Two-Photon Spectroscopy of Core Excitons in Barium Fluoride Using Synchrotron Radiation and Laser Light

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We have conducted two-photon spectroscopy of core excitons in BaF_2. Synchrotron radiation and laser light were used for $5p$ core-electron excitation and Auger-free luminescence was detected as the signal. Two-photon excitation enables access to f and p orbitals that cannot be reached by one-photon excitation of electrons in p orbitals. It has been found that the spin-orbit splittings of $4f$ and $6p$ states of the Ba ion in BaF_2 are 0.7 ± 0.1 and 1.4 ± 0.1 eV, respectively.

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Electronic structures are one of the most fundamental features necessary for understanding static and dynamic properties of condensed matter. To reveal distribution of unoccupied states, which are important in the study of excitation and deexcitation cycles, optical spectroscopy is the standard tool as well as inverse-photoemission spectroscopy. The two-photon absorption (TPA) technique is particularly attractive because it enables access to many electronic states forbidden in optical dipole transition [1,2]. Since core states are often dispersionless and have well-defined symmetry, core-exciton spectroscopy is expected to provide fruitful information on conduction-band structures [3]. However, excitation of core electrons by TPA has been a challenge because there were no appropriate light sources. Recently, combinational use of synchrotron radiation (SR) and laser light, which joins continuous and wide-ranged photon-energy distribution of SR and strong power of lasers, has been developed [4,5]. This technique is applicable to formation of a pair of a core hole and a conduction electron in condensed matter, that is, a core exciton.

The study of core excitons dates back to the early 1970s [6]. The thresholds of x-ray absorption due to deep core levels were measured and compared with calculations, since the thresholds are good indexes for identification of atomic species and environment of the atoms or ions. The excitonic effect on the thresholds was disputed for a long time before it was accepted [7]. Shallow core excitons that consist of an outermost core hole and a conduction electron are clearly observed in optical reflectivity spectra of various substances [8,9].

In this Letter, we report the first performance of TPA spectroscopy of core excitons. In order to perform the spectroscopy, we had to distinguish the true signal from false ones caused by the valence-band excitation. Detecting Auger-free luminescence (AFL) was the key to the successful observation. AFL is observed in many materials possessing a shallow outermost core level [10]. Since recombination of an outermost core hole with a valence electron causes the luminescence, AFL is a good probe for investigating the behavior of the core hole [11]. The crystal of BaF_2 is one of AFL-observed materials and has been used as a scintillator in high-energy physics. Its schematic energy diagram is depicted in Fig. 1(a). The outermost core state splits into $5p_{1/2}$ and $5p_{3/2}$ levels by spin-orbit interaction. It is widely accepted that the lowest states of the conduction band consist of $5d$ orbitals of Ba ions [8,12]. One-photon spectroscopy is not appropriate for the study of high-angular momentum states such as f orbitals, because s and p orbitals are the main constituents of core levels. Since $4f$, $6s$, and $6p$ orbitals are expected above $5d$ orbitals within a few eV, BaF_2 is an ideal material for a demonstration of the power of TPA spectroscopy. We

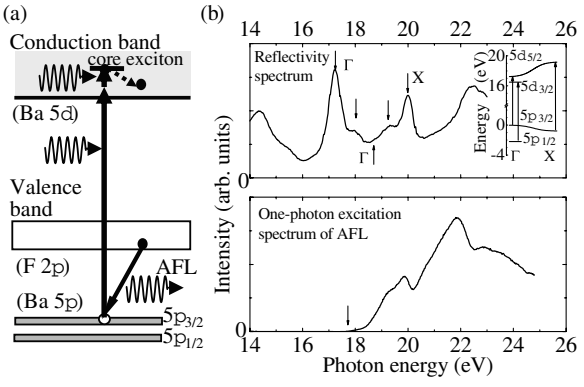

FIG. 1. (a) A schematic energy diagram of BaF_2. (b) A reflectivity spectrum (upper panel) and a one-photon excitation spectrum of AFL (lower panel) in BaF_2.

focus on two-photon excitation of $5p$ electrons to form $4f$ and $6p$ excitons in BaF_2 in this Letter.

A single crystal of BaF_2 was obtained from Horiba Ltd. Cleaved specimens with (111) planes and ones with polished (100) planes were used. Measurements were pursued at room temperature. In order to perform two-photon excitation of core excitons, SR from the storage ring at UVSOR, Institute for Molecular Science (Okazaki), was used in combination with a laser beam. Details about the experimental apparatus are written elsewhere [4]. The fundamental or the second harmonic output of a Ti:sapphire laser was guided by an optical fiber to the sample. The laser beam propagated through the sample in the direction opposite to the SR beam. The pulse duration, which was 0.2 ps at the output of the laser cavity, was enlarged to 0.3 ns during the propagation through the fiber. The bandwidth of monochromatized SR was about 0.13 eV. The average power of the fundamental and the second harmonic of the laser light were 90 and 20 mW, respectively. The pulses of SR and the laser were synchronized by an electronic device.

A single-path monochromator was used for detecting exclusively the AFL with a 5.6-eV peak by a photomultiplier tube of the microchannel plate-type. We compared the intensities of AFL between those obtained under excitation by only SR and by both SR and laser. The signal was accumulated for 10–20 min to obtain a data point at each wavelength of SR with repetition of turning on and off the laser light at 0.05 Hz. The increase of the luminescence is attributed to the extra formation of core holes by TPA and is referred to as the TPA signal hereafter in this Letter.

An ordinary reflectivity spectrum and a one-photon excitation spectrum of AFL in BaF_2 are shown in the upper and lower panels, respectively, of Fig. 1(b). The $5p$ core-exciton peaks were observed at 17.2, 18.0, 19.2, and 20.0 eV in our measurement as shown in the upper panel with downward arrows. These values are consistent with a recent measurement [13] but slightly different from a former one [8]. The peak at 14.4 eV is attributed to valence-electron excitation and that at 22.4 eV to the counterpart of the core-electron excitation [8]. According to a recent band calculation [14], the $5p$ band has a minimum at the X point by 0.7 eV below the energy of the Γ point, and the $5d$ band has a maximum at the X point by about 2 eV above the energy of the Γ point as shown schematically in the inset of the upper panel. It is suggested that the peaks at 17.2 and 20.0 eV are due to direct excitons at Γ and X points, respectively, and that the other peaks originate from indirect transitions. These peaks should be attributed to excitation of $5p_{3/2}$ electrons. It is natural that the intensities of the two direct peaks are larger than those of the indirect ones. The spectrum shows that the dispersion of the $5p$ band is 0.8 eV, which is consistent with the calculation within the experimental error.

The relativistic quantum theory tells that the spin-orbit term in the electronic Hamiltonian in a centrosymmetric electrostatic field, ϕ, is

$$H_{LS} = \frac{e}{2m^2 r}\frac{d\phi}{dr}(\boldsymbol{s}\cdot\boldsymbol{l}), \tag{1}$$

where m and e denote the mass and charge of the electron, r distance from the center, $\boldsymbol{s}$ and $\boldsymbol{l}$ spin and orbital angular momentum operators, respectively, and the natural units are used. Provided that the effective central charge is $-Ze$, $\phi = -Ze/r$. The expectation value of Eq. (1) for the (n, l) state is given by

$$\langle H_{LS}\rangle_{n,l} = \frac{Z\alpha}{2m^2}\frac{(mZ\alpha)^3}{n^3 l(l+1)(l+1/2)}\langle \boldsymbol{s}\cdot\boldsymbol{l}\rangle, \tag{2}$$

where $\alpha = e^2/4\pi$. The energy difference between the spin doublet, $\Delta_{n,l}$, is defined as $\Delta_{n,l} = E_{j=l+1/2} - E_{j=l-1/2}$, where E and j represent the energy and the total angular momentum, respectively, of the relevant state. Using Eq. (2), we have

$$\Delta_{n,l} = Z^4\alpha^2\frac{\alpha}{2a_0}\frac{1}{n^3 l(l+1)}, \tag{3}$$

where a_0 represents the Bohr radius. Applying Eq. (3), we obtain relative spin-orbit splittings of $5p$, $5d$, $4f$, and $6p$ states:

$$\Delta_{5p}{:}\Delta_{5d}{:}\Delta_{4f}{:}\Delta_{6p} \approx 3.0{:}1.0{:}1.0{:}1.7. \tag{4}$$

The spin-orbit splitting of the core $5p$ orbital was experimentally obtained to be 2.2 eV [15]. Among transitions from $5p$ to $5d$ states, $5p_{3/2}$-$5d_{5/2}$ and $5p_{1/2}$-$5d_{3/2}$ are dipole-allowed transitions. Consequently, the difference in the energies of the Γ excitons is the difference between spin-orbit splittings of the hole and electron states. Since Δ_{5d} of 0.7 eV is deduced from Eq. (4), the $5p_{1/2}$ Γ exciton should exist 1.5 eV above the corresponding $5p_{3/2}$ exciton. This exciton is found at the right position as a small structure in the reflectivity spectra of the present study (marked by an upward arrow) and the former ones [8,13]. If the 19.2-eV reflection peak might be ascribed to the $5p_{1/2}$ Γ exciton as in Ref. [8], the obtained ratio between Δ_{5p} and Δ_{5d} would be far from Eq. (4).

The excitation spectrum of AFL remains zero around the $5p_{3/2}$ Γ-exciton energy and rises at 17.7 eV, which corresponds to the core-band to conduction-band transition, as shown in the lower panel with an arrow. This implies that the hole of the core exciton does not directly recombine with a valence electron to emit AFL [10]. In other words, a core exciton must have enough energy to dissolve into a free core hole and a free conduction electron for emission of AFL. The binding energy of the exciton is obtained to be 0.5 eV from the values above. In the high-energy region, contribution from excitation of $5p_{1/2}$ electrons may be included in the spectrum, but temporal profiles of the

luminescence are unchanged for different excitation photon energies. It is indicated that a $5p_{1/2}$ hole is rapidly relaxed to the $5p_{3/2}$ level.

The intensity of the TPA signal is plotted as a function of the sum of photon energies of the two excitation light sources by filled circles in Fig. 2. The photon energy of the laser light was 3.10 eV for panel (a) and 1.55 eV for panel (b). Fine structures which are not seen in the one-photon excitation spectrum of Fig. 1(b) are found, especially in panel (b). The polarization direction of the laser light was random, and that of SR was horizontal. Cleaved (111) surfaces were used for the measurements. The TPA spectra were also measured with the use of a polished sample under the condition that the laser light was linearly polarized and that both excitation light beams entered the sample through (100) surfaces. The spectral profile was not changed much by the polarization directions of excitation light. However, the signal intensity measured under a perpendicular configuration of polarization was about 1.5 times as large as that under a parallel configuration except around 20.4 eV. This fact confirms that the signal is caused not by cascade processes but by TPA.

Resonant enhancement of TPA is expected when a real state is available as the intermediate state of the transition, since the real part of the denominator of the corresponding term vanishes in the expression of the TPA coefficient. On the high-energy side of the arrows in Fig. 2, this resonance condition of TPA is fulfilled. The TPA signal was not detected or extremely weak on the low-energy side.

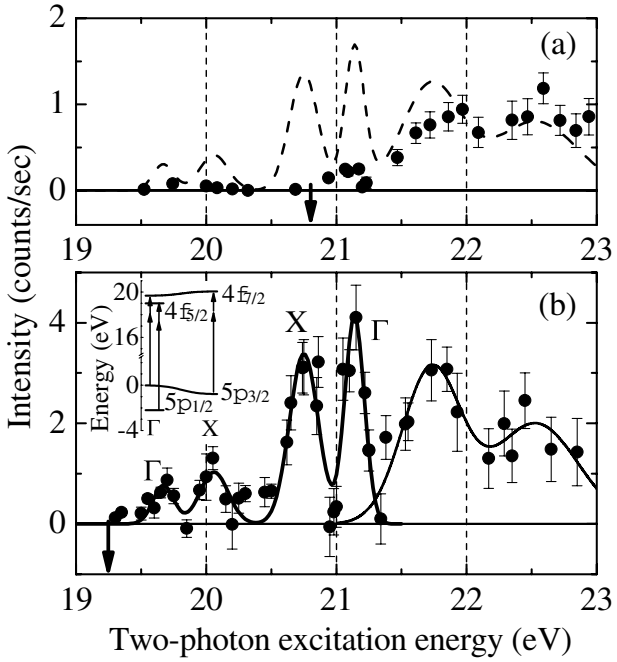

FIG. 2. Experimentally obtained TPA spectra of the crystal of BaF_2. The photon energies of the laser are (a) 3.10 eV and (b) 1.55 eV. Fine structures which are not seen in the one-photon excitation spectrum are observed. See the text for details.

There are narrow peaks at around 20 and 21 eV and two rather broad bands at around 22 eV in the TPA spectrum of Fig. 2(b) .The solid curves are the best fits to the data in the frameworks of four and two Gaussian components in the regions below and above 21.3 eV, respectively. These peaks are naturally attributed to excitons made by excitation of $5p$ core electrons. Formation of $4f$ excitons is the most probable candidate for constituents of the narrow peaks because $4f$ orbitals are the lowest to which transition by TPA is allowed. Since the next lowest states are $6p$ states, the bands around 22 eV are attributed to $6p$ excitons.

Angular momentum selection rules for TPA allow forming $5p_{1/2}$-$4f_{5/2}$, $5p_{3/2}$-$4f_{7/2}$, and $5p_{3/2}$-$4f_{5/2}$ excitons, placed in the order of decreasing energy. Since a sharp structure is not found in the higher-energy region, the peaks at around 21 eV are attributed to $5p_{1/2}$-$4f_{5/2}$ excitons and that at around 20 eV to $5p_{3/2}$-$4f_{7/2}$ excitons. These excitons are expected to show some peaks due to a dispersion effect similar to the case of $5d$ excitons. Unfortunately, we have no data of band calculation of $4f$ states. However, if it is assumed that the $4f_{7/2}$ state has a maximum at the X point by 0.4 eV above the energy of the Γ point, we can explain these peaks in a simple way taking into account that the $5p_{3/2}$ state has a minimum at the X point by 0.7 eV below the energy of the Γ point as shown schematically in the inset of Fig. 2(b); 19.7- and 20.8-eV peaks are attributed to direct excitons at Γ and X points, respectively, and the 20.1-eV peak to an indirect exciton from the Γ to the X point. The 21.1-eV peak is attributed to the $5p_{1/2}$-$4f_{5/2}$ Γ exciton. Then, we obtain $\Delta_{5p} - \Delta_{4f} = 1.5$ eV. Since $\Delta_{5p} = 2.2$ eV, it is concluded that $\Delta_{4f} = 0.7$ eV. This is consistent with Eq. (4) within the experimental error.

There might be an alternative explanation based on the crystal field effect. According to the group theory in a cubic field, the $4f_{7/2}$ level splits into sublevels expressed as Γ_6^-, Γ_7^-, and Γ_8^-, and $4f_{5/2}$ into Γ_7^- and Γ_8^-. One more peak might be found if the excitons were exposed to a strong crystal field [13]. Therefore, the crystal field effect is rejected as the cause of the narrow peaks.

TABLE I. Experimentally obtained excitonic peaks and locations of electron levels at the Γ point. The origin of the measure for the levels is set to the bottom of the conduction band made of the $5d_{3/2}$ level. The binding energy of the excitons is assumed to be the same as that of $5d$ excitons.

	Holes	Electrons	
Excitonic peaks (eV)	Orbitals	Orbitals	Locations (eV)
19.67			
20.06	$5p_{3/2}$	$4f_{7/2}$	3.2 ± 0.2
20.75			
21.14	$5p_{1/2}$	$4f_{5/2}$	2.5 ± 0.2
21.73	$5p_{3/2}$	$6p_{3/2}$	5.3 ± 0.2
22.53	$5p_{1/2}$	$6p_{1/2}$	3.9 ± 0.2

The present interpretation of $4f$-exciton peaks is summarized in Table I. Provided that the binding energies of $4f$ excitons are the same as that of $5d$ excitons, the locations of $4f_{5/2}$ and $4f_{7/2}$ levels are above the $5d_{3/2}$ level by 2.5 and 3.2 eV, respectively, at the Γ point as listed in Table I.

We discuss the two broad bands at 21.7 and 22.5 eV in Fig. 2(b). Corresponding bands are also seen in panel (a). The broken curve of panel (a) is drawn for comparison; the curve is the sum of the two solid curves in panel (b) but is normalized to the data at 21.9 eV. The two bands, as well as the narrow peak at 21.1 eV, are found for different laser photon energies. This fact strongly supports the claim that the two bands are caused by TPA due to $6p$ excitons. However, the peak positions of the lower band are not exactly the same between the two spectra. It should be pointed out that polarization dependence of the signal around 20.4 eV is different from that at other energies in spectrum (b); the signal intensity did not depend on the polarization configuration but depended on whether the surfaces of the sample were cleaved or polished. It is implied that there is absorption due to some defects near the surface. Cascade excitation of these defects may cause the peak shift from 21.7 to 21.9 eV in spectrum (a). We also attribute the weak signal at around 19.7 eV in spectrum (a) to cascade excitation, since a weak signal was also observed around 18.2 eV under excitation of 1.55-eV laser light.

The two $6p$ bands are separated by about 0.8 eV. This value corresponds to $\Delta_{5p} - \Delta_{6p}$, if the 21.7-eV band is attributed to $5p_{3/2}$-$6p_{3/2}$ excitons and the 22.5-eV band to $5p_{1/2}$-$6p_{1/2}$ excitons. Then, $\Delta_{6p} = 1.4$ eV is obtained from $\Delta_{5p} = 2.2$ eV. This is consistent with Eq. (4) within the experimental error. Since both hole and electron bands have the p character, it is conceivable that the distance between the two states does not change so much at different points in k space. This may explain the cause of the broad Gaussian shape of the $6p$ exciton bands. The locations of $6p$ exciton peaks and those of $6p$ levels are summarized in Table I, where the binding energies of $6p$ excitons are assumed to be the same as that of $5d$ excitons.

In conclusion, we have conducted two-photon spectroscopy of core excitons in the crystal of BaF_2 through excitation with SR and laser. The TPA spectra were interpreted in the frame of a band picture with a relativistic effect. Energy locations of unoccupied $4f$ and $6p$ levels have been obtained. The spin-orbit splittings of $4f$ and $6p$ states were found to be 0.7 ± 0.1 and 1.4 ± 0.1 eV, respectively. It was clarified that the dispersion effect is much stronger than crystal field splitting in the crystal of BaF_2, and the dispersion of the $4f$ state is about 0.4 eV.

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