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SUBSTITUTION EFFECTS ON THE MIXED VALENCE BEHAVIOUR OF Eu in EuCu$_2$Si$_2$

SUJATA PATIL, B.D. PADALIA, R. NAGARAJAN*, L.C. GUPTA* and R. VIJAYARAGHAVAN*

Department of Physics, Indian Institute of Technology, Bombay 400 076, India
'Tata Institute of Fundamental Research, Bombay 400 005, India

Abstract - Results of the L3 XANES and $^{151}$Eu Mossbauer measurements on EuCu$_2$(Si$_{1-x}$Sn$_x$)$_2$, Eu(Cu$_{1-x}$Au$_x$)$_2$Si$_2$ with 0<x<0.2 and Eu(Cu$_{0.8}$M$_{0.2}$)Si$_2$ where M= Au, Ag, Ru and Ni, are reported here.

Introduction:
The mixed valent (MV) systems, EuCu$_2$Si$_2$, and EuPd$_2$Si$_2$, have been extensively studied by several investigators [1-8]. Utility of Mossbauer spectroscopy (MS) and L3-X ray absorption near edge structure (L3-XANES) in studying the Eu valence state in MV systems has been established [10]. Substitution of Sn and Au in EuPd$_2$Si$_2$ has been reported to affect the valence state of Eu [10,13]. These considerations have motivated us to carry out systematic L3-XANES and MS on the substituted EuCu$_2$Si$_2$ samples. The results of our L3-XANES and MS measurements on EuCu$_2$(Si$_{1-x}$Sn$_x$)$_2$, Eu(Cu$_{1-x}$Au$_x$)$_2$Si$_2$ where 0<x<0.2 and Eu(Cu$_{0.8}$M$_{0.2}$)Si$_2$ where M= Au, Ag, Ru and Ni are reported here.

Experimental:
The samples were prepared by arc melting the constituents in argon atmosphere. Single phase formation of the samples was checked by x-ray diffraction method. L3-XANES was recorded with a conventional X-ray absorption spectroscopic setup using laboratory source of continuous X-radiation [9,14]. A transmission geometry Mossbauer spectrometer working in the constant acceleration mode was used in the present work.

Results and Discussion:
L3-XANES of a divalent or a trivalent Eu ion is, generally, dominated by a strong peak (called Raie blanche or white line) corresponding to an electron transition from 2p$_{3/2}$ core level to the first unoccupied level in the conduction band with high density of states. In a MV system, the absorption profile consists of two-peaks pertaining to divalent and trivalent components, separated by ~7 eV.

In the present work, a two-peak pattern with 7eV separation characteristic of Eu based MV systems has been observed in the L3-XANES of Eu in EuCu$_2$(Si$_{1-x}$Sn$_x$)$_2$ for each of these compositions (Fig.1). The peak positions for the $^{151}$Eu Mossbauer spectra of the same samples, appear at the same energy values as have been observed for the MV Eu (Eu$^{2+}$ and Eu$^{3+}$) in EuCu$_2$Si$_2$ [2]. This implies that Eu in EuCu$_2$(Si$_{1-x}$Sn$_x$)$_2$ samples retains its MV character. It is apparent from Fig.1 that the relative intensities of Eu$^{2+}$ and Eu$^{3+}$ components are sensitive to Sn concentration. The intensity of the divalent component is seen to increase with increasing Sn concentration. This may be due to the variation in the average local valence which cannot be identified by the L3-XANES study alone. It was, therefore desirable to record the $^{151}$Eu Mossbauer spectra of the same samples.
Fig. 2 shows the $^{151}$Eu Mossbauer spectra of EuCu$_2$(Si$_{1-x}$Sn$_x$) at 300K and 77K. The spectra of the Sn substituted samples are similar to that of the MV EuCu$_2$Si$_2$ compound except for the presence of a satellite line which appears at the position expected for Eu$^{2+}$. The isomer shift (IS) of the satellite line appears to be temperature independent but its relative intensity (with respect to the main line) seems to be temperature dependent. Also, the satellite line grows in intensity with increase in Sn concentration.

Figures 3, 4, 5 and 6 show L3-XANES and $^{151}$Eu Mossbauer spectra of Eu(Cu$_{1-x}$M$_x$)$_2$Si$_2$, with M = Au, Ag, Ru and Ni. Similar to EuCu$_2$(Si$_{1-x}$Sn$_x$), the L3-XANES data of Eu(Cu$_{1-x}$M$_x$)$_2$Si$_2$ exhibit the characteristic two-peak pattern for each of these samples. It is evident from Fig. 3 that substitution of Au has enhanced the intensity of the Eu$^{2+}$ component compared to that of EuCu$_2$Si$_2$. The L3-XANES recorded for Eu(Cu$_{1-x}$Au$_x$)$_2$Si$_2$ for O$^{2-}$X suggest that substitution of Au is driving the MV Eu(Eu$^{2+}$ and Eu$^{3+}$) towards Eu$^{2+}$. This would imply that the single Mossbauer line with IS = 7.9 mm/sec observed for 20% Au substituted sample is a mixed valent line (Fig. 5). Further, concentration of Au may stabilize the Eu in Eu$^{2+}$ state as a result of increase in the volume and reduction in screening of Eu core hole due to the 3d band of Cu. Fig. 4 indicates that for 20% Ag substituted sample, the enhancement of divalent component is less than that for 20% Au substituted sample even though they have similar electronic structure. This difference in behaviour may be due to volume effects arising out of difference in the ionic radii. It should be noted that the IS of the Mossbauer line for the 20% Ag substituted sample does not show a shift towards trivalent position as one would expect, but shows a broader line at 300K and the development of a satellite line towards trivalent position at 77K. This interesting aspect will be discussed elsewhere.

The L3-XANES (Fig. 4) of Ru substituted sample is similar to that of EuCu$_2$Si$_2$. However, the MS measurements show two lines in the MV regime; the major line is nearly at the same position as that of EuCu$_2$Si$_2$ and the minor line has IS = -6.9 mm/sec, which is more towards Eu$^{2+}$.

The substitution of Ni for Cu in EuCu$_2$Si$_2$ may not change the unit cell volume as Ni and Cu have almost the same ionic radius but may try to fill up its incomplete 3d shell demanding electrons from Eu, thereby trying to stabilize the Eu in Eu$^{3+}$ state. This has indeed been reflected in the L3-XANES and Mossbauer spectra (Fig. 4.5.6).

The mixed valence behaviour of Eu in EuCu$_2$Si$_2$ has been interpreted in terms of the excitation energy ($E_{\text{ex}}$) and a possible distribution in $E_{\text{ex}}$ either due to the width of the 4f level or due to the different local environment [8]. The present results indicate that the value and distribution of $E_{\text{ex}}$ in EuCu$_2$Si$_2$ is affected by the substitution of Sn, Au, Ag, Ru and Ni. An attempt is being made to deduce the value of $E_{\text{ex}}$ and its correlation to the substitutional atoms.

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References:

Fig. 1. L$_3$ XANES of Sn substituted EuCu$_2$Si$_2$.

Fig. 2. Mossbauer spectra of Sn substituted EuCu$_2$Si$_2$. 
Fig. 3. L₂-XANES of Au substituted EuCu₂Si₂.

Fig. 4. L₂-XANES of Eu(Cu₀.₈_M₀.₂)₂Si₂ where M = Au, Ag, Ru and Ni.

Fig. 5. Mossbauer spectra of Eu(Cu₀.₈_M₀.₂)₂Si₂ where M = Au, Ag, Ru, Ni at 300 K.

Fig. 6. Mossbauer spectra of Eu(Cu₀.₈_M₀.₂)₂Si₂ where M = Au, Ag, Ru, Ni at 77 K.