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Photoion yield spectroscopy in the 4d photoionization of Eu^+

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Abstract. Using an ion–photon merged-beam apparatus, photoion yield spectra of Eu^{2+} and Eu^{3+} from the 4d photoionization of Eu^+ were measured as a function of photon energy in the range 110–160 eV. The measured spectra look very similar to those from a neutral Eu target. Both Eu^{2+} and Eu^{3+} yield spectra, a broad 'giant resonance' appears at 140 eV with some preceding small peaks at 131.5, 132.8 and 134.7 eV. The summit of the 'giant resonance' in the Eu^{2+} spectrum is split into two peaks. This is not observed in neutral Eu photoionization.

1. Introduction

The 4d photoionization of lanthanides has been the subject of great interest in the field of atomic physics since it involves anomalous broad resonance phenomena, so-called 'giant resonances'. For metallic and atomic lanthanides, it has been revealed through experimental investigations that the $4d \rightarrow (4, \varepsilon)f$ 'giant resonance' profile changes systematically as a function of atomic number Z (see, for example, Zimkina *et al* (1967) for solids, Dzionk *et al* (1989) and Nagata *et al* (1990) for atomic vapours). Although the production mechanisms for the giant resonance are not yet totally understood, such systematic evolution of the resonance profile is often explained qualitatively by 'orbital collapse' of the f wave of the excited electron due to the increase of nuclear charge (Connerade 1987). According to the 'orbital collapse' mechanism, a change of the giant resonance profile can be caused not only by the increase of nuclear charge but also by any other change which makes the effective potential for the f electrons more attractive. In our previous work (Koizumi *et al* 1995), the measured photoion yield spectra from 4d photoionization of Ba^+ were obviously different from those from neutral Ba (Nagata *et al* 1990). Becker *et al* (1986) reported a difference in the autoionization characteristics between the '$4d \rightarrow 4f$' giant resonance and $3d \rightarrow 4f$ transitions in neutral Eu atoms. They ascribed this difference to the 'collapse' of the 4f wavefunction. The 3d hole increases the effective charge of the nucleus and makes the

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inner well of the effective potential deeper than that in the 4d hole case, therefore the 4f wavefunction is almost localized inside the centrifugal barrier. In this sense, $4d \rightarrow (4, \varepsilon)f$ photoexcitation/ionization of ionic Eu may show a difference from the neutral Eu case, since the existence of the primary ionic charge may cause the 'collapse' of the $(4, \varepsilon)f$ wavefunction.

On the other hand, it has also been revealed that the giant resonance profile of lanthanide in solid metal, where the non-local valence electrons are considered 'ionized', is almost the same as that of the isolated atom of the same element except for small structures and some preceding discrete peaks. Mansfield and Connerade (1976) reported the observed similarity between the $4d \rightarrow f$ transitions in Eu vapour and that in metallic Eu. Since this resemblance showed that the difference of the valence electron environment did not affect the resonance photoexcitation so much, they inferred that $4d^{10}4f^n \rightarrow 4d^9 4f^{n+1}$ transitions in lanthanides take place deep inside the 'ionic cores'. Following this argument, the resonance profile of ionic lanthanides is expected to be very similar to that of metallic lanthanides. However, the outer electron environment of atoms in solids is not really the same as that of isolated ions. The 4d photoabsorption spectrum of Ba^{2+} (Lucatorto *et al* 1981) is very different from that of Ba metal (Rabe *et al* 1974), whereas the photoabsorption spectrum of Ba vapour (Lucatorto *et al* 1981) looks similar to that of Ba metal. (Note that the 'ionic core' of Ba metal is Ba^{2+}.) The photoabsorption spectrum of La^{3+} in the 4d giant resonance region (Köble *et al* 1995) also shows a conspicuous discrepancy from that of La metal (Zimkina *et al* 1967). Therefore, it is important to see how the ionized (valence-electron-moved) state affects the giant resonance, yet very few experiments on $4d \rightarrow \varepsilon f$ giant resonances have been performed for ionic lanthanides.

Recently, using an ion–photon merged-beam apparatus, we have measured photoion yield spectra of singly and doubly photoionized products from the 4d photoionization of singly charged ions; Xe^+ (Sano *et al* 1996) and Ba^+ (Koizumi *et al* 1995). As a new result in this series of experiments, in this paper we present the photoion yield spectra of Eu^{2+} and Eu^{3+} from a Eu^+ target measured within the energy range of the $4d \rightarrow (4, \varepsilon)f$ giant resonance: 110–160 eV.

2. Experiment

The experimental set-up was the same as that described in Koizumi *et al* (1995). Briefly, the measurements were done using synchrotron radiation from the 2.5 GeV storage ring of the photon factory (PF) at the National Laboratory for High Energy Physics (KEK). The experimental chamber was set at the beamline BL-3B which was equipped with a 24 m spherical grating monochromator (Yagishita *et al* 1991). In this study, a 600 line/mm grating was used for the energy range 110–160 eV. Photon intensity was measured as electric current by a photodiode located at the end of the chamber. The estimated photon flux was 10^{12} s^{-1} with an energy resolution of $E/\Delta E \simeq 130$. Eu^+ ions were produced by a surface ionizer combined with an oven, and extracted with 2 kV acceleration. The ions were deflected 90° by an electrostatic quadrupole and merged into the photon beam. After passing a 15 cm reaction region which was biased by about 800 eV, the ions were demerged from the photon beam and charge analysed by electrostatic parallel plates. Eu^{2+} and Eu^{3+} produced in the reaction region were introduced into two small windows on the end plate of the charge analyser, and detected by channel electron multipliers combined with ion-to-electron converter plates. Primary ion current was monitored by a Faraday cup installed in the analyser. In order to cancel background signals, data were accumulated through temporal four-phase ion–photon ON/OFF modulation. The measured photoion

intensities were calibrated for ion current, photon intensity and efficiencies of the detectors. The vacuum of the experimental chamber was kept lower than 3×10^{-10} Torr during the measurement.

3. Results and discussion

The obtained relative photoion yield spectra with an energy resolution of $E/\Delta E \simeq 130$ are shown in figure 1. In both Eu^{2+} and Eu^{3+} spectra, a broad 'giant resonance' appears at 140 eV. The width of the resonance is much narrower than that in Xe^+ (Sano *et al* 1996) and Ba^+ (Lucatorto *et al* 1981, Koizumi *et al* 1995). In the spectra, there are also observed some preceding peaks at the onset of the giant resonance. These small peaks were, as shown in figure 2, remeasured with a higher-energy resolution of $E/\Delta E \simeq 350$, and their positions were determined as 131.5, 132.8 and 134.7 eV, respectively. As seen in these figures, although the photon energy is much higher than the double-ionization threshold of Eu^+ ($\sim$50 eV), the relative intensities of the singly photoionized product (Eu^{2+}) is almost comparable with (or even higher than) the doubly photoionized product (Eu^{3+}) in the giant-resonance energy region. This is very different from the cases of lighter elements such as Xe and Ba, where the singly photoionized yield is much less than the doubly photoionized product. Therefore, the photoexcitation and subsequent autoionization processes of Eu^+ are considered to be different from those of Xe^+ and Ba^+. This might be ascribed to the many-electron effect due to the existence of 4f electrons between the 4d and 6s subshells. The other difference in the spectra is that the Eu^{2+} yield shows a 'Beutler–Fano-type' profile, which means that the mechanism to produce Eu^{2+} contains interchannel coupling such as the interference between direct and indirect ionization. In the case of neutral Eu, photoelectron spectroscopy revealed that in the giant resonance region a large part of photoelectrons are from the 4f subshell, and that the partial cross section of 4f photoelectron emission shows a Beutler–Fano profile (Becker *et al* 1986, Richter *et al* 1989, Kukk *et al* 1994). Becker *et al* (1986) attributed the mechanisms of this process to the super-Coster–Kronig-like decay, i.e. $4d^9 4f^7(4, \varepsilon f) \rightarrow 4d^{10} 4f^6(\varepsilon d, g)$, which leaves the ion in the same final state as reached by direct 4f photoionization. This is consistent with the result of the photoion measurement where the intense singly photoionized yield is observed with a Beutler–Fano profile. As will be mentioned below, the photoion yield spectra from Eu^+ are very similar to those from neutral Eu, so that the same mechanisms are expected for the photoexcitation/ionization of Eu^+.

For comparison with the total photoion yield spectrum for a neutral Eu target (Nagata *et al* 1990), the sum of the Eu^{2+} and Eu^{3+} products is shown in figure 3. Note that Eu^+ photoionization not only yields Eu^{2+} and Eu^{3+} but also Eu^{4+}, not Eu^{5+}, therefore the sum of Eu^{2+} and Eu^{3+} is not completely equivalent to the *total* ion yield, but the intensity of Eu^{4+} is relatively small. As seen in figure 3, differing from the cases of Xe^+ and Ba^+, the spectral profile and peak positions look very similar to those observed in neutral Eu photoionization, despite the existence of the initial ionic charge. From the aspect of the 'orbital collapse' picture, this implies that the change of one charge state does not affect the effective potential so much, and hence there is no further collapse of the orbital. This is almost the same as the observed similarity between atomic and metallic Eu reported by Mansfield and Connerade (1976). They concluded that their result strongly supported the assumption that in lanthanide metals the $4d \rightarrow 4f$ transitions occur deep inside the doubly or triply 'ionized' cores, i.e. Eu^{2+} for Eu metal, which are screened from the electrons of the conduction band. Since the 4f orbital in neutral Eu is considered to be moderately collapsed already and localized deep inside the inner well at such a high atomic number

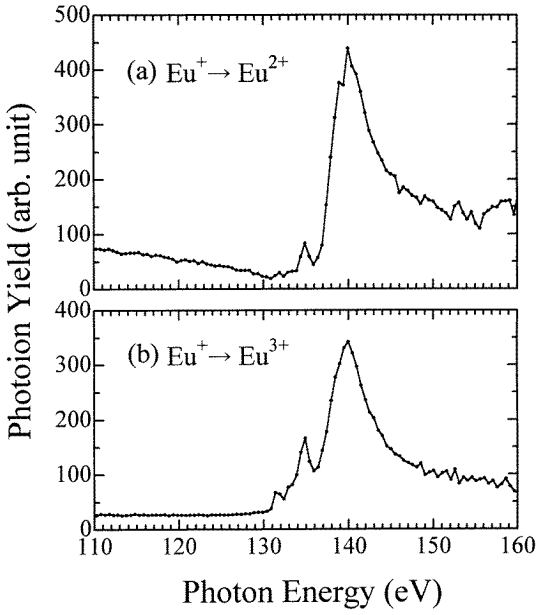

Figure 1. The relative photoion yield spectra of (*a*) Eu^{2+} and (*b*) Eu^{3+} obtained from a Eu^{+} target with an energy resolution of $E/\Delta E \simeq 130$. Both (*a*) and (*b*) are on the same scale.

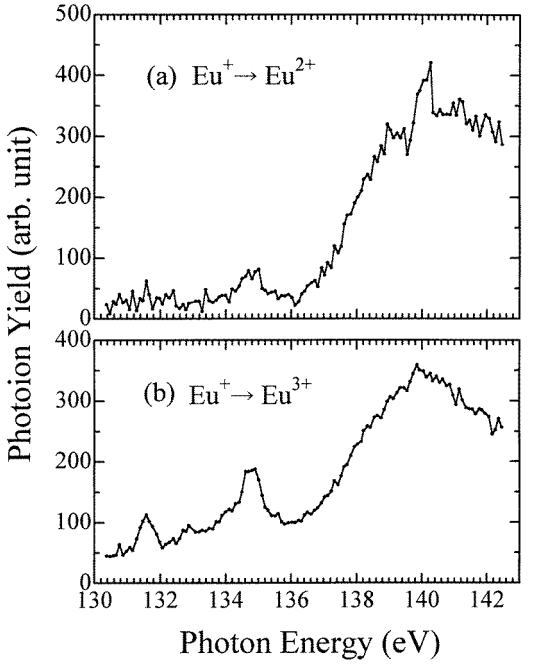

Figure 2. The measured relative photoion yield spectra of (*a*) Eu^{2+} and (*b*) Eu^{3+} from a Eu^{+} target with an energy resolution of $E/\Delta E \simeq 350$. The vertical scale is common to both (*a*) and (*b*).

$Z = 63$, this assumption seems valid even for Eu^{+} by substituting the outer 6s electrons for the band electrons. Namely, the $4d \rightarrow (4, \varepsilon)f$ transitions and subsequent decay processes take place deep inside the Eu atom, therefore are not affected so much by removal of one electron from the outer 6s orbital.

Finally, it is worth noting that the summit of the broad peak for the singly ionized product (Eu^{2+}) seems split (clearly seen in figure 2). This is *not* observed for a neutral Eu

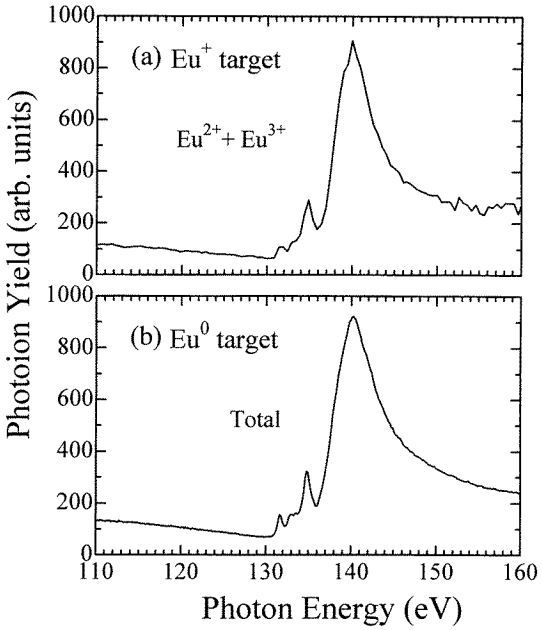

Figure 3. Comparison of photoion yield spectra from Eu^{+} and neutral Eu. (*a*) The sum of the Eu^{2+} and Eu^{3+} yield from a Eu^{+} target. (*b*) Total photoion yield from neutral Eu (Nagata *et al* 1990). The vertical scales are not normalized in the same way.

target (Nagata *et al* 1990), and considered as possible evidence for further collapse caused by removal of one 6s electron, though the total profile is not obviously changed.

4. Summary

Photoion yield spectra for a Eu^{+} target were measured in the energy range 110–160 eV. In the partial photoion yields of both Eu^{2+} and Eu^{3+}, a broad 'giant resonance' profile was observed at 140 eV with some preceding small peaks at 131.5, 132.8 and 134.7 eV. The spectra look very similar to those from a neutral Eu target. This implies that in Eu the contribution of 6s electrons to the $4d \rightarrow (4, \varepsilon)f$ 'giant resonance' is very small. However, a split was observed in the peak of the 'giant resonance' of the Eu^{2+} spectra. This was not observed in the neutral Eu case and considered as modest evidence of partial collapse of the f orbital due to the change of charge state.

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