X-ray-absorption near-edge-structure study of $EuPd_3B_x$: A mixed-valence system

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L_3 absorption spectra of Eu in boron-containing alloys, $EuPd_3B_x$ ($x=0$, 0.25, 0.5, and 1.0) have been recorded. Direct evidence for the mixed-valence (Eu^{3+} and Eu^{2+}) behavior of Eu in $EuPd_3B_{0.5}$ and $EuPd_3B$ has been provided by x-ray-absorption near-edge structure (XANES). The value of the average valence of Eu in $EuPd_3B$ and $EuPd_3B_{0.5}$ alloys is estimated and it is found to be temperature independent. The XANES results in conjunction with the Mössbauer measurements lead to the conclusion that $EuPd_3B$ is an inhomogeneous mixed-valence system.

INTRODUCTION

Recently it has been reported[1] that alloying boron with RPd_3 (R = rare earth) compounds results in the formation of a new series of compounds of formula, RPd_3B_x ($0 \leq x \leq 1$). The addition of boron leads to an expansion of the cell volume in almost all cases and the increase is much larger for $EuPd_3B_x$ alloys (and also for $CePd_3B_x$) compared with other members of the series. The magnetic susceptibility of $EuPd_3$ alloys has been found to increase with increase in boron content, changing from almost temperature independent (for $x=0$) to strongly temperature dependent (for $x=1$). These features have been interpreted in terms of a change in the valence state of the Eu ion from Eu^{3+} to mixed valence (Eu^{3+} and Eu^{2+}) in $EuPd_3B_x$ alloys.[2] Further, the Mössbauer spectrum of ^{151}Eu in $EuPd_3B$ at 300 K exhibits a single line which lies in between the values expected for Eu^{2+} and Eu^{3+} systems. At low temperatures (~ 112 K), splitting of the Mössbauer spectrum into two lines has been observed and this phenomenon (not observed earlier in any metallic system) has been attributed to reduction in the valence fluctuation frequency.[3] It may be noted that the valence fluctuation time ($\sim 10^{-13}$ sec) is faster than the Mössbauer probing time ($\sim 10^{-9}$ sec), so that in this respect Mössbauer is a slow technique and provides an average effect in the case of systems exhibiting valence fluctuation phenomenon.

X-ray-absorption near-edge structure (XANES) studies offer a simple and powerful method for the investigation of the phenomenon of valence fluctuation, mixed valence, or interconfiguration fluctuation. It is a fast (probing time $\sim 10^{-16}$ sec) technique and provides signatures of the two different ionic configurations in a mixed-valence system. Unlike x-ray photoelectron spectroscopy (XPS), the results obtained from XANES are free from surface effects. The XANES method has been effectvely employed in our laboratory to understand the valence fluctuation phenomenon in some mixed-valence systems.[4–6] We present here, the results of the L_3 absorption near-edge structure studies of Eu in $EuPd_3B_x$ ($x=0$, 0.25, 0.5, and 1.0).

EXPERIMENT

The $EuPd_3B_x$ ($x=0$, 0.25, 0.50, and 1.0) alloys were prepared by arc melting the constituent elements in argon atmosphere. An x-ray diffraction method was used to check the formation of single phase materials. The L_3 absorption spectra were recorded using a focusing x-ray spectrograph of Cauchois type. A molybdenum target x-ray tube was used as a laboratory source of continuous radiation. For low-temperature studies, a cold-finger-type liquid nitrogen cryostat was employed. Other details regarding experimental setup are described elsewhere.[4]

RESULTS AND DISCUSSIONS

The L_3 absorption near-edge spectra of Eu in $EuPd_3B_x$ ($x=0$, 0.5, and 1.0) are shown in Fig. 1. The single absorption peak corresponding to the trivalent state of Eu in $EuPd_3$ is evident. This peak arises due to an electron transition from $2p_{3/2}$ core level to the first unoccupied level in the $5d6s$ conduction band, above the Fermi level, E_f. A single absorption peak (not shown in the figure) has also been observed for $EuPd_3B_{0.25}$ at the same energy position as that of Eu^{3+} in $EuPd_3$. This implies that Eu in $EuPd_3B_{0.25}$ exists in the trivalent state. The present result is consistent with the susceptibility[2] and Mössbauer measurements[3] on $EuPd_3B_{0.25}$.

The L_3 absorption curves for $EuPd_3B_{0.5}$ and $EuPd_3B$ each show two distinct peaks separated by ~ 7 eV. One of these peaks is at the same energy position as that of trivalent Eu in $EuPd_3$. The second peak appears on the lower energy side of the Eu^{3+} peak and is assigned to Eu^{2+}. It is interesting to note that the measured value of the energy separation (~ 7 eV) between the two absorption peaks assigned to Eu^{3+} and Eu^{2+} agrees with the theoretical results of Herbst and Wilkins[7] and also with the experimental reports[5,6] on other Eu-based mixed-valence systems. The present study suggests that the Eu ions have undergone valence change from Eu^{3+} in pure $EuPd_3$ to mixed-valence state (Eu^{3+} and Eu^{2+}) in $EuPd_3B_x$ ($x=0.5$ and 1).

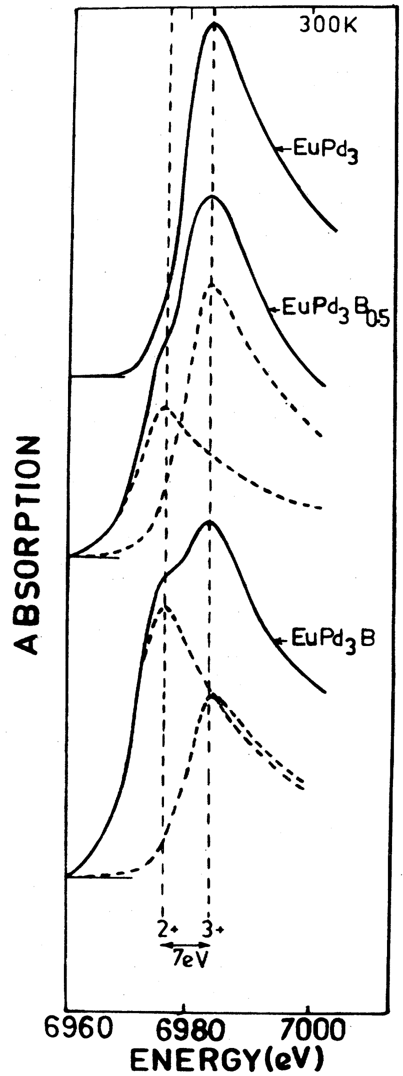

FIG. 1. L_3 absorption spectra of Eu in $EuPd_3B_x$ ($x=0$, 0.5, and 1) at 300 K. The intensities have been normalized with respect to the peak position of the curves. The dotted curves represent the deconvoluted Eu^{2+} and Eu^{3+} components.

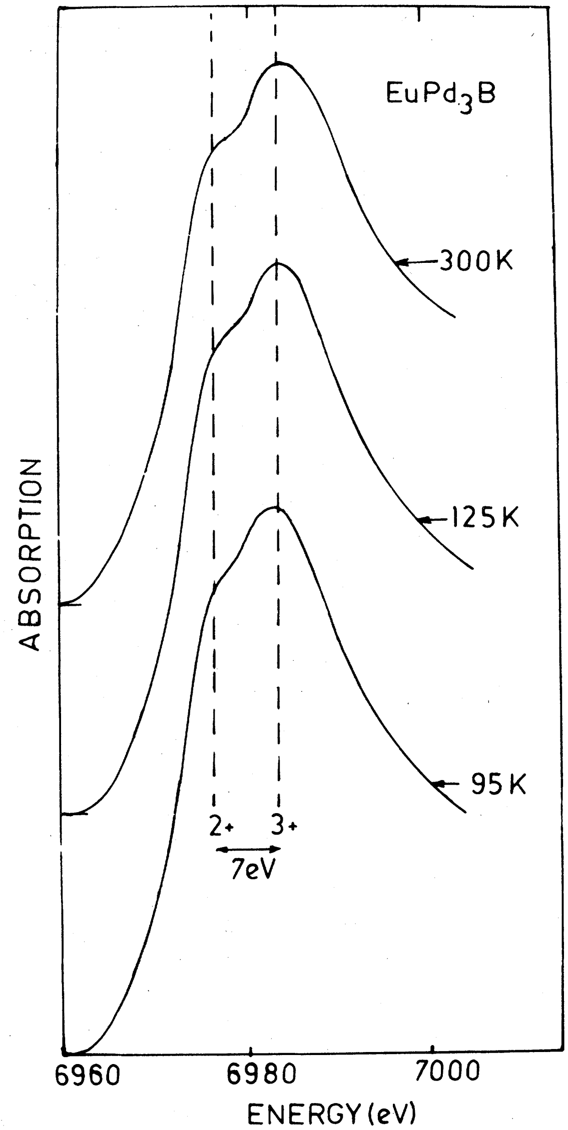

FIG. 2. L_3 absorption spectra of Eu in $EuPd_3B$ at 300, 125, and 95 K. The intensities have been normalized with respect to the peak position of the curves.

The L_3 absorption profiles for $EuPd_3B_{0.5}$ and $EuPd_3B$ are deconvoluted assuming that (i) the line shape of Eu^{3+} corresponds to that of Eu^{3+} in $EuPd_3$ and (ii) the line shape for Eu^{2+} is also the same but it is shifted from that of Eu^{3+}. Similar procedure was adopted in an earlier work.[6] The deconvoluted spectra shown in Fig. 1 reveal that the relative population of Eu^{2+}/Eu^{3+} increases with increasing boron concentration. This analysis at 300 K yields the values of the average valence of Eu in $EuPd_3B_{0.5}$ and $EuPd_3B$ as 2.6 ± 0.1 and 2.4 ± 0.1, respectively.

It is of interest to see if the average valence of $EuPd_3B_{0.5}$ and $EuPd_3B$ is affected by the variation of temperature. For this purpose, L_3 absorption spectra of these samples were recorded at low temperature (~ 95 K). Figure 2 shows that the (Eu^{2+} to Eu^{3+}) intensity ratio of the two peaks for $EuPd_3B$ at 95 and 300 K remains the same. This implies that the average valence of Eu in $EuPd_3B$ is temperature independent. It is found that the average valence of Eu in $EuPd_3B_{0.5}$ is also temperature independent.

Although the XANES study establishes the fact that Eu in $EuPd_3B_{0.5}$ and $EuPd_3B$ is in a mixed-valence state, it is not possible to identify the homogeneous or inhomogeneous mixed-valence character in these compounds by XANES alone. It is, therefore, desirable to consider the present XANES results in conjunction with the Mössbauer measurements[3] on the same sample, $EuPd_3B$. Figure 3 shows the ^{151}Eu Mössbauer spectrum of $EuPd_3B$ at 300 K (upper curve), 115 K (middle curve), and 88 K (lower curve). A single line at 300 K is apparent from the figure and the isomer shift (~ -2.7 mm sec^{-1} with respect to EuF_3) is intermediate between trivalent and divalent europium. It is noted that the line width increases from 3.1 mm sec^{-1} at 300 K to 5.1 mm sec^{-1} at 115 K with no change in the isomer shift. Around 112 K, the single-line spectra of $EuPd_3B$ starts splitting into two lines. On further lowering the temperature to 88 K, the spectrum splits into two lines with isomer shift of ~ -5.4 mm sec^{-1} and $\sim +1$ mm sec^{-1}.

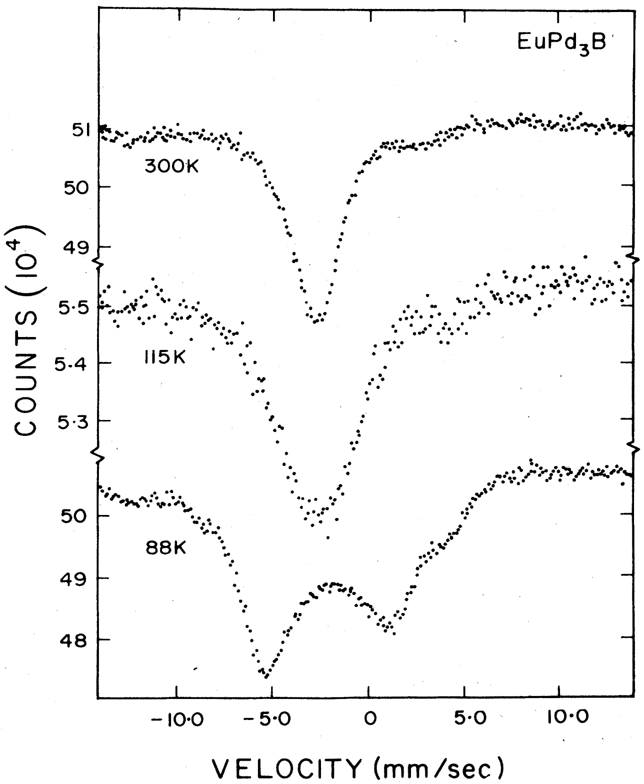

FIG. 3. ^{151}Eu Mössbauer spectra of $EuPd_3B$ at 300, 115, and 88 K.

Similar behavior has been noted for Eu_3S_4 by others.[8]

The observed splitting of Mössbauer spectrum of ^{151}Eu in $EuPd_3B$ at ~ 112 K requires some discussion. If the observed splitting is due to reduction in the valence fluctuation frequency so that it becomes comparable with the Mössbauer probing time ($\sim 10^{-9}$ sec), the x-ray absorption spectra (probe time $\sim 10^{-16}$ sec) should not exhibit change in the spectral features around 112 K. It is noted that the L_3 absorption spectra recorded at 95 and 125 K (Fig. 2) indeed show no change in the L_3 absorption near-edge structure, as is expected.

Further Mössbauer work[9] on $EuPd_3B$ at 4.2 K, exhibits two lines at ~ -6.7 mm sec^{-1} and 3.5 mm sec^{-1} corresponding to Eu^{2+} and Eu^{3+} ions. Below 4.2 K, $EuPd_3B$ orders magnetically, and at 1.4 K the Mössbauer absorption corresponding to Eu^{2+} ions shows magnetic hyperfine splitting. It is likely that the crystal structure of $EuPd_3B$ undergoes a lattice distortion at low temperatures, stabilizing europium ions in two different valence states (mixed integral valence or inhomogeneous mixed valence).

It may be noted that the average valence of Eu in $EuPd_3B$ as deduced from the relative areas under the two peaks in the Mössbauer spectrum at 88 K is 2.4 ± 0.1 which is in excellent agreement with the present XAS results.

It may be stated that the XANES results, in conjunction with the Mössbauer measurements, lead to the conclusion that $EuPd_3B$ is an inhomogeneous mixed-valence system.

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