PHYSICAL REVIEW B VOLUME 29, NUMBER 10 15 MAY 1984

Valence behavior of europium in $EuPd_3B_x$ ($0 \leq x \leq 1$) alloys: Possible charge ordering in $EuPd_3B$

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(Received 18 May 1983; revised manuscript received 8 November 1983)

Extensive ^{151}Eu Mössbauer-effect studies in a wide range of temperatures (700–1.4 K) are reported for the samples $EuPd_3B_{0.5}$ and $EuPd_3B$. The valence of europium, which is trivalent in $EuPd_3$, is observed to change with boron content. The temperature dependence of the Mössbauer spectrum in $EuPd_3B$ suggests that europium ions undergo charge ordering at low temperature.

The synthesis of new alloys of the formula RPd_3B_x ($0 \leq x \leq 1$), where R is from La to Lu, has recently been reported in the literature.[1] The x-ray diffraction patterns of these alloys are found to be similar to the parent RPd_3 compounds which crystallize in the $AuCu_3$-type structure. However, alloying with boron results in the expansion of cell volume. The lattice expansion is observed to be much larger for $CePd_3B_x$ and $EuPd_3B_x$ alloys compared with that in other RPd_3B_x alloys, implying thereby a change of valence of cerium and europium ions. Magnetic-susceptibility measurements on $CePd_3B_x$ alloys showed conclusively that cerium ions undergo a valence change from mixed valent in $CePd_3$ to largely trivalent in $CePd_3B_x$ alloys.[2] Preliminary ^{151}Eu Mössbauer[3] and susceptibility measurements down to 77 K (Ref. 4) on $EuPd_3B_x$ alloys revealed that the valence of europium, which is trivalent in $EuPd_3$, changes as a function of boron concentration. However, more information is needed in order to have a deeper insight into the behavior of this system. In the present work the Mössbauer investigations have been extended to higher and lower temperatures (700–1.4 K). Furthermore, resistivity measurements (for $EuPd_3B$) were performed between 300 and 4.2 K. The present Mössbauer studies reveal that both $EuPd_3B_{0.5}$ and $EuPd_3B$ undergo magnetic ordering at low temperatures. In the compound $EuPd_3B$, low-temperature measurements suggest charge ordering of europium ions though at 300 K all the europium ions are in a valence fluctuating state. To our knowledge, such a behavior has been observed for the first time in a metallic system. The magnetic ordering temperatures for both $EuPd_3B$ and $EuPd_3B_{0.5}$ were determined by specific-heat measurements.

The alloys $EuPd_3B_x$ ($x = 0$, 0.25, 0.5, and 1.0) were prepared by arc melting the constituents in an argon atmosphere. To offset the loss in europium due to evaporation, an excess amount of europium was taken. Powder x-ray diffraction patterns using Cu $K\alpha$ radiation showed all the samples to be single phase. It may be mentioned that in the Mössbauer spectrum of some of our samples we observe the presence of small impurity phases which could not be detected in the x-ray diffraction patterns. The diffraction patterns of $EuPd_3B_x$ alloys are similar to $EuPd_3$ which crystallizes in the $AuCu_3$-type structure, but the lattice constant is seen to increase with boron concentration. From earlier investigations it is known that metalloids like boron, carbon, etc., can occupy the interstitial body-center position in the $AuCu_3$-type crystal structure to give rise to an antiperovskitelike arrangement.[5] Therefore it is likely that the smaller boron atoms occupy the vacant body-centered position in the $EuPd_3$ unit cell. The increase in the lattice constant in $EuPd_3B_x$ alloys is larger relative to that observed in other compounds. Figure 1 depicts the lattice constants of RPd_3 and RPd_3B (R = La to Gd). A strong deviation from the value determined by the usual lanthanide contraction for trivalent rare-earth ions is observed in $EuPd_3B$. The larger cell volume change observed in the Eu alloys indicates a possible change in the valence of europium as the ionic radius of divalent europium exceeds that of trivalent europium.

Since there is an appreciable difference in the isomer shift (S) of europium ion in the divalent and trivalent state, the Mössbauer measurement can be used to extract information about the valence state of the europium ion at a microscopic level. The Mössbauer spectrum obtained in $EuPd_3$ (300 K) shows a single line with an S of 4.5 ± 0.1 mm/s (with respect to EuF_3), in agreement with that reported earlier in literature.[6] The absorption in $EuPd_3B_{0.25}$ occurs at the same position as in $EuPd_3$ and is observed to be temperature independent down to 1.4 K. This is a further confirmation of the susceptibility result which indicates the trivalent character of europium ions in this alloy. On further addition of boron, which results in further expansion of the lattice, the change in the valence state of europium ions is clearly ob-

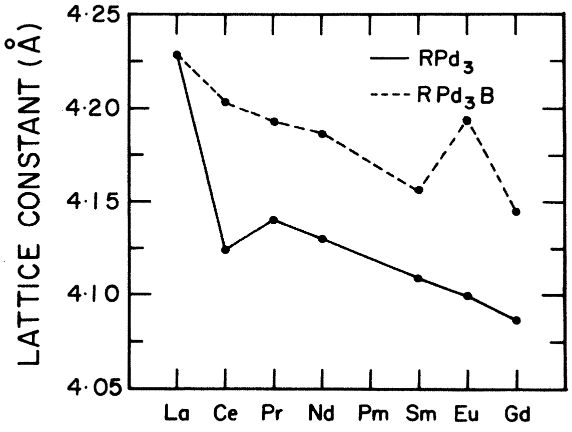

FIG. 1. Lattice constants of RPd_3 and RPd_3B (R = La to Gd).

served in the Mössbauer spectrum. In $EuPd_3B_{0.5}$ two peaks with S of $-3.62(5)$ and $+3.13(5)$ mm/s occur at 300 K (Fig. 2). These peaks show strong temperature dependence and, as the temperature is lowered to 4.2 K, the lines shift further apart to $-5.90(5)$ and $+4.10(5)$ mm/s. The behavior observed here is very similar to that reported in the alloys $Eu_xLa_{1-x}Rh_2$, where the spectra consist of a few lines exhibiting strongly temperature-dependent isomer shifts, which has been interpreted on the basis of near-neighbor environment-dependent excitation energy for the fluctuation of electrons between the conduction band and the localized $4f$ level.[7] In a certain temperature range the excitation energy is also found to be temperature dependent.[7,8] We feel that a similar situation exists in the $EuPd_3B_{0.5}$ alloy and that the experimentally observed Mössbauer spectrum is a composite of a number of subspectra where each subspectrum arises from a different europium site characterized by the number of nearest neighbors of boron. From the temperature dependence of the S it is clear that decreasing the temperature stabilizes the europium ions into "divalent- and trivalentlike" states. Extension of measurements down to 1.4 K revealed, besides a peak at 4.10 mm/s corresponding to trivalent or nearly trivalent europium, a magnetically split spectrum arising as a result of the ordering of Eu^{2+} ions. From specific-heat measurements, the magnetic ordering temperature T_c is found to be 1.7 ±0.1 K.

A very novel and rather puzzling Mössbauer behavior is observed in $EuPd_3B$. We have mentioned above that com-

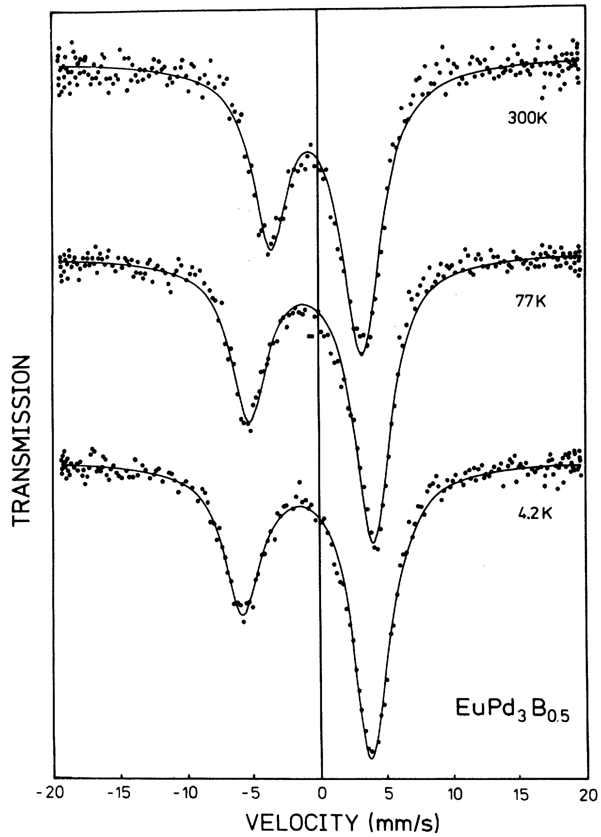

FIG. 2. Mössbauer absorption spectra of $EuPd_3B_{0.5}$ at different temperatures.

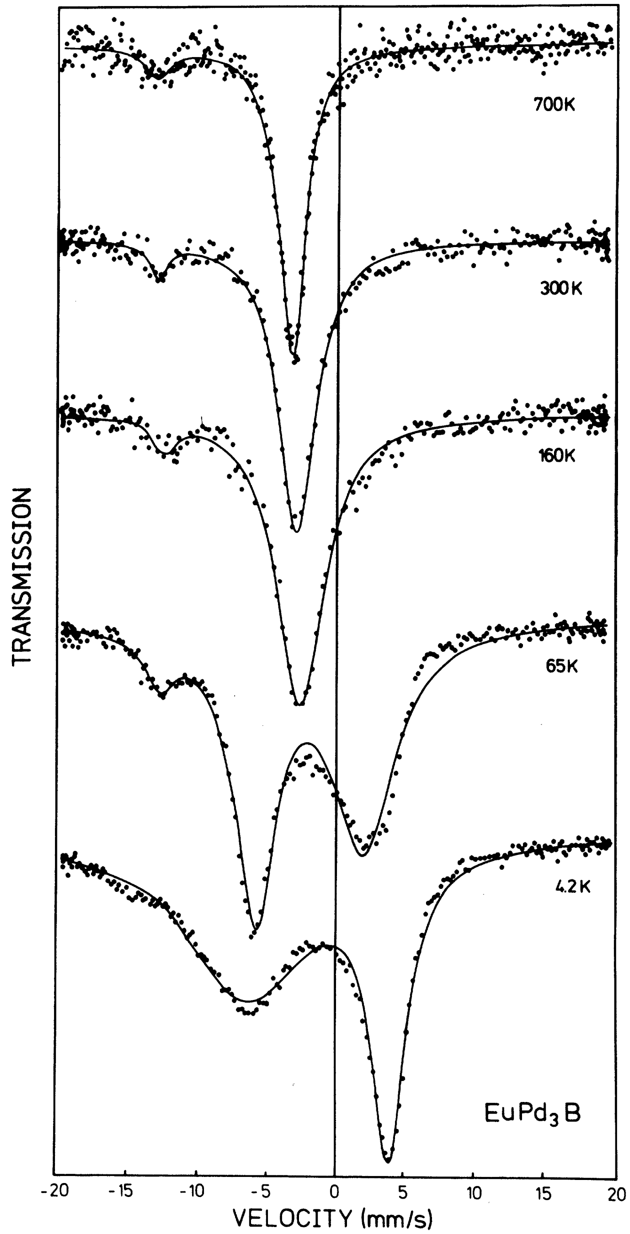

FIG. 3. Mössbauer absorption spectra of $EuPd_3B$ at different temperatures.

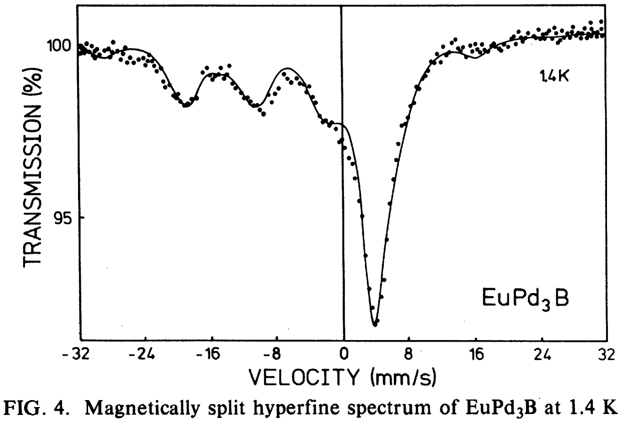

FIG. 4. Magnetically split hyperfine spectrum of $EuPd_3B$ at 1.4 K.

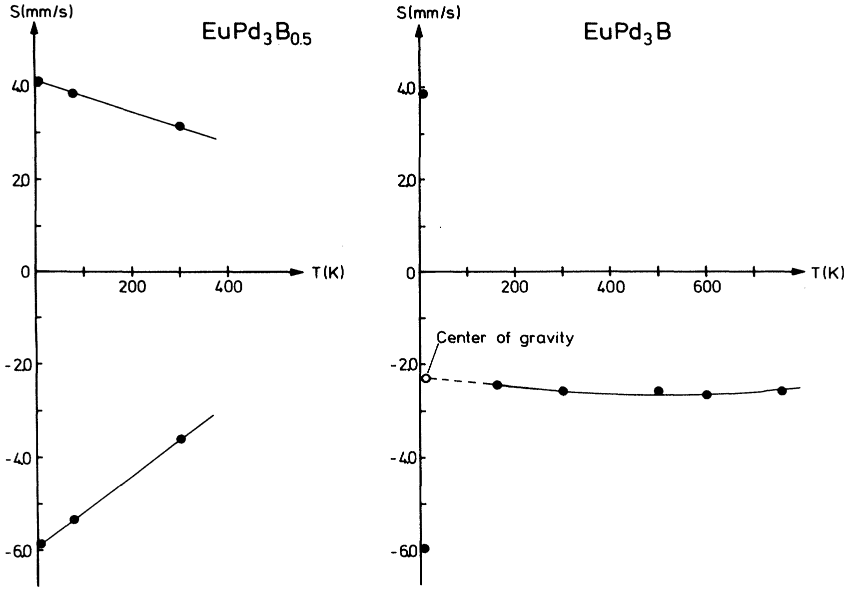

FIG. 5. Isomer shift values S for both $EuPd_3B_{0.5}$ and $EuPd_3B$ as a function of temperature.

pounds with $AuCu_3$-type structure can give rise to antiperovskite-type arrangement if alloyed with suitable elements. The alloying element occupies the body-centered position of the unit cell. This fact makes us presume that a well-defined chemical order exists in $EuPd_3B$ in contrast to $EuPd_3B_{0.5}$ where some of the body-center positions will be unoccupied. Therefore, in $EuPd_3B$ where as per stoichiometry each unit cell of the lattice has a boron atom at the center, all europium ions are crystallographically equivalent and should exist in the same valence state. This is, indeed, observed at 300 K where a single Mössbauer absorption with an S of -2.59 mm/s characteristic of europium ions in the valence fluctuating state is observed (Fig. 3). The small peak at $\simeq -12$ mm/s is due to the divalent impurity phase. Normally, valence fluctuating europium compounds exhibit a single motionally narrowed Mössbauer line with a temperature-dependent isomer shift that tracks the change in the average valence as a function of temperature. An entirely different behavior is observed in $EuPd_3B$: the linewidth increases from 2.2 mm/s at 700 K to 3.1 mm/s at 300 K and 5.1 mm/s at 115 K without any change in the isomer shift. On decreasing the temperature further, the spectrum splits into two lines (see Fig. 3). The center of gravity of these two lines coincides very well with the position of the single line observed for $T=160$ K extrapolated to 4.2 K. The compound orders magnetically at 4.35 K (determined from specific-heat measurements). An effective hyperfine field of 31.3 T is inferred from the magnetically split Mössbauer spectrum at 1.4 K (Fig. 4). The temperature dependence of the isomer shifts in $EuPd_3B_{0.5}$ and $EuPd_3B$ is plotted in Fig. 5. One gets an apparent impression from Fig. 5 that the two separate peaks observed in $EuPd_3B_{0.5}$ up to 300 K might collapse into a single absorption peak at higher temperatures. To check this, efforts were made to record a Mössbauer-effect (ME) spectrum at 800 K but the sample decomposed.

The behavior of the $EuPd_3B$ ME spectrum at various temperatures is very similar to that observed in the ME spectrum of Eu_3S_4.[9] Thus we suggest that similar to Eu_3S_4 charge ordering of the Eu ions occurs in $EuPd_3B$. However, there are some important differences. Conductivity of Eu_3S_4 between 77 and 300 K shows an exponential behavior. Our resistivity measurements for $EuPd_3B$, on the other hand, show metallic behavior in the temperature range from 300 to 4.2 K. No anomaly is detected within an accuracy of about 2–3%. The values of the resistivity at 300 and 4.2 K are 1.6×10^{-4} and 5.5×10^{-5} Ω cm, respectively. It is not yet clear to us what triggers the low-temperature behavior of $EuPd_3B$. Preliminary x-ray diffraction experiments (at 6 K, using V-filtered Cr radiation) were performed to look for a possible structural phase transition at low temperatures. The analysis of the diffraction patterns at 300 and 6 K did not show within our experimental accuracy any change in the crystal structure. However, more careful x-ray diffraction studies are needed to verify if the compound undergoes any structural distortion at low temperatures as is found in Eu_3S_4.[10]

To summarize, alloying boron with $EuPd_3$ leads to the formation of new alloys $EuPd_3B_x$ $(0\leqslant x\leqslant 1)$. Depending on the boron concentration, $EuPd_3B_x$ alloys show very different physical properties relative to those of $EuPd_3$. Thus while $EuPd_3$ is a Van Vleck paramagnet, $EuPd_3B_{0.5}$ and $EuPd_3B$ order magnetically at low temperatures. In $EuPd_3B$ a charge ordering of the Eu ions seems to occur at low temperatures. This is the first metallic rare-earth system known to exhibit such a behavior.

ACKNOWLEDGMENTS

We wish to thank K. Westerholt for performing the specific-heat and conductivity measurements and J. P. Sanchez for the high-temperature Mössbauer measurements.

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