Chemical Shifts in Europium Studied by ESCA

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(30. IV. 68)

Abstract. Electron spectroscopic measurements have been performed on the $4\,s$, $4\,p$, $4\,d$ and $4\,f$ levels of Eu. Shifts in binding energies of about 7 eV are reported between Eu in Eu_2O_3 and Eu in a lower valence state. The $4\,f$ level is shifted less than the $4\,p$ and $4\,d$ levels.

Introduction

Professor BUSCH and associates at the Laboratory for Solid State Physics at ETH, Zürich, have carried out a large number of investigations on rare earth compounds. The physical properties of these compounds have been studied by use of different techniques and a wealth of data has been published. For example, the magnetic and magneto-optic properties of the semiconducting europium chalcogenides have been the subject of several studies [1, 2, 3]. One piece of information that is relevant to such studies is the energy level schemes of the elements in the compounds, particularly the outermost levels which constitute the energy bands of the solid. It has been shown, both by X-ray and electron spectroscopy, that not only the outer levels, but also the core electron energies, depend on the chemical state of the element. We shall illustrate this in the present paper by some electron spectroscopic measurements on europium in different valence states.

Experimental Procedure

By the ESCA-method the electron binding energies of an element are determined through an energy (or momentum) analysis of electrons expelled by characteristic X-radiation [4]. In the present investigation the electrons were expelled by aluminium $K\alpha$-radiation and analysed in a 50 cm ironfree spectrometer [5]. Detection was performed by five channel electron multipliers placed close to each other in the focal plane of the spectrometer. The momentum separation between adjacent detectors was 0.2% and the entrance to each detector was defined by a slit, 0.4×9 mm². Each detector was connected to a preamplifier and a scaler, thus forming a separate counting system. Because of this multidetector arrangement the amount of information obtained per unit time was increased considerably as compared with single channel detection.

Measurements were performed on europium in different states of oxidation. Most of the specimens used for studies of Eu in Eu_2O_3 were produced by evaporating Eu_2O_3 onto thin aluminium backings or by pressing Eu_2O_3 powder into a copper mesh.

Eu_2O_3 spectra were also obtained from metallic Eu, due to the rapid oxidation of the surface.

For studies of europium in a lower valence state, a metallic Eu specimen was used. It was carefully polished before each measurement so that a clean, shining surface was obtained. The polishing was first performed in an inert gas atmosphere, but it was later found that the lines corresponding to the lower valence state could be studied even if the polishing was carried out in air at atmospheric pressure. Electron lines from europium in the lower valence state were also found in specimens obtained by evaporation of Eu metal onto thin aluminium backings, which were placed in the spectrometer vacuum chamber immediately after the evaporation.
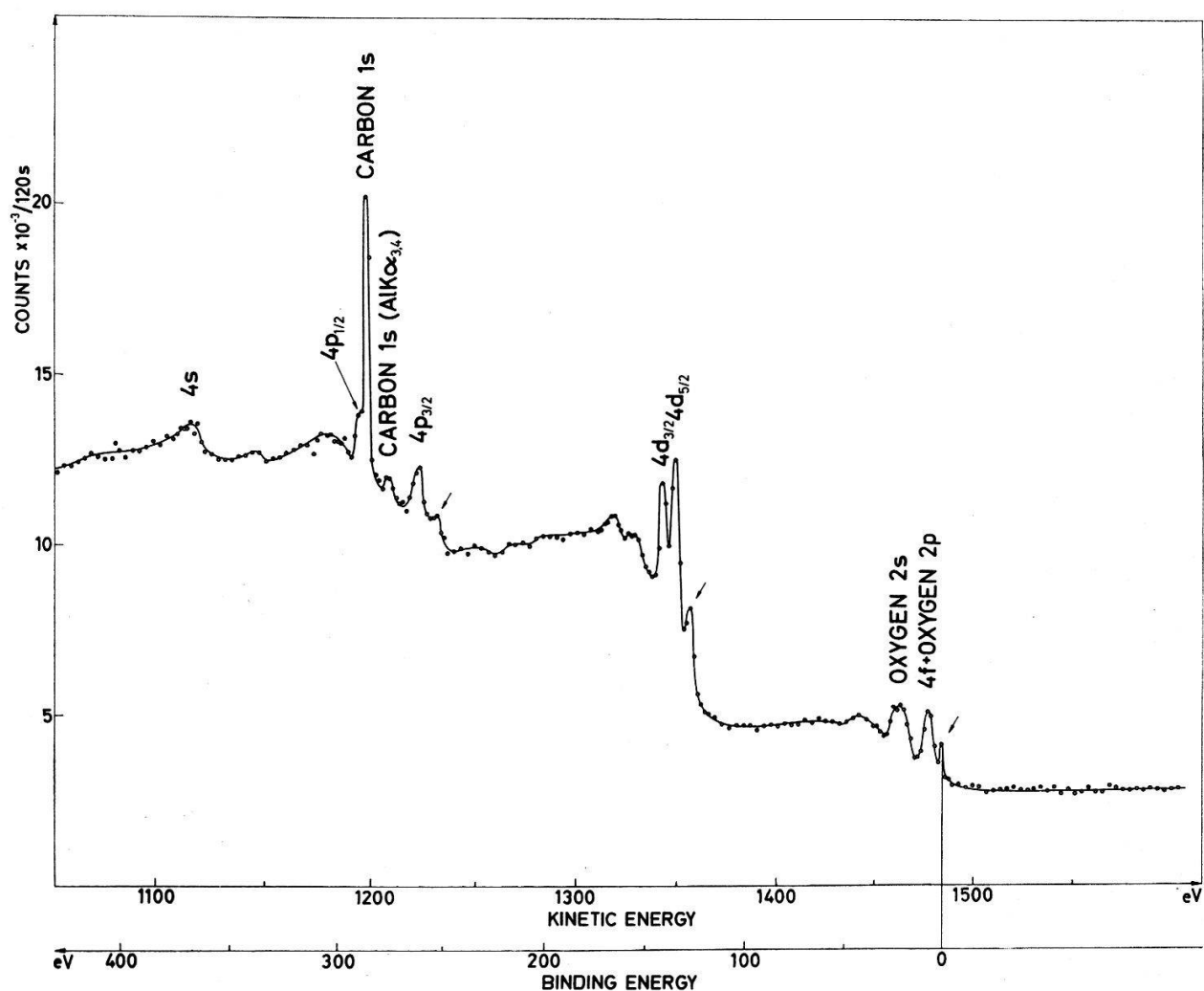
Figure 1

Electron spectrum of europium excited by Al Kα-radiation.
The spectrum was obtained from a polished Eu metal specimen. The lines with the notations $4s$ $4p_{1/2}$, $4p_{3/2}$, $4d_{3/2}$, $4d_{5/2}$ and $4f$ originate from levels of Eu in Eu_2O_3 while the lines marked with arrows originate from Eu in a lower valence state. All measured points are not shown.

Electrons expelled from the $1s$ level of carbon were used for calibration of the electron spectra. This carbon line appears in the spectra because of a small accumulation of pump oil on the specimens and it is convenient for use as a calibration line [4].

Experimental Results and Discussion

An electron spectrum from a polished metal specimen is shown in Figure 1. It shows electron lines from the 4 s, 4 p, 4 d and 4 f levels of europium and also electron lines from carbon and oxygen. An electron spectrum from an evaporated Eu_2O_3 specimen recorded in the same energy region gave similar structures with the important exception that the lines marked with arrows in Figure 1 did not appear.

Figure 2

Electron lines from the 4 d levels of europium. The spectra (a), (b), (c) and (d) were obtained from an Eu metal specimen.

(a) Shortly after polishing. (b) After exposure to a pressure of 10^{-5} torr for 20 hours. (c) After exposure to air at atmospheric pressure for 10 hours. (d) Immediately after repolishing. The spectrum (e) was obtained from an evaporated Eu_2O_3 specimen. In all recordings the 4 $d_{3/2}$ and 4 $d_{5/2}$ lines of Eu in Eu_2O_3 are seen. Spectra (a), (b) and (d) also show the 4 $d_{5/2}$ line of Eu in the lower valence state.

The regions where the extra peaks were found were studied in detail with special attention to the time variation of the line intensities. The results are illustrated in Figures 2 and 3. Figure 2 shows the $4 d_{3/2}$ and $4 d_{5/2}$ lines. Spectrum (a) was recorded shortly after polishing the metal piece and the same energy region recorded after 20 hours' exposure to vacuum chamber pressure (10^{-5} torr) is shown in (b). The specimen was then exposed to air at atmospheric pressure for 10 hours and the spectrum was recorded again (c). The decrease (b) and disappearance (c) of the extra line are clearly seen in the figure. After spectrum (c) had been recorded, the metal piece was polished again and spectrum (d) was recorded. The extra line was found
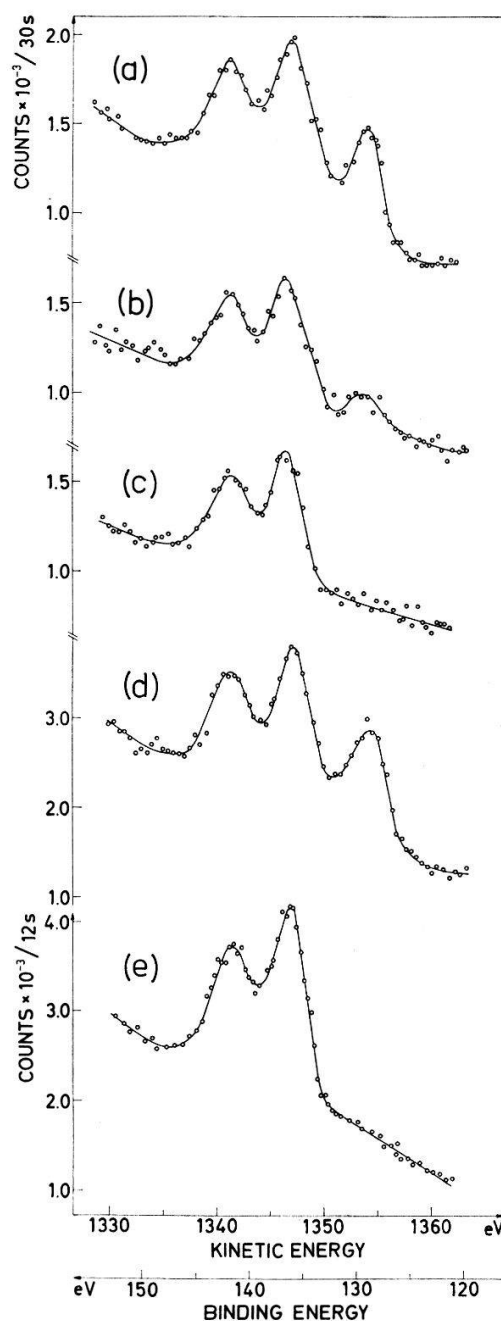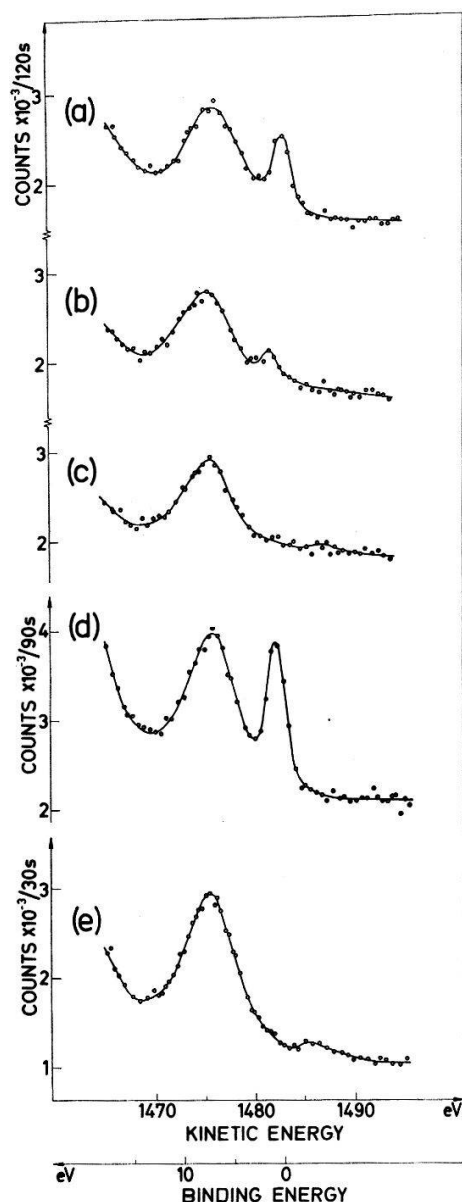

Figure 3

Electron lines from the $4 f$ level of Eu. The spectra (a), (b), (c) and (d) were recorded with an Eu metal specimen.
(a) Shortly after polishing. (b) After exposure to a pressure of 10^{-5} torr for 18 hours. (c) After exposure to air at atmospheric pressure for 10 hours. (d) Immediately after repolishing. The spectrum (e) was obtained from an evaporated Eu_2O_3 specimen. In all recordings the $4 f$ line of Eu in Eu_2O_3 are seen. Spectra (a), (b) and (d) also show the $4 f$ line of Eu in the lower valence state.

again. Besides the spectra (a), (b) and (c) in Figure 2 several other recordings were made at intermediate times and these recordings confirmed the gradual decrease in intensity of the extra line. For comparison, a spectrum in the same energy region from an Eu_2O_3 specimen is shown in Figure 2 (e). Figure 3 shows a similar sequence of recordings for the $4f$ electron line of europium.

The intensities of the lines marked with arrows in Figure 1 all showed the same time-dependence during the measurements and these lines are interpreted as emanating from europium in the same valence state. Both EuO and Eu metal seem to be a possible origin of the extra lines (see below). The more intense europium lines are due to Eu_2O_3. No extra lines can be seen in Figure 1 close to the $4s$ and $4p_{1/2}$ lines. In the latter case this is due to the overlapping of the intense carbon line $1s$ and in the $4s$ case the line is too broad to reveal a structure on the high energy side.

In the recordings shown in Figures 2 and 3 it is easy to identify the lines which emanate from europium in Eu_2O_3 but it is more doubtful to which state of oxidation the lines with the highest kinetic energy in these spectra should be attributed. The electron configuration of the neutral europium atom is $\ldots 4f^7 5s^2 5p^6 6s^2$ and the valence band is probably formed by electrons with f and s symmetries. At the photon energy used in this investigation (1.5 keV), the outer s electrons generally have a comparatively low photoelectric cross-section and neither the $5s$ electrons (binding energy 39 eV [6]) nor the $6s$ electrons give rise to a marked peak in the electron spectra. Since the s part of the valence band is not seen in our recordings, it is not possible to make a definite determination of the energy difference between the valence band and the Fermi level (zero binding energy). If, however, the $4f$ electrons are the outermost electrons, the upper limit of the valence band is defined by the high energy side of the $4f$ line. After estimated corrections for instrumental broadening and inherent width of the X-radiation, the energy difference between the Fermi level and the high energy side of the line with the highest kinetic energy in Figure 3 is found to be ~ 0.5 eV. Then, assuming the Fermi level to be situated halfway between the valence and conduction bands, a gap width of about 1 eV is obtained for the compound which is the origin of the extra lines. It has earlier been found that the compound EuO is a semiconductor at room temperature and by absorption measurements BUSCH et al. [1] have determined the gap width to be 1.115 eV at room temperature. Thus it might seem natural to interpret the extra lines as emanating from europium in EuO.

Table 1

Electron binding energies of europium

Atomic level	Number of recordings	Electron binding energy (eV) Present (Eu_2O_3)	BEARDEN and BURR [6]
$4s$	9	366.3 ± 0.8	360.2 ± 0.7
$4p_{1/2}$	20	289.1 ± 0.7	283.9 ± 1.0
$4p_{3/2}$	20	260.7 ± 0.6	256.6 ± 0.8
$4d_{3/2}$	25	141.4 ± 0.6	133.2 ± 0.6
$4d_{5/2}$	25	135.7 ± 0.6	
$4f$	19	7.3 ± 0.7	0.0 ± 3.2

On the other hand it is possible that the $4f$ line reflects the lower part of the valence band only and that the $6s$ electrons fill the valence band up to the Fermi level. (Compare Ag in Chapter IV of Reference [4].) The extra lines would then originate from Eu metal.

The binding energies of the europium $4s$, $4p$, $4d$ and $4f$ levels in Eu_2O_3 are given in Table 1. The energies were calculated using a weighted energy value for the $AlK\alpha_{1,2}$ line of 1486.56 eV [7]. The $B\varrho$-value used for the calibration line C $1s(AlK\alpha_{1,2})$ was 116.769 ± 0.020 G cm [8]. The errors given are twice the standard deviation of the mean, to which the error for the calibration line and the error for the work function of the vacuum chamber material [8] have been quadratically added. The value obtained for the binding energy of the $4f$ electrons in Eu_2O_3 might be influenced by the presence of the oxygen $2p$ line.

Table 1 also gives the electron binding energies for Eu according to the tabulation by BEARDEN and BURR [6]. The energies of the outer levels in the rare earth elements have not previously been measured by the ESCA method and in the tabulation by BEARDEN and BURR the M, N and O levels have been calculated using X-ray emission data together with the L binding energies measured by electron spectroscopy. The accuracy is not very high, for example the $4d_{3/2}$ and $4d_{5/2}$ levels are not separated in the tabulation [6], although the spin-doublet splitting amounts to several eV (see Table 1). The binding energies for Eu in Eu_2O_3 obtained in the present investigation deviate significantly from the tabulated values [6].

The shifts in binding energy between the lines marked with arrows in Figure 1 and the lines corresponding to Eu_2O_3 are given in Table 2. If these shifts are taken into account, the binding energies for Eu in the lower valence state can be calculated. The agreement between these binding energies and the values given by BEARDEN and BURR is better, but significant discrepancies remain.

Table 2

Differences in binding energies obtained with the use of Eu_2O_3 specimen and Eu metal specimen.

Atomic level	Difference (eV)
$4p_{3/2}$	7.8 ± 0.2
$4d_{5/2}$	7.5 ± 0.2
$4f$	6.4 ± 0.1

The atomic levels of Eu are shifted by ~ 7 eV towards higher binding energies when going from the lower valence state to Eu_2O_3 (see Table 2). A shift towards higher binding energies upon oxidation is expected due to the higher electronegativity of oxygen as discussed in Chapter V of Reference [4]. In Figure 2 only three lines are seen in spectra (a), (b) and (c) which means that the $4d_{3/2}$ line of Eu in the lower valence state and the $4d_{5/2}$ line of Eu in Eu_2O_3 must overlap. The spectra in Figure 2 show that the chemical shift of the $4d$ level is even larger than the spin-doublet splitting of the same level.

Chemical shifts of Eu have previously been studied by FADLEY et al. [9]. The levels studied were $3\,d_{3/2}$, $3\,d_{5/2}$ and $4\,p_{3/2}$. For the $4\,p_{3/2}$ level a shift in binding energy between Eu in Eu_2O_3 and $EuAl_2$ amounting to 9.2 eV was reported. The same shift within experimental errors ($\pm$ 0.5 eV) was reported for a measurement on Eu in Eu_2O_3 and EuO. In the present investigation a shift of (7.8 $\pm$ 0.2) eV is reported for this level. The discrepancy may be explained by the difficulties in measuring shifts at higher kinetic energies of the photoelectrons as was the case in the experiment by FADLEY et al.

As long as the valence electrons do not penetrate into the atomic core, one would expect the same shift in electron binding energy for all core electrons. However, if there is a penetration of valence electrons into the core, different shifts for different core electrons are expected [4]. The smallest shift would be found for the valence electrons themselves. As seen in Table 2 the $4\,f$ electrons are shifted about 1 eV less than the $4\,p$ and $4\,d$ electrons, and the observed shifts are thus in agreement with the prediction.

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On the Problem
of Tabular Reduction of Crystal Chemical Information:
Metals and Semiconductors

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Abstract. Difficulties are emphasized of bearing in mind the great amount of crystal chemical information now existing, and using it in order to select materials most likely to provide desired electrical, magnetic or other physical properties. Regarding structures as formed by the stacking of layer networks of atoms, a tabular reduction of structural information on atomic arrangement