

(BL6A2)

## Photoelectron spectroscopic study of core-exciton decay in BaF<sub>2</sub>

Masao Kamada, Minoru Itoh,<sup>A</sup> and Yukinori Kiyota<sup>A</sup>

*UVSOR Facility, Institute for Molecular Science, Myodaiji, Okazaki 444-8585*

*<sup>A</sup>Faculty of Engineering, Shinshu University, Nagano 380-8553*

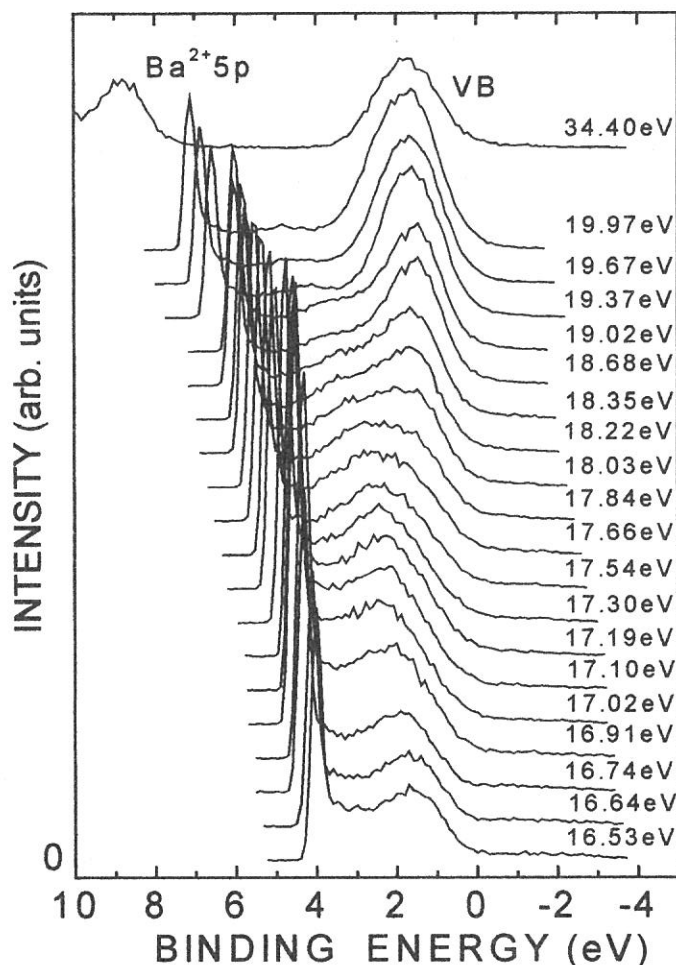
In recent decade, new luminescence, so-called Auger-free luminescence or cross luminescence, was discovered by the core-level excitations in the wide-band gap materials, where the band-gap energy ( $E_g$ ) is larger than the energy difference ( $E_{VC}$ ) between a valence band and an outer-most core level.<sup>1)</sup> The luminescence is attributed to the transition from the valence band to the core level. There is no Auger process when the condition  $E_g > E_{VC}$  is satisfied, and then the Auger-free luminescence is so strong and useful for fast scintillation in the vacuum ultraviolet and soft x-ray regions. The Auger-free luminescence appears with the excitation of the core level. It is known that there are no exciton peaks in the excitation spectra, but the reason is not fully understood yet. The present work has been conducted to understand why core-exciton peaks are missing in the excitation spectra of Auger-free luminescence.

Experiments have been conducted at plane-grating monochromator beamline BL6A2 of the UVSOR facility, Institute for Molecular Science. Photoelectron spectra of BaF<sub>2</sub> were observed with an angle-resolved hemi-spherical energy analyzer. Specimens were prepared by evaporation in a preparation chamber and were transferred to an analyzing chamber. The base pressures of the preparation and analyzing chambers were  $5 \times 10^{-10}$  and  $2.5 \times 10^{-10}$  Torr, respectively, while the pressure was raised to  $2 \times 10^{-8}$  Torr during evaporation. Special cares were taken to make thin films of about 10 nm in thickness. No charging effects were observed in the present experiments.

Luminescence spectra of the same thin films were observed in the analyzing chamber by using a quartz lens and a Spex 270M monochromator with a princeton LN-532CCD detector. The luminescence and excitation spectra of single crystals were also measured for comparison. The luminescence spectra consist of two different luminescence bands, the Auger-free luminescence and the luminescence due to a self-trapped exciton. The energy positions of these luminescence bands in films are almost the same as those in the single crystals, but the intensity ratios are not the same between films and crystals.

Figure 1 shows a set of EDCs of a BaF<sub>2</sub> film which was obtained with excitation photon energies of 16.5-20 eV. The peak position and intensity of the valence band photoelectrons change drastically around the excitation photon energy of Ba-5p core exciton (17.1 eV). One of the present authors (M. K.) has been studying the decay process of the core-excitons in alkali halides by using photoelectron spectroscopy and proposed the following two non-radiative decay processes of the Li K-exciton in LiF; (1) direct-recombination process and (2)  $K_{ex}$ -VV Auger process.<sup>2)</sup> In the direct-recombination process, an excited electron and a core hole forming a core exciton recombine with one another, transferring the energy to a valence electron. This causes the resonant enhancement of the valence photoelectrons. The probability of the direct-recombination process can be estimated by using CIS and absorption (reflection) spectra. The obtained value is about 27-54 % for the Ba-5p exciton peak of BaF<sub>2</sub>. It should be noted that the value is not 100 %, while there is no core-exciton peak in the excitation spectra of Auger-free luminescence. This indicates that there is another non-radiative decay of the core-exciton.

Previously kamada et al. proposed that in the  $K_{ex}$ -VV Auger process, a valence electron recombines with a core hole, transferring the energy to another valence electron.<sup>2)</sup> This produces the two-holes and one-electron bound state consisting of two-holes in the valence band



and an electron in the excited state, resulting in the resonant enhancement of the Auger electrons and the energy shift of the Auger electrons. The present material BaF<sub>2</sub> has an energy gap ( $E_g=10.8$  eV) larger than the energy difference ( $E_{VC}=7.9$  eV) between the valence band and an outer-most core-level. Therefore, in order to explain the present result, the two-holes and one-electron bound state may be produced at the final state of the core-exciton decay. The typical energy shift of the Auger electrons due to the two-holes and one-electron bound state is about 1.0 eV. Thus the kinetic energy of the Auger electrons produced at the final stage of the core-exciton decay is roughly estimated to be 8.9 eV. Since the exciton absorption band has a long tail down to 8.8 eV and also there are unknown bound states around 8 eV, the Auger transition may be possible, resulting in the suppression of the Auger-free luminescence at the excitation photon energy of the core-exciton.

It is also found that the resonance enhancement due to the core-exciton decay is large in the higher-binding energy part of the valence band. This fact indicates that the partial density of states of barium ions locates on the higher-binding energy side of the valence band or that the relaxed excited state of the core-exciton in BaF<sub>2</sub> is shifted by about 0.9 eV. The detailed analyses will be reported in near future.

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## Laser-induced core-level shifts in GaAs (100)

Masao Kamada, Jun-ichi Murakami<sup>A</sup>, Senku Tanaka<sup>B</sup>, Sam Dylan More,  
Shuji Asaka<sup>C</sup>, Minoru Itoh<sup>A</sup>, and Yasuo Fujii<sup>B</sup>

*UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585*

<sup>A</sup>*Faculty of Engineering, Shinshu University, Nagano 380-8553*

<sup>B</sup>*College of Engineering, Osaka City University, Osaka 558-8585*

<sup>C</sup>*Equipment Develop Center, Institute for Molecular Science, Okazaki 444-8585*

Electric potentials at semiconductor surfaces and interfaces are very important to understand a variety of electrical properties and phenomena of semiconductors and to control semiconductor devices. Lots of works have been conducted to know the equilibrium electronic states at the semiconductor surfaces and interfaces, but few works have been carried out to understand the dynamics of non-equilibrium charge distribution. Long *et al.* have first reported the transient surface photo-voltage on Si (111) using synchrotron radiation (SR) and laser pulses.<sup>1)</sup> They obtained non-equilibrium electron density induced by laser pulses in the space charge layer. An agreement between their experiments and theoretical simulations is good for a high power laser, but not for a low power laser. In recent years, Marsi *et al.* have conducted the similar experiment to study the transient surface photo-voltage on Si (111)2x1 and GaAs (110) surfaces,<sup>2)</sup> and reported the difference in dynamics between Si and GaAs surfaces. The purpose of the present work is to investigate the photo-induced carrier dynamics on GaAs (100), since this surface provides spin-polarized electrons after Cs- and oxygen treatments.<sup>3)</sup>

Figure 1 shows a schematic arrangement of the present experiments at BL6A2, where a plane-grating monochromator (PGM) and a hemi-spherical electron analyzer were installed. We used a mode-locked Nd:YAG laser with a pulse width of about 300ps, which was triggered with a signal from a master oscillator of the UVSOR storage ring. Second-harmonic light of the laser (photon energy 2.33 eV) was focused on the sample in a vacuum chamber, having a spot size of 2 mm, which covered well the SR spot size of 1 mm. The temporal overlap was also carefully adjusted by using a MCP-PM/TAC system. The energy distribution curves with and without laser excitation were measured in single scan by using an optical shutter. The clean surface of p-type GaAs (100) doped with Zn was prepared *in situ* using Ne-sputtering and thermal annealing procedures.

Figure 2 shows Ga-3*d* photoelectron spectra at 165 K. It is clearly observed that the Ga-3*d* level under laser excitation is shifted by about 0.33 eV to higher kinetic energy side. The As-3*d* level is also shifted by the same amount. Any change in spectral shape was not appreciable in both cases. Therefore, the present core level shift induced by laser excitation can be attributed to the transient photo-voltage effect. Namely, hot electrons and holes produced by laser pulses are separately distributed in the surface space-charge layer, and then their redistribution may change the band bending of GaAs. The dependences of the core-level shifts on the incident photon flux and the sample temperature are well explained by this idea.

This work was partially supported by a Grant-in-Aid from the Ministry of Education, Science, Culture, and Sports.

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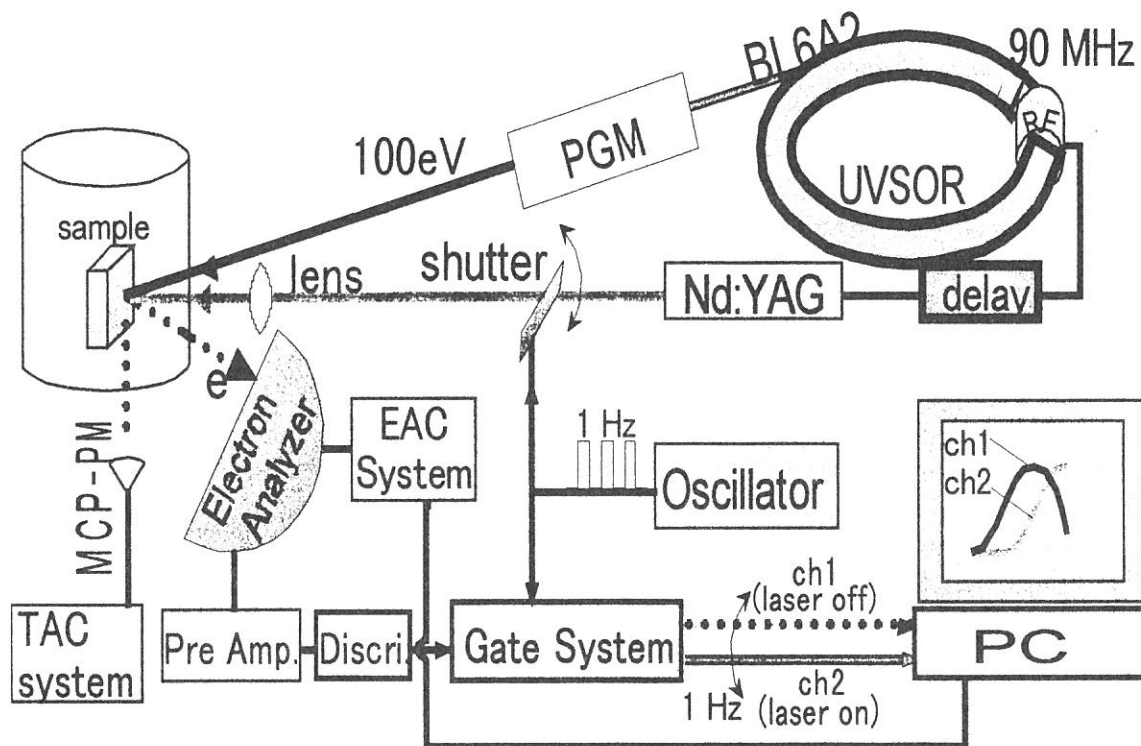


Fig. 1. Schematic experimental setup

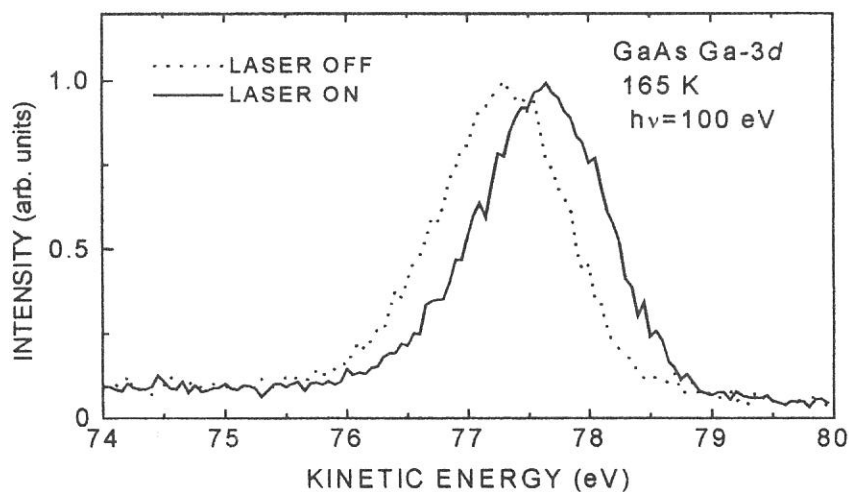


Fig. 2. Ga-3d photoelectron spectra with and without laser excitation.

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## Photoemission Studies on binary alloys CrPt<sub>3</sub> and MnPt<sub>3</sub>

Hitoshi SATO, Shinya SENBA, Kozo TERAMOTO,  
Masaki TANIGUCHI, Hiroshi MARUYAMA\* and Masao KAMADA#

*Faculty of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima 739-8526*

*\*Faculty of Science, Okayama University, Tsushima-Naka 3-1-1, Okayama 700-8530*

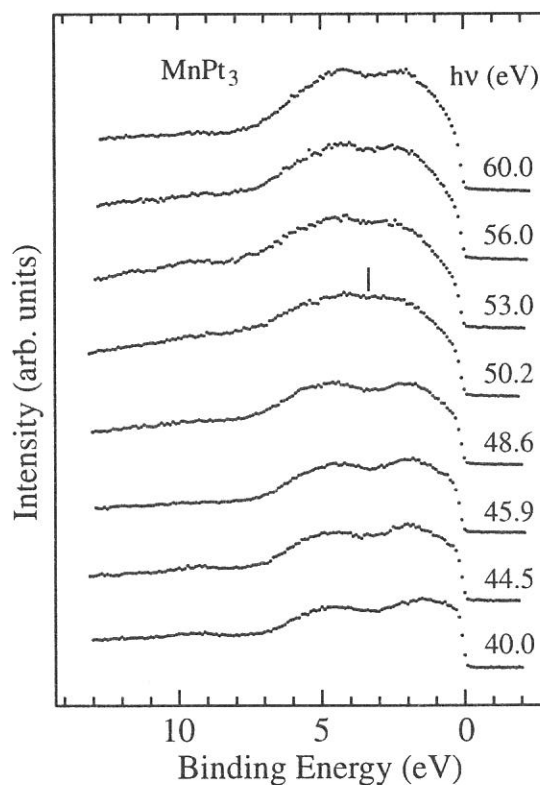
*#Institute for Molecular Science, Myodaiji, Okazaki 444-8585*

Transition metal intermetallic compounds TPt<sub>3</sub> (T=V, Cr, Mn, Fe, Co) have Cu<sub>3</sub>Au-type crystal structure and reveal a wide variety of magnetism. For VPt<sub>3</sub> and CrPt<sub>3</sub>, the magnetic moments on the Pt sites align in an antiparallel direction to those on the T sites, forming a ferrimagnetic ordering. MnPt<sub>3</sub> and CoPt<sub>3</sub> are ferromagnetic compounds, while FePt<sub>3</sub> exhibits antiferromagnetism with a (1/2,1/2,0) magnetic reflection. In this study, we have carried out the photoemission experiments on CrPt<sub>3</sub> and MnPt<sub>3</sub> in the Cr and Mn 3p-3d excitation region.

Samples used for the experiments were prepared by the arc-melting method under an Ar atmosphere. Photoemission experiments were carried out on plane-grating monochromator beam line BL6A2. Photoelectrons were collected with a hemi-spherical analyzer. Clean surfaces were obtained by scraping with a diamond file under ultrahigh vacuum. All experiments were performed at room temperature.

Figure 1 shows a series of photoemission spectra of MnPt<sub>3</sub> in the Mn 3p-3d excitation region (~ 50 eV). The photoemission intensities have been normalized to the monochromator output. Binding energy is referred to the Fermi level. We notice that the Mn 3d and Pt 5d hybridization band spreads over the top 7 eV region of the valence bands. It is noted that the resonant enhancement is not observed clearly. This means that the Mn 3d electrons in MnPt<sub>3</sub> have extremely itinerant character and strongly hybridize with the Pt 5d states. However, a small amount of enhancement is observed around 3.2 eV as indicated by a bar in the figure. The Mn 3d states are considered to contribute to the valence bands mainly around this energy. As for CrPt<sub>3</sub> also, the resonant enhancement was not observed (not shown here), but the energy position of the Cr 3d states seems to be just below the Fermi level.

In the Cr and Mn 3d excitation region, the photoionization cross-section of the Pt 5d states is larger than those of the 3d states. In order to separate more clearly the Cr/Mn 3d and Pt 5d partial densities of states in the valence bands, we plan to measure the photoemission spectra at the Cooper minimum in the Pt 5d cross-section.



**Fig.1** A series of photoemission spectra of MnPt<sub>3</sub> in the Mn 3p-3d excitation region.