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Valence band of metal europium studied with synchrotron radiation photoemission spectroscopy

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Abstract

We have measured the photoemission spectra of Eu film prepared in an ultra-high vacuum chamber within the photon energy range from 21.2 to 177.7 eV. The 4f core level is located at ~ 2.1 eV below the Fermi level with some fine structures. The occupied part of the 5d6s valence band distributes between the Fermi level and ~ 6.5 eV binding energy. The 5d state extends from the Fermi level to the bottom of the valence band, while the 6s state has its maximum of the density of states at ~ 5.2 eV. The 5p–5d resonance has significant effects on the spectral lines acquired with photon energies lower than ~ 30 eV. The 5d photoemission is enhanced and accompanied by Auger emission around the threshold of the 5p–5d resonance.

1. Introduction

The 5d, 6s and 4f states are the foundation of understanding various physical properties of rare-earth (RE) metals and their compounds. Photoemission spectroscopy (PES) is the principal method to measure directly the electronic structure, and a large amount of PES data have been reported for RE metals in the literature. The localized 4f level can be easily observed and studied with the PES technique, while it is rather intricate to study the valence band of RE metals. There has been a general consensus that the strongly mixed 5d and 6s states constitute the valence band and the 5d state distributes at the Fermi level [1–7]. However, the density of states of the 6s state has not yet been clearly observed and thoroughly understood. Since 6s is the outermost shell of RE metals, the precise knowledge of its energy distribution is of great importance in understanding the bonding, the charge transfer, and the 4f-valence band interaction in RE metals and their compounds.

We selected Eu to study the valence band because Eu exhibits the simplest and narrowest 4f photoemission among RE metals [1, 4, 8]. Eu is one of the two divalent RE metals (the

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other is Yb), and there is no trivalent 4f photoemission superimposing on the valence band as is usually observed in trivalent or mixed valent RE metals. Moreover, the divalent 4f state of Eu ($^8S_{1/2}$) has no spin-orbit splitting, in contrast to the case of Yb. Therefore Eu is the most appropriate RE metal for studying the valence band. In this paper, we report the valence band and 4f level photoemission spectra of metal Eu film acquired with photon energies from 21.2 to 177.7 eV. The photon energies cover the characteristic energies of the 4d–4f resonance (around 140 eV), the 5p–5d resonance (lower than ~ 30 eV) and the maximum of the 4f photoionization cross section (~ 95 eV). The present work, together with the re-examination of Eu 4d [9] and 3d [10] photoemission and some recent band calculations [11, 12], constitutes the current status of the knowledge about the electronic structure of metal Eu.

2. Experimental details

Sample preparation and measurements were performed in the Surface Science Station of the National Synchrotron Radiation Laboratory of China (NSRL), where the radiation energy ranges from 15 to 190 eV. Al $K\alpha$ and Mg $K\alpha$ sources are also equipped as supplements. The base pressure was 8×10^{-11} mbar. An angle-resolved energy analyser was used to record the photoelectrons at normal emission. The total energy resolution is ~ 0.1 eV, with the incident photon energies around 21.0 eV. The resolution gets slightly worse with higher photon energies. The spectra reported here were measured with photon energy ranging from 21.2 to 177.7 eV, with increments of 2 eV (below the photon energy of 50 eV and around the 4d–4f resonant photoemission) or 5 eV.

Thoroughly degassed Eu was sublimated from a ceramic crucible onto a Si:H(111) substrate. The high-purity Eu (99.99%) was purchased from Beijing Research Institute for Nonferrous Metals. The substrate was transferred into the preparation chamber immediately after HF acid etching and subjected to an annealing at 300 °C for 1 h.

We first prepared a Eu film with a thickness of ~ 200 Å for synchrotron radiation PES (SR-PES) measurements. The thickness was estimated according to the x-ray photoemission (XPS, Mg $K\alpha$ source) signals of Si 2p and Eu 3d and the inelastic-scattering-mean-free-path (IMFP) data [13]. No O 1s signal was detected in the XPS measurements, which ensured the cleanness of the sample surface. Several hours later (about the mid-time of the total experimental procedure), we deposited ~ 100 Å more Eu onto the sample to keep the sample fresh, though we did not find any O 1s signal at that time. After the accomplishment of the SR-PES measurements, we checked the sample again with the XPS measurement and did not observe any O 1s signal.

3. Results and discussion

Figure 1 exhibits some selected photoemission spectra of Eu film between the Fermi level and 10.5 eV binding energy. There are three main features in each line, located at the Fermi level, at 2.10 eV and at 5.15 eV, respectively. The spectra in figure 1 were normalized to the height of the peak at 2.10 eV (4f photoemission), and the incident photon energies are indicated next to the lines.

Figure 2 presents the detailed spectral evolution near the 4d–4f resonance with the photon energy increment of 2 eV for most lines. The spectral lines were normalized to the incident photon fluxes and thus represent the actual intensity variations. The most intensive 4f photoemission was observed at the photon energy of 140.9 eV, which coincides with the main giant resonance occurring around 140 eV [8]. The 4f photoemission comprises some fine structures that were first observed at low temperature on Eu(110) by Weschke *et al* [6]. The

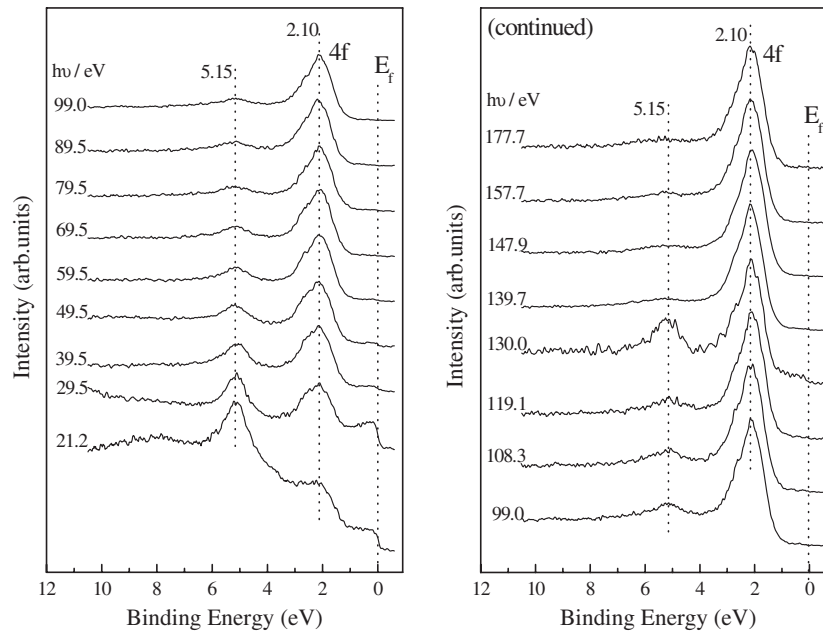


Figure 1. Synchrotron radiation photoemission spectra of Eu film within the photon energy range from 21.2 to 177.7 eV. The spectral lines were normalized to the heights of the 4f peak.

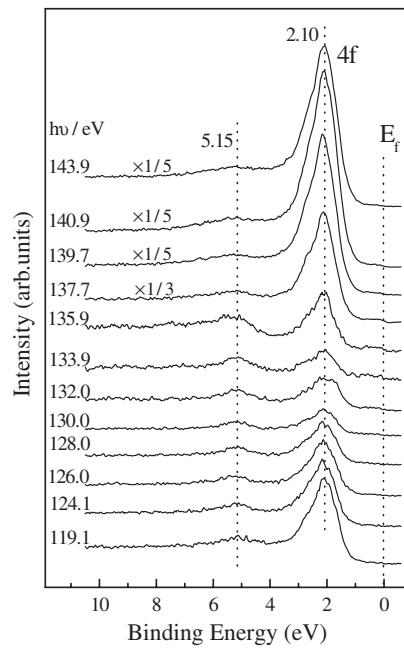


Figure 2. Spectra evolution around the 4d–4f resonance. The spectral lines were normalized to the incident photon flux.

subpeak at higher binding energy (than 2.10 eV) is the surface component, and the remaining subpeaks are due to the $4f^6$ final-state multiplet [6].

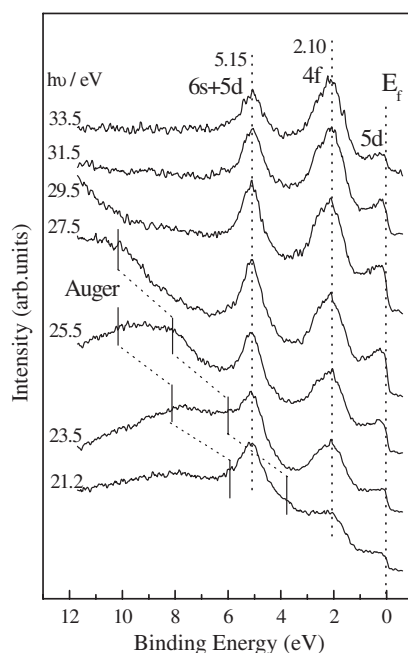


Figure 3. Spectra evolution within the photon energy range from 21.2 eV to 33.5 eV. The spectral lines were normalized to the incident photon flux. The short vertical lines represent the Auger emission as the decay channel of the 5p–5d resonance.

The 4f photoemission superimposes on the valence band of RE metals, which is the reason why the valence band has not been thoroughly understood in PES researches. However, divalent Eu has the simplest 4f photoemission spectrum among RE metals, as mentioned in section 1. Therefore we can for the first time observe the bottom of the valence band of Eu in figure 1. The occupied part of the valence band has a width of ~ 6.5 eV, with two dominant features. One of the features is located at the Fermi level. The other is the peak at 5.15 eV. The spectral weight of the valence band between the two features is concealed by the 4f photoemission and cannot be resolved.

To study the valence band in detail, we exhibit in figure 3 the spectral evolution below the incident photon energy of 34 eV with the increment of 2.0 eV, since the photoionization cross section of the 5d6s states is larger at lower photon energies [14]. The spectral lines were normalized to the photon fluxes. To the best of our knowledge, there are no photoemission data for Eu in the literature with incident photon energy as low as that in figure 3. This might be because Eu is very easily oxidized. The photoionization cross section of O 2p is rather large within the photon energy range of figure 3 [14], and even a slight oxidation would preclude the reliable information of the valence band. In this work, we can be sure that the PES data are free from oxidation for two reasons. First, the XPS measurements did not find any O 1s signal. Second, there is no trivalent (oxidized) 4f signal, which is located at 7 eV binding energy [7, 15–17], if it exists. Therefore the spectra are intrinsic to divalent Eu.

The spectral lines acquired with photon energies lower than 30 eV are especially complicated. It seems that additional spectral features superimpose on the 4f and the valence band photoemission. A close inspection of the spectra can find that the additional features (indicated with short vertical lines in figure 3) have constant kinetic energies. So we ascribe them to Auger emission as a decay channel of 5p–5d resonance.

The Eu 5p doublet is located at ~ 18.5 eV ($5p_{3/2}$) and ~ 24.5 eV ($5p_{5/2}$) [7]. The 5p–5d resonant photoemission not only presents the accompanying Auger emission but also surely enhances the 5d photoemission. Thus we observe the remarkably intense valence band photoemission in figure 3. The spectral features of the valence band have their highest intensities at the photon energy of 27.5 eV, and then decrease monotonically with higher photon energies. The simultaneously enhanced intensities of the features at the Fermi level and at 5.15 eV indicate that the occupied 5d state extends from the Fermi level to the bottom of the valence band. However, the spectral weight at the Fermi level decreases more rapidly than that at 5.15 eV with higher photon energies (figure 1). Therefore the feature at 5.15 eV has other origination, besides the contribution from the 5d state.

We suggest that the feature at 5.15 eV is mainly the 6s state, based on the following reasons. First, this feature cannot be the shake-up of the 4f photoemission. If the feature is the shake-up, the spectral intensity should vary in proportion to that of the 4f main peak. However, figure 1 does not show this relationship. On the contrary, the stronger 4f photoemission is accompanied with a weaker feature at 5.15 eV (figure 2). Second, the spectral lines acquired with photon energies from 132.0 to 135.9 eV (figure 2) exhibit relatively strong intensities of the feature at 5.15 eV. This observation coincides with the result [8] that the valence band autoionization process is strong with photon energies near but lower than the threshold of the 4d–4f resonance, which implies that the feature at 5.15 eV is part of the valence band. Last, the binding energy of the feature at 5.15 eV coincides with theoretical results that the 6s state is distributed at the lower part of the valence band [11, 12]. However, the hybridization between the 5d and 6s states was underestimated in band calculations that predicted that the 5d state is distributed only at the top of the occupied part of the valence band [12]. The SR-PES measurements in the present work reveal that the 5d state extends from the Fermi level to the bottom of the valence band, as discussed above.

4. Conclusions

The occupied part of the valence band of metal Eu has a width of ~ 6.5 eV. The 5d state has its highest density of states at the Fermi level and extends to the bottom of the valence band. The 6s state is distributed at the lower part of the valence band with the highest density of states at 5.15 eV. The facts that the 5d state, which was considered to be located at the top of the occupied part of the valence band, extends to the bottom of the valence band and that the outermost shell (6s) has a binding energy far below the Fermi level should help in understanding various properties of Eu and its compounds. The Auger decay of the 5p–5d resonance has significant effects on the spectral lines recorded with photon energies lower than ~ 30 eV. The PES data of metal Eu in a wide photon energy range (21.2–177.7.0 eV) reported in this work can also be a good reference for the PES studies of Eu compounds.

Acknowledgments

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