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ESCA studies of some mixed-valence rare-earth intermetallics

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Abstract. ESCA (or XPS) studies of some rare-earth intermetallics were carried out using ESCA (3) Mark II and 'ESCALAB' machines from V G Scientific. The mixed valence nature of $EuCu_2Si_2$ and $EuNi_2P_2$ intermetallic compounds has been established. The 3*d* core-level photoemission spectra of Eu in $EuCu_2Si_2$ and $EuNi_2P_2$ exhibit two sets of structures corresponding to two different valence states of the rare-earth ions. Each of these sets shows simple spin-orbit splitting. The replicate splitting measured by us agrees well with those calculated by Herbst and Wilkins. The 3*d* core-level photoemission spectra of Eu is free from the multiplet splitting and satellite structure. The importance of 3*d* core-level photoemission studies in the understanding of valence fluctuation phenomenon has been emphasized.

Keywords. Photoemission spectra; ESCA; XPS; rare earth intermetallics; valence fluctuation.

1. Introduction

Rare-earths include a group of lanthanides (La to Lu) with atomic numbers, $Z = 57$ to 71. The normal electron configuration of rare earths is represented by $[Xe]\ 4f^n5d^16s^2$ except for europium and ytterbium. The 4*f* shell prefers to be half-filled ($4f^7$) in europium while ytterbium metal has a tendency to retain the completely filled ($4f^{14}$) shell. The magnetic moment is determined by the number of 4*f* electrons in rare earths. The available reports on the crystal structures, melting points, phase changes, room temperature densities and the lattice parameter measurements in the rare earths indicate that europium and ytterbium are anomalous in their physical properties.

Rare-earths form a large number of compounds of different composition and crystal structure with metals and nonmetals (Wallace 1973). Rare-earth intermetallics offer a fascinating field for research due to their interesting structural and physical properties. Possible applications of rare-earth intermetallics for hydrogen storage, development of permanent magnets of outstanding quality and their use in computer

technology as memory elements have stimulated interest in the fundamental research on rare earths intermetallics.

Normally, rare-earth ions exist in tripositive state in rare earth compounds including intermetallics. However, in some rare earth compounds, the $4f$ levels and the $5d6s$ band coexist at the Fermi-level. Under these conditions it becomes energetically possible for the rare earth ion to fluctuate fast ($\sim 10^{-11}$ sec) between the two integral $4f^n$ and $4f^{n-1}$ states separated by very small energy difference. This phenomenon is known as 'valence fluctuation', 'mixed valence' or 'interconfiguration fluctuation (ICF)'. Valence instabilities occur in some rare earth compounds when the $4f$ level is moved to the Fermi level by the application of pressure or alloying. Such compounds show a variety of unique thermal and magnetic properties. Therefore, the understanding of valence fluctuation phenomenon is of considerable importance.

An indication of the mixed-valence is provided by the deviation of the lattice parameter from the usual lanthanide contraction. As an example take the case of $EuCu_2Si_2$ (Sampathkumaran *et al* 1979). Figure 1 shows that $EuCu_2Si_2$ is neither in tripositive state nor in the divalent state. Similar is the behaviour of Yb in $YbCu_2Si_2$. These compounds are therefore expected to be valence-fluctuating systems. Another distinguishing feature of these systems is the demagnetization of rare earth ions at low temperatures. Information on such valence fluctuating materials is obtained from magnetic susceptibility measurements. Measurement of Mössbauer isomer shifts is an unequivocal tool for the study of valence fluctuation phenomenon. If the time, Γ of transition between $4f^n$ and $4f^{n-1}$ configuration is larger compared to the life time of the excited state (10^{-8} sec) of the Mössbauer nucleus, there will be two Mössbauer lines. If on the other hand, Γ is smaller than 10^{-8} sec as is the case with ICF the two lines are pulled together to form a single broad line. Other techniques used for the study of ICF phenomenon are the NMR, X-ray absorption and X-ray photoelectron spectroscopy.

X-ray photoelectron spectroscopy (XPS) is a powerful technique for the study of mixed-valence compounds (Campagna *et al* 1979). The measuring time of XPS is $\sim 10^{-16}$ sec whereas the valence fluctuation phenomenon occurs on a time scale ($\sim 10^{-11}$ sec) much greater than the measuring time of XPS. It is expected that XPS should provide signatures of the two different configurations, $4f^n$ and $4f^{n-1}$ of

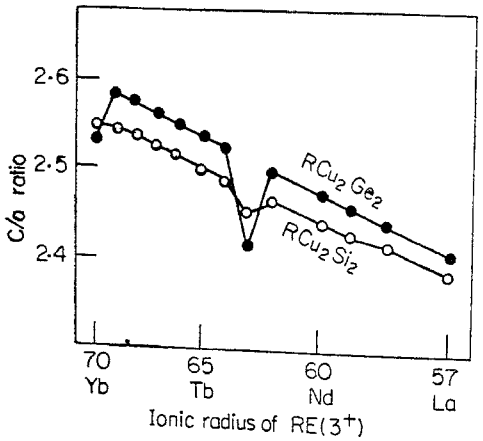

Figure 1. Plot of c/a ratio versus the rare earth ions.

the rare earth ion in a valence fluctuating compounds. This has indeed been observed in the 4*f* photoemission spectra of SmB_6 (Campagna *et al* 1976), $YbAl_3$ and $EuCu_2Si_2$ (Buschow *et al* 1977) and other systems (Campagna *et al* 1979). The photoionization of a $4f^n$ shell produces complex final state spectra with structure characteristic of the initial 4*f* state occupancy. Two distinct structures corresponding to two different 4*f* occupancy are recorded by XPS technique.

Besides 4*f*, the 3*d* and 4*d* core-level photoemission spectra can be used for the study of mixed-valence compounds. For rare earth ion with two different configuration $4f^n$ and $4f^{n-1}$ in the same compound, the 3*d* and 4*d* core level photoemission spectra are expected to exhibit two sets of structures (or replicate splittings) each corresponding to one of the 4*f* configuration (Herbst and Wilkins 1979). The average values of the 3*d* and 4*d* binding energies and the replicate splittings, ρ have been calculated for two valence states of the rare earth metals Ce, Sm, Eu, Tm and Yb which form valence fluctuating compounds. It is shown that the XPS results on 4*d* and 3*d* photoemission spectra of CeN agree well with the theoretical predictions (Herbst and Wilkins 1979) indicating that these core level XPS studies can be used effectively for the study of valence fluctuation phenomenon.

It is noted that the complex multiplet structure is always associated with the photoionization of a $4f^n$ shell. In those situations when the 4*f* multiplet structure of the rare earth ion interferes with the valence band spectra of the 3*d* metal ion (as an example take the case of $EuCu_2Si_2$), the analysis of the spectra becomes difficult. Further in the case of Ce intermetallics, XPS study of the 4*f* levels does not provide reliable information regarding the ICF phenomenon. In such cases 4*d* and 3*d* core-level studies are used. The photoemission spectra of 4d–core levels of SmB_6 (Chazalviel *et al* 1976), CeN (Baer and Zurcher 1977), Eu Pt_{2-x} Rh_x (Nowik *et al* 1977) and $CePd_3$ (Gupta *et al* 1980) have been employed in recent years to establish the mixed-valence nature of these compounds. However, 4*d* spectrum has complex structure due to multiplet splitting. We have, therefore, investigated the relatively simpler 3*d* core-level photoemission spectra of rare earth ions in $EuCu_2Si_2$ and $EuNi_2P_2$. The results of such studies are discussed here.

2. Experimental

The sample of $EuCu_2Si_2$ was prepared by arc melting constituent elements in proper proportions followed by vacuum annealing. $EuNi_2P_2$ was prepared by tin matrix method (Nagarajan *et al* 1981). The x-ray diffraction analysis showed single phase formation.

The 3*d* core-level photoemission spectra of Eu in $EuCu_2Si_2$ and $EuNi_2P_2$ were measured using V.G. ESCA (3) mark II machine with AlK_α as excitation source. The samples were mounted on to the tip of a sample probe and were then cleaned by ion-etching inside the sample preparation chamber. Ultra high vacuum $\sim 10^{-10}$ torr was maintained throughout the experiment. The samples were checked after ion etching and these showed no change in their structure and composition. The O(1s) and C(1s) peaks were monitored to ensure the cleanliness of the samples.

3. Results and Discussion

(*i*) 3*d* core-level XPS of $EuCu_2Si_2$

$EuCu_2Si_2$ has been studied using a number of techniques including XPS (Buschow *et al* 1977; Sampathkumaran *et al* 1979). Due to the interference of 3*d* spectrum

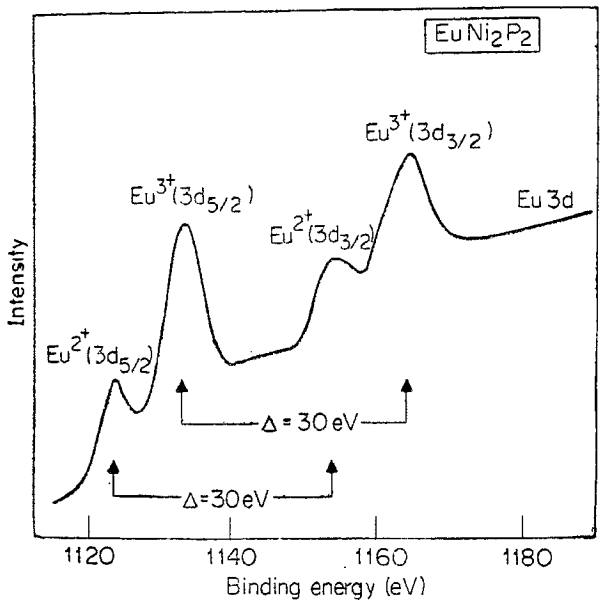

Figure 2. 3*d* XPS spectrum of Eu in $EuCu_2Si_2$.

of copper with the 4*f* multiplet structure of europium ion, the assignment of the photoemission peaks to different valence states is rather a difficult exercise (Buschow 1977). Further, the 4*d* spectrum of europium has complex multiplet structure. However, the 3*d* photoemission spectra of europium is simpler than the 4*f* and 4*d* photoemission spectra. It exhibits two sets of structure (figure 2), each of these sets consists of a simple spin-orbit doublet. The structure corresponding to $4f^7$ configuration is replicated at higher binding energy side of $4f^6$ configuration, as the effective nuclear charge increases in the latter case. The replicate 3*d* splitting measured by us agrees well with the theoretical value of Herbst and Wilkins (1979). We have, therefore, assigned the observed two sets of structures to divalent and trivalent europium in $EuCu_2Si_2$. The detailed discussion on this sample together with the temperature-dependent results will be discussed elsewhere.

(*ii*) 3*d core-level XPS of* $EuNi_2P_2$

$EuNi_2P_2$ is a sample which has not been studied by others using XPS technique. The 3*d* core-level photoemission spectra of Eu in this compound is shown in figure 3. It is apparent from the figure that the spectral features are similar to those reported for Eu in $EuCu_2Si_2$. The two sets of structures are assigned to divalent and trivalent europium. The values of average binding energies for divalent and trivalent europium are $\sim$1139 eV and $\sim$1149 eV, respectively. The replicate splitting which agrees well with the theoretical calculation (Herbst and Wilkins 1979) is $\sim$10 eV. The spin-orbit splitting is found to be $\sim$ 30 eV. The complete results on this system using Mössbauer, magnetic susceptibility, x-ray absorption and XPS techniques will be published elsewhere.

The present study establishes the mixed-valence character of $EuCu_2Si_2$ and $EuNi_2P_2$. It is recognised that the 3d core-level photoemission spectra can be used as a 'Finger-

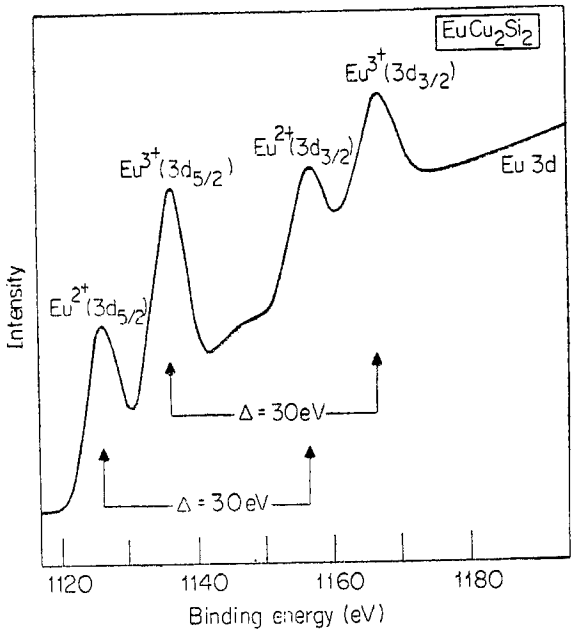

Figure 3. 3*d* XPS spectrum of Eu in $EuNi_2P_2$.

Print' for the identification of valence fluctuating systems. The present report amply emphasises the importance of 3*d*-core-level XPS studies in the understanding of valence fluctuation phenomenon in rare earth intermetallics.

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