absorption edge jump to be about 5×10^{-4} cm. The mirrorlike surfaces were manufactured in the pellet specimen due to applying pressure. The thinner powdered specimen was used for the measurements of both absorption and optical-luminescence yield spectra.

The observations of the spectra were performed on Beamline 7C at the Photon Factory³⁹ with a positron energy of 2.5 GeV and a ring current of 350–250 mA. A fixed exit slit monochromator with two Si(111) flat crystals was employed. The resolution is about 0.8 eV with a vertical slit size of 1 mm at 4 keV. Higher harmonics were rejected by using a pair of the fused quartz mirrors at a grazing incidence. The x rays incident on the specimens were monitored by an ionization chamber with flowing gas of 30% N₂+70% He. For the absorption measurement, the transmitted x rays were detected by another ionization chamber with flowing pure N₂ gas.

The absorption measurements were carried out at room temperature. All the specimens for the opticalluminescence yield spectra were mounted on the cold finger of a closed-cycle He cryostat. A schematic diagram of the experimental arrangement used for the measurements of the optical-luminescence yield spectra is illustrated in Fig. 9. The spectra were observed in a reflection mode. The incident angle of the x rays was 45° to the specimen. The beam size of the incident x rays was restricted within a slit width of an analyzing grating monochromator (Jobin Yvon H-20, f = 200 mm). The optical luminescences from the front surface of the specimen were monitored through a quartz window of the cryostat and focused by a quartz lens (50 mm diameter, f = 100 mm) onto the entrance slit of the analyzing grat-



FIG. 9. A schematic diagram of experimental arrangement used for the measurement of optical-luminescence yield spectra. The specimen is mounted on the cold finger of a cryostat.

ing monochromator. The optical luminescences were detected with a Hamamatsu R928 photomultiplier. With exciting x rays around the Ca K-edge region, a general view of the luminescence spectrum was first taken by scanning the grating monochromator. The wavelength of the grating monochromator is fixed at the peak energy of the luminescence band (4.36 eV, 284 nm at 90 K), and then the exciting x rays were scanned to observe the yield spectra. The signals from the photomultiplier were accumulated for 3-5 s per data point.

B. Experimental results

The optical-luminescence spectrum of CaF_2 at 30 K produced by x-ray excitations in the region of the Ca K edge is shown in Fig. 10. The luminescence band is identified to the intrinsic luminescence of CaF_2 .⁴⁰ Additional bands on the lower-energy side are also observed. No change in the relative spectral shape of the luminescence band was confirmed by changing the exciting photon energy.

Figure 11(a) shows the near-edge absorption spectrum at the Ca K edge in CaF₂ measured at room temperature. Comparing with the previously observed spectrum,¹ rich structures can be seen particularly in the region of the first prominent peak, owing to the higher resolution. The structures on the lower-energy side of this strong peak may be assigned to the transitions to s- or d-like excited states.³³

Various features are observed in the specimen from the differently treated forms of the specimen. Figures 11(b), 11(c), and 11(d) show the optical-luminescence yield spectra from the thin powdered layer, the pellet, and the single crystal at 90 K, respectively. All the spectra are corrected for the spectral response of the ionization chamber, polyimide-film windows, and air path. Note here that the yield spectra for the thin and thick layers



FIG. 10. A luminescence spectrum of CaF_2 at 30 K produced by x-ray excitation in the region of the Ca K edge.

are not normalized by the intensity of the absorbed x rays but by the relative intensity of the incident x rays. This procedure is usually adopted in the literature. The yield spectrum (b) well reproduces the absorption spectrum except for a slight suppression of the height of the first prominent peak. When attention is directed to the region below the K-shell excitation threshold, the first preedge peak is magnified in comparison with the absorption spectrum. In contrast to the powdered specimen, the single crystal shows a shallow negative-jump spectrum which is of the same nature as the one observed previously.¹ The pellet also shows a shallow negative jump around the absorption edge followed by the totally inverted form. However, at the higher-energy region, no depression is noticed. It suggests that the absorption magnitudes in this energy region lie in the vicinity of $R(\mu')=1$. In both spectra from the single crystal and the pellet, the contrast to the oscillatory part with the jump appears to be low.

Figures 12(a)-12(d) show the yield spectra from the thin powdered layer, the thick powdered layer, the pellet, and the single crystal at 30 K, respectively. The spectrum from the thick powdered layer has lower contrast compared to the thin powdered specimen. In particular, the first prominent peak is remarkably suppressed. In the thin powdered specimen, although the nature of the spectrum remains unaltered, the edge jump slightly enlarges when compared to that at 90 K. Both the pellet (c) and the single crystal (d) exhibit drastic changes at 30 K; the jump at the edge being positive in both the specimens. In the pellet, a portion corresponding to the prominent peak in the absorption spectrum shows a dip. The change in the edge-jump direction with decreasing temperature is

the first observation in the optical-luminescence yield spectra. The detailed comparison around the K-shell absorption edge with the absorption spectrum is given in Figs. 13 and 14 for the pellet specimen and the single crystal at 30 and 90 K, respectively. The vertical lines are drawn to help the precise comparison.

A notable general feature of all yield spectra is seen in the almost linear increases of the intensities with photon energy. This is attributed to the increasing yield $\eta's$ (Refs. 13 and 27) as a result of the electron multiscatterings from a high-energy photoelectron into many lowenergy electrons.

We briefly summarize the experimental results as follows: (i) The powdered layers show the yield spectra similar to the absorption spectrum. The peak heights are, however, suppressed more or less depending on the thickness of the layer. The thicker the layer is the stronger the suppression of the peak height. (ii) The pellet shows a positive edge jump at 30 K, but converts to a negative feature with an inverted oscillation part at 90 K. (iii) The thick single crystal exhibits a positive jump with a normal oscillation part at 30 K, but completely switches to negative direction at 90 K. (iv) The yields



FIG. 11. The absorption spectrum of CaF_2 near the Ca K edge at room temperature (a), and the optical-luminescence yield spectra of CaF_2 at 90 K for a thin powdered layer (b), for a pressed pellet, (c) and for a single crystal (d). The dotted curve in (d) refers to theory. The rich structures on the lower-energy side of the K-shell excitation threshold are observed.

(luminescence intensities) of all the specimens show a linear increase with the incident photon energy.

C. Analysis of the spectra

In this section, we discuss semiquantitatively the observed original spectra utilizing the present model. The single-crystal specimen in the present study is sufficiently thick compared to x-ray penetration depth, meaning that it is under the condition of total absorption, and the first factor in Eq. (12) or (7) is almost unity. From Figs. 11(d) and 12(d), the values of the intensity ratio R at the Ca Kedge are 0.94 at 90 K and 1.06 at 30 K. At the Ca K edge of CaF₂, three components, the K-shell and L-shell absorptions of the Ca atom and the K-shell absorption of the F atom, must be taken into account. The energies of the F K-edge absorption and the Ca L_1 -edge absorption are not much different and both the energies are far away from the Ca K-absorption edge. Assuming the yield of the optical luminescence for the L-shell excitation of the Ca atom to be the same as that of the K-shell excitation of the F atom, the yield ratio B's can be calculated from





FIG. 13. The detailed comparison of the yield spectra of the pellet specimen at 90 and 30 K with the absorption spectrum of the thin powdered layer at room temperature. The prominent peaks inversely correspond in both spectra as indicated by lines.



FIG. 12. The optical-luminescence yield spectra of CaF_2 at 30 K for a thin powdered layer (a), for a thick powdered layer (b), a pressed pellet (c), and a single crystal (d). The dotted curves in (a) and (d) refer to theory.

FIG. 14. The detailed comparison of the yield spectra of the single-crystal specimen at 90 and 30 K with the absorption spectrum of the thin powdered layer at room temperature.

Eq. (7). The values obtained are 0.93 at 90 K and 1.07 at 30 K using atomic absorption coefficients just below and above the Ca K edge of the Ca atom and of the F atoms at the Ca K edge. As seen in Fig. 2, the thickness of the specimen alters the magnitude of the edge jump as well as its direction under the constant yield ratio. It should be pointed out that by thickness we essentially mean the escape depth of the emitted light and not the actual thickness of the specimen.⁴¹ In the opaque powdered specimen, random scattering and diffuse reflection prevent the light emitted from deeper sites to reach the surface. In the reflection mode of the observation, where the optical luminescence is detected at the front of the specimen, since the escape depth of the optical (uv, visible) luminescence is shallower than the penetration depth of x rays, a thick powdered specimen is equivalent to a thin transparent one. The effective thickness critically depends on how the specimen is handled, and it increases in thin powdered layer, thick powdered layer, pellet, and single crystal, in that order.

In Fig. 15, the intensity ratio $R(\mu')$ as a function of the Ca absorption coefficient μ' is plotted for the values of B = 0.93 (solid curves) and B = 1.07 (broken curves) for various thicknesses under a fixed absorption coefficient

FIG. 15. The dependence of the luminescence intensity ratio $R(\mu')$ on the absorption coefficient (μ') of Ca in CaF₂ for suitable thicknesses which are chosen to fit the observed edge jump at 90 K around the absorption edge. Curves 1 (1') through 4 (4') correspond to thicknesses of 2.5 (2.5)×10⁻⁴, 12.5 (12.5)×10⁻⁴, 78 (45)×10⁻⁴, and 1 (1)×10⁻¹ cm, respectively. The solid curves are calculated with B = 0.93 and $\mu = 392.1$ cm⁻¹, and the broken curves with B = 1.07 and the same value of μ . The values *B*'s are estimated from the spectra of the single crystal at 90 and 30 K.

 μ =392.1 cm⁻¹, which is the total amount of the Ca *L*-shell absorption and the F *K*-shell absorption at the Ca *K* edge in CaF₂.⁴² The thickness of the thin layer is rather small. Therefore, the first factor in Eq. (7) is greater than unity. The thin layer showing the prominent positive jump corresponds to the curve 1 (t=2.5×10⁻⁴ cm) in Fig. 15. The change of *B* from 1.07 at 30 K to 0.93 at 90 K in the second factor does not affect the spectrum shape, since the first factor dominates the shape in the thin-layer case.

In the case of the thick layer at 30 K, the observed jump is about R = 2.21 at the absorption edge, and at $\mu' = 1551 \text{ cm}^{-1}$, which is the absorption coefficient due to the Ca K shell at the K edge in CaF₂,⁴² the curve 2' indicates about the same amount. The totally suppressed spectrum is well described by the curve 2'. The effective thicknesses of both layers are found to be 2.5×10^{-4} cm for the thin one and 12.5×10^{-4} cm for the thick one. The single crystal ($t \simeq 0.1$ cm) at 90 K exhibits a totally inverted spectrum. The change of B from 0.93 to 1.07 compels the inverted spectra to revert to the normal ones in the thick specimens and also enlarges the edge jump of normal spectra in the thin layers as seen in the spectra at 90 and 30 K.

In the pellet specimen, the situation is somewhat complicated. The spectral features are well explained along the curve 3. This corresponds to the case R = 1. However, the spectrum at 30 K shows one shallow dip portion in an otherwise positive scheme. The similar diminution can be recognized in the excitation spectra in the energy region of a vacuum ultraviolet, or that in the ultraviolet region. $^{22-26}$ In all the spectra in the present study, this portion strongly suppressed in the positive-jump spectra and in those with the negative jump more deeply decreases. To explain the behavior of this portion, the smaller values of B must be assigned in Eq. (7) compared to the values used, i.e., 1.07 at 30 K and 0.93 at 90 K. The various competitive excitations for an identical luminescence band result in different yields for the luminescence in which the optically excited states strongly affect those through nonradiative relaxation channels such as electron-phonon scattering as discussed in the next section.

On the basis of above description, we try a partial least-squares fitting for a few yield spectra using the experimental absorption spectrum as input and adjusting the model parameters. The calculated intensities from Eqs. (5) and (6),

$$P + P' = I'_0 [1 - \exp\{-(\mu + \mu')t\}] \eta \frac{\mu + \mu'B}{\mu + \mu'} + \gamma \quad (18)$$

are directly compared with the measured intensities (not R), which are relative values, and are corrected for the spectral response of the experimental system as described in Sec. III B. Therefore, I'_0 is an overall adjustable parameter. The K-shell absorption coefficient $\mu'(E)$ is obtained by subtracting $\mu(E)$, extrapolated to the energy region of the K-shell absorption, from the experimental absorption spectrum, using the table by McMaster, Kerr Del Grande, and Hubbell.⁴⁸ The quantity γ is a (small) shift that must be applied because the dark current

(offset) measurement for the ionization chamber was not reliable and the stray light in the optical system is included in the detected light. It is assumed that the yields $\eta(E)$ and $\eta'(E)$ linearly depend on the exciting photon energy as follows,

$$\eta = \alpha + \beta (E - E_K) \tag{19}$$

and

$$\eta' = \alpha' + \beta'(E - E_K) , \qquad (20)$$

respectively, where E_K is K-shell threshold energy. The yield ratio B is rewritten as

$$B = \frac{\eta'}{\eta} = \frac{\alpha B_K + \beta'(E - E_K)}{\alpha + \beta(E - E_K)} .$$
(21)

The values of B_K (= α'/α) are determined from the jump magnitude in the single-crystal spectra, independently at 30 K (1.07) and 90 K (0.93). Thus, the fitting parameters are I'_{0} , α , β , β' , and γ . The results are given with dotted curves in Figs. 11(d), 12(a), and 12(d). The obtained values of the main parameters are $\beta = 4.3/\text{keV}$ and $\beta' = 4.6/\text{keV}$ for the thin layer. (These are not absolute values and we merely see the qualitative tendency of the increasing yield with the exciting photon energy.) The agreement with experiment in the thin layer is fairly good except in the portion of the prominent peak, and the spectral outline in the single-crystal spectra is reproducible. However, the contrast in the oscillatory part is relatively low. It may originate from the difference of the experimental temperature between the absorption (RT) and the optical-luminescence yield spectra (90 and 30 K) and furthermore from our assumption that the yields for the L-shell excitation of the Ca atom and for the K-shell excitation of the F atom are identical. The disagreement of the prominent peak is consistent in the spectra from the pellet specimen. A full least-squares fit using Eq. (12) is presently in progress.

IV. DISCUSSION

In the present model, the distinctive luminescence yields are assigned to the independent excitationluminescence cycles [see Eqs. (7), (12), and (15) and also Fig. 1]. In our measurements for the intrinsic luminescence of CaF₂, it is found that the yield at the most prominent absorption peak assigned to transitions to the *p*-like molecular states³³ is smaller than that in the excitation to the free electron states. That is, optical luminescence from excitations to the different optically excited states does not give rise to the same yields and provides an evidence of support. This fact certifies to our model. This has also been seen clearly in the previous photo-current^{18,19} and photoluminescence^{22,23} measurements in the fundamental absorption region of alkali halides. The yields for the identical intrinsic luminescence at low temperature are different between the excitations in the band-to-band region and in the exciton region. The former is larger than the latter below 100 K and the latter shows a peculiar temperature behavior, so that the photocurrent and photoluminescence intensities apparently diminish at the first exciton absorption peak. For the same intrinsic luminescence, the excitation spectra in the wide energy interval²⁷ show the stepwise increases in the intensity following troughs at each threshold energy which is in a similar feature to the spectra observed in the fundamental absorption region. (Sharp dips at core exciton energy are also observed.) The stepwise increase has been qualitatively explained in terms of multiplication of the free electron-hole pairs due to inelastic scatterings of the photoexcited electron with a valence electron. These observations of dips, stepwise increases, and troughs mean that the yield depends on the initial and final electronic states of the optical transition. There are some processes which tend to complicate the situation in the x-ray region. The photoexcited luminescence consists of three stages: core electron excitation (photoabsorption), relaxation of the excited electron to the initial state of luminescence, and radiative decay. In this cycle, the luminescence yields may be substantially governed by the four processes in the relation of three stages; first, xray fluorescence; second, Auger cascade processes following from photoabsorption; third, energy conversion mechanism due to the electron-electron inelastic scatterings from a high-energy excited electron to many lowenergy electrons following the simultaneous production of holes; fourth, nonradiative decays such as electronphonon scatterings, photoelectron emissions, and defect formations. These four mechanisms are competitive in the yield for each excitation, and illustrated in the three kinds of the excitation-luminescence cycle in Fig. 1.

fluorescence reduces The x-ray the opticalluminescence yield. The deeper the excited core level is, the larger is the yield of the x-ray fluorescence. Therefore, this process works to be B < 1. The Auger processes are advantageous to the inner-core excitations, especially in the K-shell excitation, which produces a more energetic electron and more excited electrons. The third process leading the electrons to an initial state of luminescence makes the yields for the outer-core excitations increase more because an excited photoelectron from the outercore level is of a higher kinetic energy than that from the inner-core level with the same incident photon energy. A KLL Auger electron resultant in the K-shell excitation has less kinetic energy than the photoelectron by the Lshell excitation as schematically drawn in Fig. 1. The increasing yield with the kinetic energy of the excited electron is found in our measurement and directly measured in the energy region from 5.9 to 29.2 keV.¹³ Therefore, this mechanism is advantageous to the outer-core excitations.

Some of the electrons dropping down onto the vicinity of an initial state of luminescence may recombine with holes passing through the nonradiative channels due to the electron-phonon scatterings. This event could give the temperature-dependent behaviors of the yields or the yield ratios. However, the temperature effect is relatively weak and may be masked by the former two processes because the energetic Auger electrons and the inelastic scatterings produce many electron-hole pairs (and also create many phonons). The decay channels depend on the optically excited states, as is well known. (The other radiationless decay channels may not universally affect the quantum yields; the defect formations are hardly created in liquids, the photoelectron emissions play important roles in the vacuum ultraviolet region but may be weak in the hard x-ray region.) Thus, the different values of *B* for the identical luminescence band are inevitably placed in each excitation-luminescence cycle. The value of *B* should be analyzed in individual cases. In the case of CaF₂, the four processes are in delicate balance. The fourth process may have weak initiative, and then the change of *B* from 1.07 at 30 K to 0.93 at 90 K is possibly interpreted by the fourth process.

V. SUMMARY

We have presented a phenomenological theory, based on a microscopic consideration, to explain the experimentally observed anomalies in various yield spectra. When different excitation-luminescence channels, each having different yields, compete for a particular luminescence band, an anticorrelation behavior with respect to the absorption is seen in the yield spectra. Furthermore, the nature of these spectra strongly depends on the luminescence-yield ratio between the individual coreelectron excitations as well as on the effective thickness which is introduced to explain the spectra of the opaque powdered specimen. Using yield ratio and effective thickness as the variable parameters, several features in the optical-luminescence yield spectra accompanied by EXAFS oscillations in the deep-core-electron excitation region such as a totally inverted spectrum, an inverted oscillatory behavior in the positive jump, an overtone oscillation, and a negative jump with a small hump at the threshold energy, are presented in simulation. No additional EXAFS oscillations or the suppressed and vague

- *Present address: Department of Chemical Science and Technology, Faculty of Engineering, Tokushima University, Tokushima 770, Japan.
- ¹A. Bianconi, D. Jackson, and K. Monahan, Phys. Rev. B 17, 2021 (1978).
- ²J. Jaklevic, J. A. Kirby, M. P. Klein, A. S. Robertson, G. S. Brown, and P. Eisenberger, Solid State Commun. 23, 679 (1977).
- ³G. Martens, P. Rabe, G. Tolkiehn, and A. Werner, Phys. Status Solidi A 55, 105 (1979).
- ⁴J. Stöhr, in X-Ray Absorption: Principles, Applications and Techniques of EXAFS, SEXAFS, and XANES, edited by R. Prins and D. C. Koningsberger (Wiley, New York, 1985).
- ⁵A. Erbil, G. S. Cargill III, R. Frahm, and R. F. Boehme, Phys. Rev. B **37**, 2450 (1988).
- ⁶J. Goulon, P. Tola, J. C. Brochon, M. Lemonnier, J. Dexpert-Ghys, and R. Guillard, in *EXAFS and Near Edge Structure III*, Vol. 2 of *Springer Proceedings in Physics*, edited by K. O. Hodgson, B. Hedman, and J. E. Penner-Hahn (Springer-Verlag, Berlin, 1984), p. 490.
- ⁷J. Goulon, C. Goulon-Ginet, R. Cortès, and J. M. Dubois, J. Phys. (Paris) **43**, 539 (1982).
- ⁸J. Goulon, P. Tola, M. Lemonnier, and J. Dexpert-Ghys, Chem. Phys. 78, 347 (1983).
- ⁹R. F. Pettifer and A. J. Bourdillon, J. Phys. C 20, 329 (1987).

oscillation are predicted for thin or thick specimens in the simulated spectra.

To examine the model further, we measured the yield spectra monitored by the optical luminescence at different temperatures (30 and 90 K) from the selftrapped exciton in the CaF2 specimen prepared in the different physical forms and effective thickness, i.e., powdered layers of varying thickness which were loosely heaped on a membrane filter, a pressed powder in the form of a pellet, and a cleaved single crystal. The observed yield spectra are strongly sensitive to the physical state of the specimen; the powdered layers generally reproduce the absorption spectrum, the pellet specimen displays a positive feature at lower temperature (30 K) but a negative feature at higher temperature (90 K) while the thick single crystal exhibits nearly the same tendency as the pellet specimen, but more clearly. These specific features of the optical-luminescence yield spectra, which can be fairly well reproduced from the absorption spectrum, are semiquantitatively analyzed.

Different yield ratio in a preedge region from the higher-energy region must be assigned in order to fit the spectra. This provides an evidence that an individual yield results from an independent excitationluminescence cycle.

ACKNOWLEDGMENTS

One of the authors (K.R.B.) is grateful to the Japan Society for the Promotion of Science (JSPS) for the financial support. This work has been performed with support from the Photon Factory, through Proposals No. 89-123 and No. 91-178. Some part of the calculations were carried out at the computer center of Osaka University.

- ¹⁰T. K. Sham and S. M. Heald, J. Am. Chem. Soc. **105**, 5142 (1983).
- ¹¹T. K. Sham and R. A. Holroyd, J. Chem. Phys. **80**, 1026 (1984).
- ¹²B. X. Yang, J. Kirz, and T. K. Sham, Nucl. Instrum. Methods Phys. Res., Sect. A 236, 419 (1985).
- ¹³R. A. Holroyd and T. K. Sham, J. Phys. Chem. 89, 2909 (1985).
- ¹⁴T. K. Sham, R. A. Holroyd, and R. C. Munoz, Nucl. Instrum. Methods Phys. Res., Sect. A 249, 530 (1985).
- ¹⁵T. K. Sham, R. A. Holroyd, and R. C. Munoz, J. Phys. (Paris) Colloq. 47, C8-153 (1986).
- ¹⁶T. K. Sham and R. A. Holroyd, Phys. Rev. B 39, 8257 (1989).
- ¹⁷T. Murata, S. Emura, T. Moriga, H. Maeda, and M. Nomura, in *X-Ray Absorption Fine Structure*, edited by S. Samar Hasnain (Ellis Horwood, London, 1991), p. 653.
- ¹⁸Y. Nakai and K. Teegarden, J. Phys. Chem. Solids 22, 327 (1961).
- ¹⁹G. R. Huggett and K. Teegarden, Phys. Rev. 141, 797 (1966).
- ²⁰H. Sugawara and T. Sasaki, J. Phys. Soc. Jpn. 46, 132 (1979).
- ²¹T. Goto, T. Takahashi, and M. Ueta, J. Phys. Soc. Jpn. **24**, 314 (1968).
- ²²J. Ramamurti and K. Teegarden, Phys. Rev. 145, 698 (1966).
- ²³M. P. Fontana, H. Blume, and W. J. van Sciver, Phys. Status Solidi 29, 159 (1968).

- ²⁴H. Blume, M. P. Fontana, and W. J. van Sciver, Phys. Status Solidi **31**, 133 (1969).
- ²⁵M. Ikezawa and T. Kojima, J. Phys. Soc. Jpn. 27, 1551 (1969).
- ²⁶H. Onuki and R. Onaka, J. Phys. Soc. Jpn. 34, 720 (1973).
- ²⁷J. H. Beaumont, A. J. Bourdillon, and M. N. Kabler, J. Phys. C 9, 2961 (1976).
- ²⁸M. Yanagihara, Y. Kondo, and M. Kanzaki, J. Phys. Soc. Jpn. **52**, 4397 (1983).
- ²⁹K. M. Monahan and W. C. Walker, Phys. Rev. B 15, 2303 (1977).
- ³⁰H. Möller, R. Brodmann, and G. Zimmerer, Solid State Commun. 20, 401 (1976).
- ³¹Ch. Ackermann, R. Brodmann, U. Hahn, A. Susuki, and G. Zimmerer, Phys. Status Solidi B 74, 579 (1976).
- ³²M. Elango, J. Pruulmann, and A. P. Zhurakovskii, Phys. Status Solidi B 115, 399 (1983).
- ³³A. J. Bourdillon and J. H. Beaumont, J. Phys. C 9, L479 (1976).
- ³⁴A. Bosacchi, B. Bosacchi, and S. Franchi, Phys. Rev. Lett. **36**, 1086 (1976).
- ³⁵M. P. Fontana, Phys. Rev. Lett. **37**, 789 (1976).
- ³⁶M. Yanagihara, Y. Kondo, T. Hanyu, and S. Yamaguchi,

Solid State Commun. 68, 345 (1988).

- ³⁷Y. Kondo, S. Hoshina, M. Yanagihara, H. Kimura, T. Hanyuu, and S. Yamaguchi, Solid State Commun. 80, 431 (1991).
- ³⁸E. D. Eanes, J. L. Costa, A. MacKenzie, and W. Warburton, Rev. Sci. Instrum. **51**, 1579 (1980).
- ³⁹M. Nomura and A. Koyama, in *X-Ray Absorption Fine Structure* (Ref. 17), p. 666. The specifications of the Beamline 7C are described by M. Nomura, A. Koyama, and M. Sakurai (unpublished).
- ⁴⁰J. H. Beaumont, W. Hayes, D. L. Kirk, and G. P. Summers, Proc. R. Soc. London, Ser. A **315**, 69 (1970).
- ⁴¹In the strict sense, the effective thickness is not identical with the escape depth of the emitted light. In place of Eq. (2), the equation $dP(x,E) = \eta(x,E)\mu(E)I(x)dx$ should be solved to obtain the exact luminescence intensity for an opaque specimen. In the present discussion, we ignore the dependence of η on x for simplicity.
- ⁴²The linear absorption coefficients on CaF₂ used here are estimated from the table by W. H. McMaster, N. Kerr Del Grande, and J. H. Hubbell, *Compilation of X-Ray Cross Section* (National Technical Information Service, Springfield, 1969).