Time-Resolved Auger Decay in CsBr Using High Harmonics

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The temperature-dependent decay dynamics of innershell holes in CsBr was measured by using high harmonics. The measured lifetime was as short as 1.5 ps at 340 K due to increasing the Auger-allowed final state density in the Urbach exciton tail, whereas it is 1.1 ns at 10 K, determined by radiative recombination. The temperature-dependent Auger lifetime extrapolated to a high temperature corresponds to the fully energy-allowed Auger decay. In the model to be presented, this yields an interatomic Auger decay lifetime of $2.4 + 3.8/-1.5$ fs, in line with a theoretical calculation for NaF.

A vacant state in an inner shell relaxes with time constants ranging from a few attoseconds (as) to a few femtoseconds (fs), depending on the binding energy. The inner-shell holes created vanish through an ultrafast rearrangement of the electronic system, leaving two holes in the outer levels. This process, known as an Auger process, is a universal phenomenon in atoms, molecules, and condensed matter. The lifetime of core holes has been estimated from the full width at half maximum of the photoelectron spectra [1]. However, spectral measurements can provide only indirect information on the Auger decay process. Real time measurements are greatly needed to study Auger dynamics. The time-resolved spectroscopy of core holes needs high temporal resolution along with high photon energy to excite the inner shell. Synchrotron radiation (SR) is a standard high-energy light source, but its temporal resolution has so far been limited to several picoseconds (ps). On the other hand, high harmonics (HH) of a fs laser have a pulse width down to sub-fs in the extreme-ultraviolet and soft-x-ray regions [2–4]. Therefore, HH are eminently suitable for time-resolved spectroscopy following core-hole creation [5,6].

Very recently, the Auger decay time of gaseous Kr was measured in the fs regime from the shift of the photoelectron spectrum by an intense fundamental laser field [7]. In the gas phase, the Auger decay occurs mainly through the intra-atomic transition within a given atom. On the other hand, in condensed matter, interatomic Auger transitions are possible among neighboring atoms. Such interatomic Auger processes could be largely affected by the environment of created holes, such as lattice deformation or vibration (i.e., temperature or injected carrier density), and are a challenging subject in solid-state physics. CsBr is of special interest for the study of the Auger process, because it has two competing relaxation channels of holes created in the Cs^+ $5p$ outermost-core band, radiative decay and nonradiative Auger decay

[8]. At low temperatures, Auger decay is energetically forbidden because the energy difference E_{VC} between the top of the outermost-core band and the top of the valence band is smaller than the band gap energy E_g. However, the Urbach exciton tail states can provide suitable final states for Auger decay products, causing the rate to increase with temperature [9]. In the present experiment, we measured the temperature-dependent decay time of the luminescence arising from the radiative decay of Cs^+ $5p$ core holes, and determined the Auger decay probability at the high-temperature limit. The interatomic Auger decay time was, for the first time, estimated to be $2.4 + 3.8/-1.5$ fs in condensed matter, in good agreement with a theoretical calculation of alkali halides [10]. The present work verified that HH enable time-resolved spectroscopy with high temporal resolution that was not accessible before by SR.

We first briefly describe the relaxation processes of a hole created in an outermost-core band. An outermost-core hole is filled by a valence electron and transfers the released energy to another valence electron that is ejected to the continuum state. This process is much faster than the competing radiative process. However, the situation is quite different in CsBr; the Auger decay of core holes is energetically forbidden at low temperatures, because $E_{VC} < E_g$. Instead of Auger electrons, we observe a new type of luminescence originating from an interatomic radiative transition between the Br^- $4p$ valence band and the Cs^+ $5p$ outermost-core band. This luminescence is called the cross luminescence [11] or Auger-free luminescence (AFL) [12]. Figure 1 shows a schematic energy-level diagram of CsBr, with $E_{VC} = 6.5$ eV [13] and $E_g = 7.3$ eV [14]. The Auger-free condition is still satisfied, even though we consider the existence of the exciton band at $E_{VX} = 6.9$ eV [15]. When the sample temperature is increased, the exciton absorption band trails to the forbidden gap (Urbach tail) due to the exciton-phonon interaction, resulting in substantial band gap shrinkage.
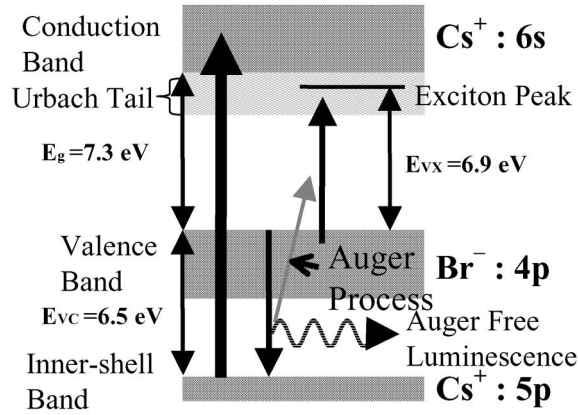
FIG. 1. Schematic energy-level diagram of CsBr. E_{VC} is the energy difference between the top of the valence band and that of the outermost core band. E_g is the band gap energy. At room temperature, even though E_g is a little larger than E_{VC}, the Auger decay process is partially allowed because of the existence of the Urbach tail.

Consequently, the Auger process becomes partially allowed and coexists with AFL. The temperature-dependent Auger decay time is, therefore, measured by observing the decay dynamics of AFL at different temperatures. At the high-temperature limit, we can estimate the Auger decay probability in the situation where $E_{VC} > E_g$.

In the present experiment, we used HH of a Ti:sapphire laser for inner-shell excitation. Details about the Ti:sapphire laser employed are described in Ref. [16]. The pulse width and output energy were 40 fs and 8 mJ at 1 kHz, respectively. The laser beam was focused into a Kr gas tube by a 1-m radius-of-curvature concave mirror for HH generation. The gas tube and the sample were placed in a vacuum chamber. An electric heater attached to the sample holder was used to change the sample temperature from 300 to 340 K in an increment of 20 K. The HH beam was focused on the sample surface by a gold-coated toroidal mirror. The fundamental and low-order harmonics were eliminated by a beam splitter and an Al filter, as described in Ref. [6]. Seven HH from the 11th (16.6 eV) to 23rd (37.5 eV) were used for the outermost-core band excitation of CsBr, in which the onset of the transition from the Cs^+ $5p$ state to the conduction band lies at around 14.1 eV [12].

We used a difference frequency mixing method for time-resolved spectroscopy of AFL [6]. The AFL emitted from a CsBr crystal was focused by a parabolic mirror into a 500-μm thick β-barium borate (BBO) crystal placed outside the vacuum chamber. The luminescence light was mixed with the fundamental beam of the Ti:sapphire laser delayed by an optical stage. The difference frequency wave was detected by a photomultiplier through a monochromator as a broadband filter. The signals were integrated by a boxcar averager and pro-

cessed by a computer. The luminescence spectrum was measured directly by a spectrometer equipped with an intensified charge-coupled device (ICCD) camera.

As a first step, we measured the luminescence spectrum of CsBr at 300 K. The result is shown in Fig. 2(a). The spectrum consists of two bands peaking at 5.0 and 6.0 eV, in good agreement with the previous result obtained under electron beam excitation [11].

The temporal behaviors detected at the peak positions of 6.0 and 5.0 eV are shown in Figs. 2(b) and 2(c), respectively. The high-energy band rises up almost instantaneously, as in the case of CsCl [6]. The data were fitted well to a single-exponential decay, convolved with a response function with a temporal width of 140 fs. On the other hand, the data of the low-energy band were fitted to a convolved double exponential which determined both the rise and decay times. The decay time was 5.0 ± 0.5 ps, which was the same for both bands. This fact clearly indicates that the decay time is governed only by the lifetime of a hole created in the core band [8]. The
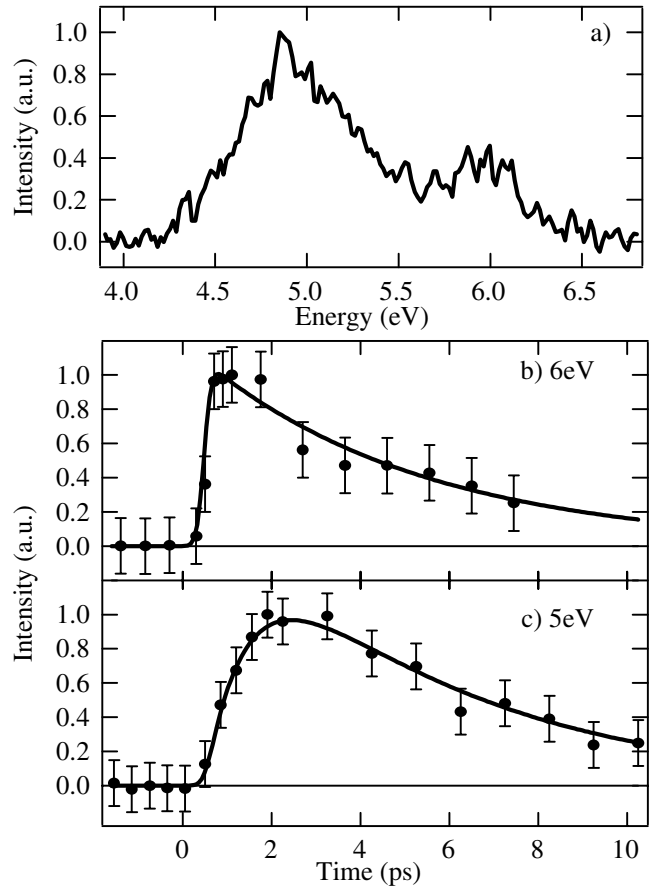

FIG. 2. Luminescence spectrum of CsBr excited by HH at 300 K (a). Decay dynamics of the luminescence detected at 5.0 eV (b) and at 6.0 eV (c) at 300 K. Solid lines are the fitting curves. The decay times are 5.0 ± 0.5 ps in both cases. The high-energy band rises instantaneously, while the low-energy band grows with a rise time of 950 ± 100 fs.

rise time of the low-energy band was estimated to be 950 ± 100 fs.

The temporal shapes of AFL at 320 and 340 K are shown in Figs. 3(a) and 3(b), respectively. The low-energy band at 5.0 eV was chosen for these measurements, because the decay time does not depend on the detection energy. The decay times were 2.5 ± 0.2 ps at 320 K and 1.5 ± 0.2 ps at 340 K. The rise time was the same as that at 300 K. The decay time decreased with increasing temperature.

There are two main differences between the present result of CsBr and the previous result of CsCl [6]. One difference is the appearance of a fast decay in CsBr due to the partially allowed Auger transition, as will be discussed later. The other is the slower rise of the low-energy band in CsBr than in CsCl. An extended deformable cluster model of AFL gives a good description of the rise component of the low-energy band [17]. According to this model, the low-energy band is ascribed to the transition from the self-trapped state of the core hole to the extended state in the valence band. The time scale of this relaxation will be of the order of the LO phonon period, as substantiated in CsCl (250 fs) [6]. Interestingly enough, we observed the rise time 950 ± 100 fs in CsBr, which is longer than the lattice vibration period (300 fs) [18]. This fact suggests that the core hole is required to overcome the potential barrier to relax into the self-trapped state. The existence of the potential barrier for self-trapping of core holes has been pointed out in Ref. [19]. The potential barrier is probably higher in CsBr than in CsCl, so that the core-hole relaxation in CsBr
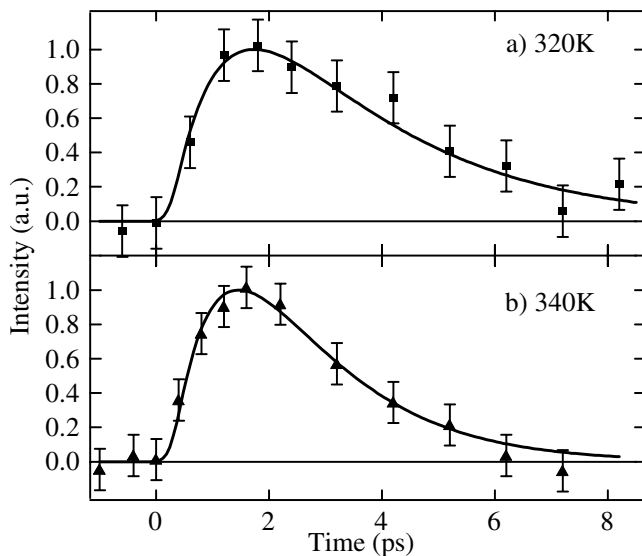
needs some vibration periods. The instantaneous rise of the high-energy luminescence in CsBr is explained as in CsCl [6] by assuming that the "hot" luminescence without Stokes shift, due to the optical transition taking place before the lattice relaxation, overlaps with the high-energy band.

We will now focus on the luminescence decay. The observed decay times in CsBr are much faster than those in CsCl (~ 1 ns [8]). Since the Auger relaxation of core holes does not occur in CsCl because $E_{VC} < E_g$ even at room temperature, the luminescence lifetime is determined only by the radiative transition probability. On the other hand, the core-hole relaxation in CsBr at 300 K contains the Auger process besides the radiative transition, because E_{VC} is close to E_g. When there are two relaxation processes of core holes, the decay rate $1/\tau(T)$ is expressed as follows:

$$\frac{1}{\tau(T)} = \frac{1}{\tau_r} + \frac{1}{\tau_a(T)}, \qquad (1)$$

where τ_r and $\tau_a(T)$ are the temperature-independent radiative decay time and the Auger decay time at temperature T, respectively. At low temperatures below 100 K, the decay process is governed by the radiative transition, because the Auger process is forbidden ($E_g > E_{VC}$). The radiative lifetime τ_r has been determined to be 1.1 ns from the previous experiment by SR [8]. The Auger decay rate increases rapidly with increasing temperature, so that $\tau(T) \rightarrow \tau_a(T)$. Thus, we can get the Auger decay time from the AFL decay dynamics at sufficiently high T.

The temperature dependence of the decay time of AFL in CsBr is presented in Fig. 4, where closed circles correspond to the present data and closed triangles to the data measured by SR [8]. The data point by SR at 300 K should be omitted, because it is limited by the time resolution of SR. We propose a simplified Urbach tail model to explain the experimental result of Fig. 4. In this model, the core

FIG. 3. Temporal shapes of the low-energy luminescence at 320 K (a) and at 340 K (b). Solid lines are the fitting curves, with decay times of 2.5 ± 0.2 ps at 320 K and 1.5 ± 0.2 ps at 340 K. The rise times of (a) and (b) are the same as that at 300 K.
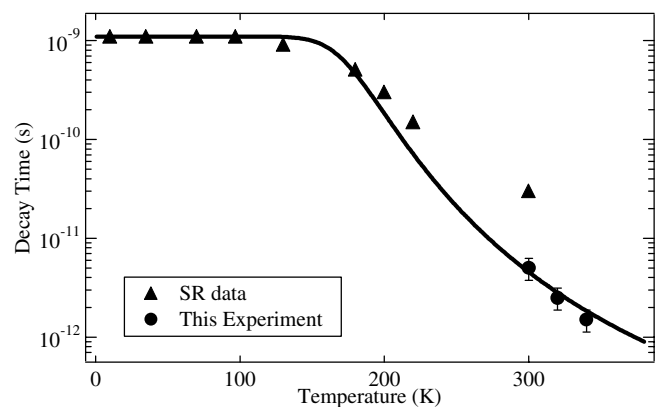

FIG. 4. Temperature dependence of the decay time of AFL in CsBr. Closed triangles correspond to the data obtained by SR [8] and closed circles to the present data. Solid line is the best fit of Eq. (1) to the experimental result.

hole recombines with a valence electron by kicking up another valence electron into the Urbach tail. The absorption coefficient at photon energy E in the Urbach tail region is described as

$$A(E, T) \propto \exp[-\sigma(E_0 - E)/k_B T], \qquad (2)$$

where σ is the steepness parameter, E_0 the converging energy, and k_B the Boltzmann constant. The values of σ and E_0 are determined experimentally. In the Urbach tail model, the Auger decay rate is described as the product of the Auger transition probability $1/\tau_{a0}$ and the joint density of state of Auger electrons, which is considered to be proportional to $A(E_{VC}, T)$. Here, τ_{a0} is the Auger decay time at the high-temperature limit, corresponding to fully energy-allowed Auger decay. Therefore, the temperature-dependent Auger decay time $\tau_a(T)$ is given as

$$\frac{1}{\tau_a(T)} = \frac{1}{\tau_{a0}}\exp[-\sigma(E_0 - E_{VC})/k_B T]. \qquad (3)$$

We set $E_{VC} = 6.5$ eV from the photoemission data [13], and $E_0 = 6.9$ eV and $\sigma = 0.5$ from the measurement of the absorption-edge spectra [20]. The data points of Fig. 4 are fitted well to Eq. (3), with one adjusting parameter τ_{a0}. From this fit, we get $\tau_{a0} = 2.4$ fs. We evaluated the uncertainty of τ_{a0} coming from the experimental inaccuracies of the parameter values. The experimental errors of σ and $E_0 - E_{VC}$ are $\pm 6\%$ and $\pm 5\%$, respectively. From these errors, we get $\tau_{a0} = 2.4 + 3.8/ - 1.5$ fs.

Because charge is transferred from metal ions to ligand valence states in the formation of an ionic compound, the outermost cation core-hole states in many ionic materials such as CsBr decay mainly by interatomic Auger processes involving anion valence electrons. The interatomic Auger process is expressed as transitions of the types $A(x)A(y)B(z)$ and $A(x)B(y)B(z)$ [21]. Here, A and B are metal and halogen ions, respectively, x is the orbit of the hole in the initial state, and y and z are those in the final state. If the final-state holes are left in two different ions, the prime is attached to distinguish one from the other. The former type is called an intra-inter transition and the latter is called an inter-inter transition. Following this notation, the Auger process of interest here is the inter-inter transition, $Cs(5p)Br(4p)Br(4p)'$. In Ref. [10], Green and Jennison calculated the Auger decay rates for various orbit patterns in NaF. The transition in CsBr is similar to the case of $Na(2p)F(2p)F(2p)'$ among their calculations, because, in both cases, holes in the initial state are on the p orbits of the outermost-core band of cations and holes in the final state are on the p orbits of the valence band of anions. The Auger decay time of the $Na(2p)F(2p)F(2p)'$ transition in NaF was evaluated to be 4.3 fs. The value is compared with the observed linewidth 1 eV of the photoelectron spectra [22], which is equivalent to 0.66 fs ac-

cording to the uncertainty principle. This lifetime is a lower limit because the linewidth is broadened by other effects such as the instrumental resolution and a valence-band width. Unfortunately, there are no available data about the linewidth in CsBr. The present value of $2.4 + 3.8/ - 1.5$ fs is in good agreement with the theoretical calculation. In NaF, the relaxation process of core holes is purely of the Auger decay character, because $E_g \ll E_{VC}$ ($E_g = 11.6$ eV [23] and $E_{VC} = 24.2$ eV [24]). We thus determined the decay time of the actual Auger process in CsBr.

In conclusion, we excited electrons in the outermost-core band into the conduction band in CsBr by HH and measured the decay time of AFL at room temperature and above. By extrapolating the temperature-dependent Auger lifetime to a high temperature, we determined the Auger decay time at the high-temperature limit, corresponding to the fully energy-allowed Auger decay. The obtained value of $2.4 + 3.8/ - 1.5$ fs is in line with the theoretical calculation for NaF, and is the first report of the interatomic Auger decay time in condensed matter by a decay dynamics experiment.

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