

### 3d core-level x-ray photoelectron spectroscopy of $\text{EuCu}_2\text{Si}_2$ , a mixed-valence system

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3d core-level x-ray photoelectron spectrum (XPS) of Eu in  $\text{EuCu}_2\text{Si}_2$  exhibits two sets of *simple* spin-orbit split structures. We have assigned these structures to two different valence states of Eu ( $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ ) in  $\text{EuCu}_2\text{Si}_2$ . The relative intensities of 2+ and 3+ peaks are strong functions of temperature. XPS in the 3d region of Eu has been employed for the first time to study the phenomenon of valence fluctuation. The relative advantage of 3d core-level spectroscopy of Eu over 4d and 4f spectral studies is brought out.

The compound  $\text{EuCu}_2\text{Si}_2$ , crystallizing in the  $\text{ThCr}_2\text{Si}_2$ -type tetragonal structure,<sup>1</sup> has attracted considerable attention in recent years because of some unusual properties of this system. The Mössbauer isomer shift lies in between the values expected for  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  systems and it is found to be strongly temperature dependent.<sup>2</sup> This system does not order magnetically at low temperatures.<sup>3</sup> These features have been interpreted in terms of fast fluctuations ( $\approx 10^{12} \text{ sec}^{-1}$ ) of Eu ions between the two different valence states (2+ and 3+). This phenomenon which is known as "valence fluctuation," "mixed-valence" or "interconfiguration fluctuation," is exhibited by some other rare-earth (Ce, Sm, Tm, and Yb) systems also.<sup>4</sup>

$\text{EuCu}_2\text{Si}_2$  has been further investigated by a number of other techniques like NMR,<sup>5</sup> resistivity,<sup>3</sup> thermoelectric power,<sup>3</sup> specific heat,<sup>3</sup> x-ray absorption,<sup>6</sup> etc. X-ray photoelectron spectroscopy (XPS) has also been widely used to understand this phenomenon in rare earths.<sup>7</sup> In this technique, one normally measures 4f-level spectra and two sets of 4f multiplet structures corresponding to two different valence states of the rare-earth ion are observed. However, the 4f-level spectra of Eu in  $\text{EuCu}_2\text{Si}_2$  get complicated due to the interference from Cu(3d) spectrum, as the photoelectric cross section of Cu(3d) and Eu(4f) signals are comparable,  $\sigma(\text{Cu } 3d^{10})/\sigma(\text{Eu } 4f^7) \approx 0.5$ . Hence the analysis of 4f spectra in  $\text{EuCu}_2\text{Si}_2$  is not simple and straightforward.<sup>8</sup> Under such circumstances, the 3d or 4d core-level study is very useful in understanding the phenomenon of valence fluctuation. The structure corresponding to  $f^n$  configuration is replicated at the higher-binding-energy side for  $f^{n-1}$  configuration, as the effective nuclear charge increases for the  $f^{n-1}$  case.<sup>9</sup> In recent years, core-level XPS spectra have been effectively employed in understanding the

mixed-valence character of Ce, Sm, and Yb systems.<sup>10-12</sup> In fact, the 4d core-level spectral studies were used for the first time to establish the presence of Eu ions in the fluctuating-valence state in the  $\text{EuPt}_{2-x}\text{Rh}_x$  (Ref. 13) system. However, the 4d spectrum has a complex structure due to multiplet splitting. Thus 4d core-level studies are also not simple in the case of Eu systems. In this paper, we report, for the first time, the XPS studies in the 3d region of Eu in a mixed-valence system, viz.,  $\text{EuCu}_2\text{Si}_2$ , thereby establishing the importance of 3d core-level spectroscopic studies in studying Eu-based mixed-valence systems.

The sample was prepared by arc-melting constituent elements in the proper proportions. X-ray diffraction analysis showed that the sample was single phase. 3d core-level photoelectron spectra of Eu in  $\text{EuCu}_2\text{Si}_2$  were measured using Vacuum Generators ESCA 2 (II) machine, with Al  $K\alpha$  and Mg  $K\alpha$  as excitation sources. The sample was mounted on to the tip of a sample probe and it was then cleaned by ion etching for an hour. The intensities of C(1s) and O(1s) peaks monitored after ion etching were insignificant. The vacuum in the analyzer chamber was maintained at  $\sim 10^{-10}$  torr.

Figure 1 shows the 3d spectra of Eu in  $\text{EuCu}_2\text{Si}_2$  (recorded with Al  $K\alpha$  radiation) at three different temperatures: 77, 300, and 750 K. At each of these temperatures, two sets of structures corresponding to two different valence states of Eu ions have been observed. Each of these sets exhibits *simple* spin-orbit doublet assigned to  $3d_{5/2}$  and  $3d_{3/2}$ . The spin-orbit splitting is found to be  $\sim 30$  eV. The weighted average of 3d binding energies for  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  in  $\text{EuCu}_2\text{Si}_2$  as obtained from the spectra are  $\sim 1138$  and  $\sim 1148$  eV, respectively. These values are in good agreement with those estimated theoretically by Herbst and Wilkins.<sup>9</sup> Incidentally, the value of the

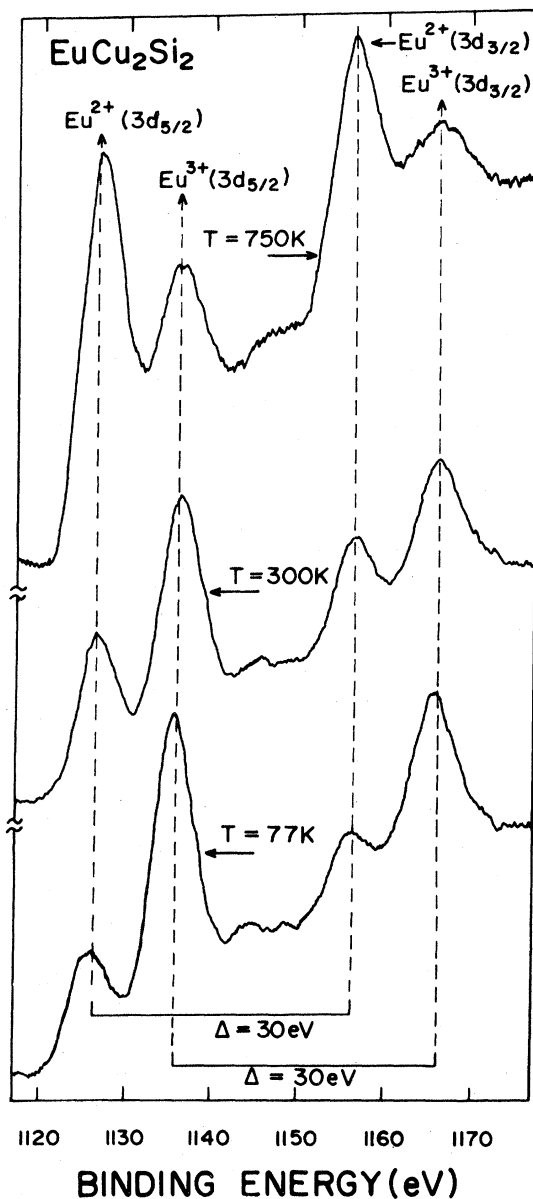


FIG. 1.  $3d$  core-level spectra of the Eu ion in  $\text{EuCu}_2\text{Si}_2$  at 77, 300, and 750 K;  $\Delta$  represents spin-orbit splitting. It is evident that the relative intensities of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  peaks are strong functions of temperature.

spin-orbit splitting of  $3d$  core level of Eu in  $\text{EuCu}_2\text{Si}_2$  is also in agreement with that reported by Siegbahn *et al.*<sup>14</sup> in Eu. It is apparent from the spectra that the relative intensities of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  peaks are strong functions of temperature. The average valency was calculated by measuring the area under the peaks. The values of the average valency of Eu thus obtained are: 2.8 at 77 K,  $\sim 2.6$  at 300 K, and  $\sim 2.2$  at 750 K, which are in good agreement with those obtained from other measurements such as NMR,<sup>5</sup> Mössbauer,<sup>2</sup> and susceptibility.<sup>3</sup>

In the case of rare-earth metals other than Eu, the  $4f$  unoccupied level is pulled down below the Fermi level under the influence of the  $3d$  core hole resulting in an electron transfer from the conduction band to the unoccupied  $4f$  level.<sup>15</sup> This process results in a gain in energy giving rise to a shakedown satellite structure with smaller binding energy compared to the main line. It has been shown recently<sup>16</sup> that in Eu metal, in which Eu is in the divalent state, the unoccupied  $4f$  level is well above the Fermi energy even in the presence of the core hole and hence the electron transfer from the conduction band to an unoccupied  $4f$  level is not energetically favorable. However, this cannot be said for the Eu ion in a trivalent state. In this case, it is possible that shakedown satellite from the trivalent signal may transfer some intensity in the vicinity of the divalent signal. If this transferred intensity were significant, the average valency obtained in the present investigations would not be in agreement with that obtained from other techniques. In view of the good agreement that we get, we infer that the shakedown-satellite intensity from the trivalent signal is not very significant.

In conclusion, it may be stated that the  $3d$  core-level x-ray photoelectron spectroscopy has not been used so far for the study of the mixed-valence phenomenon in Eu systems and this is the first successful attempt in that direction. The  $3d$  spectral studies of the Eu ion are free from complexities arising from multiplet structures, which are usually troublesome in the analysis of  $4d$  spectra. These studies are particularly useful in those Eu systems where valence-band spectra interfere seriously with the  $4f$  spectra. We hope this work will motivate further XPS studies in the  $3d$  region of the europium ion to understand the phenomenon of valence fluctuation in Eu systems.

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