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The influence of boron distribution on the valence of Eu in EuPd_3B

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Abstract. The valence states of europium in EuPd_3B are studied in connection with the distribution of boron atoms in the neighbourhood of the Eu ion.

The temperature dependence of this distribution, which determines the populations of the Eu^{3+} and Eu^{2+} states, is analysed. The results are compared with the experimental intensity ratios of the Mössbauer lines. Fairly satisfactory agreement is obtained.

1. Introduction

The Mössbauer spectra of ^{151}Eu in EuPd_3B have been investigated at different temperatures by several workers. As is well known they consist of two lines arising from Eu^{2+} and Eu^{3+} , respectively (Dhar *et al* 1981, 1982, 1984).

In recent work, Cianchi *et al* (1989) studied the valence state of europium in EuPd_3B by collecting spectra in the range of temperatures between 77 and 300 K at small temperature intervals. The experimental data have been interpreted on the basis of a relaxation process between two non-equivalent sites of europium.

The line intensities were assumed to be proportional to the populations of the two valence states and the transition probabilities between them were evaluated; the one concerning the transition from the $|3+\rangle$ to the $|2+\rangle$ valence state turned out to be strongly dependent on T while the other was nearly independent. The order of magnitude of the transition probability shows that the mechanism is associated with conformational motions and not electronic transitions. The ratio of the population of the $|2+\rangle$ to that of the $|3+\rangle$ states depends on the temperature. Figure 1 shows the relative intensities of the two lines according to Dhar *et al* (1981), and Cianchi *et al* (1989) for the point at 4 K. Although we attempted a qualitative interpretation of this behaviour, several problems remain unresolved as of course their solution needed a detailed investigation of the mechanisms from which the two states originate.

In this paper it is shown that the two conformational states introduced in our previous work (Cianchi *et al* 1989) originate from different boron distributions around the Eu ions.

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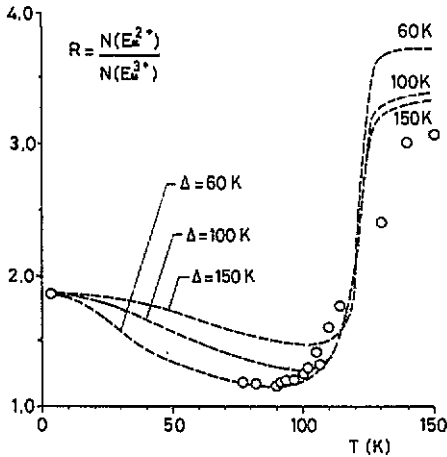


Figure 1. Fitting of the temperature variation in the intensity ratio for different values of Δ . The experimental values were obtained from the Mössbauer spectra (Cianchi *et al* 1989, Dhar *et al* 1981).

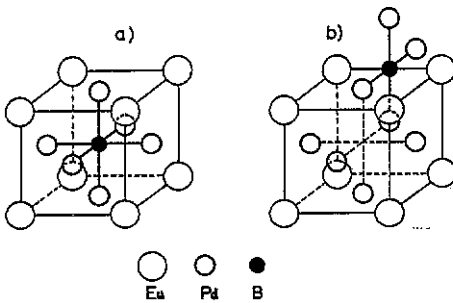


Figure 2. Sites of a boron atom in the elementary cell. (a) Site at the centre of the cell; the boron atom is surrounded by six palladium ions in octahedral coordination. (b) Site at the centre of the edge; the boron atom is surrounded by two europium ions and four palladium ions.

A simple theory for the line intensities, where the temperature dependence of the distribution of boron atoms is taken into account, is developed here; fair agreement with the line intensities obtained from fitting the spectra is achieved (Cianchi *et al* 1989).

2. Theory

The EuPd_3B compounds are observed to crystallize in the same structure as EuPd_3 (AuCu_3 type). The light boron atoms do not have a definite position in the lattice but can reasonably be accommodated at the centre of the cubic cell or at the middle points of the edges. Therefore one has four equilibrium positions for boron atoms in each cell. In the first case each boron atom is coordinated by six palladium ions and in the second case by four palladium ions and two europium ions as is shown in figure 2.

We can decide as follows that the highest-energy configuration is the one with the boron atom at the centre of the cell. There are the same number of these sites as there are boron atoms. Therefore, if such sites had low energy, at sufficiently low temperatures they should all be occupied. Under these conditions each Eu ion would be equally coordinated and therefore the Mössbauer spectrum should consist of a single line. In contrast, below $T \approx 80$ K the spectrum consists of two well resolved lines; therefore this allows us to establish that the configuration of lower energy is the one with the boron atom at the centre of one of the cube edges.

One has three equivalent sites of this type for each elementary cell so that different boron distributions, which give place to different coordinations for the Eu ions, can be realized. Since the two different kinds of boron position correspond to different energies, the boron distribution, and consequently the Eu coordination, will be temperature dependent.

It will be shown that both the presence of the two lines and the evolution with T of the line intensities are accounted for on the basis of these considerations. First we recall that the relation between the stoichiometric percentage of boron and the valence of europium in EuPd_3B_x compounds ($0 \leq x \leq 1$) is such that for $x < 0.3$ the europium ion is present only in the trivalent state while for $x \geq 0.5$ it exists both with 3+ valence and with an intermediate valence between 2+ and 3+ (Darshan *et al* 1984) which for simplicity we shall from now on indicate as 2+. Moreover for $x = 1$ the Mössbauer spectra collapse into a single line at $T \approx 112$ K, which is not observed for $x = 0.5$.

We can thus affirm that the presence of the boron atoms in the neighbourhood of the europium ions produces the occurrence of mixed valence and that this effect increases by increasing the number of neighbouring boron atoms for the Eu ion. We shall take into account first and second neighbours since their distances from the Eu ion are of the same order of magnitude (half-diagonal and half-edge of the cube). A europium ion can have up to six boron first neighbours and up to eight boron second neighbours. Let us denote these numbers by K and H ($0 \leq K \leq 6$, $0 \leq H \leq 8$). Therefore it seems reasonable to connect directly the valence of europium with the number of boron neighbours. Moreover the absence of the valence 2+ for $x \leq 0.3$ suggests that a threshold number of neighbouring boron atoms exists which, at a given temperature T , marks the border between the regions of single- and two-valence spectra.

Let M be the total number of boron atoms in the crystal and N the number of elementary cells ($0 \leq M \leq N$). Let $n(T)$ denote the number of boron ions that, at the temperature T , occupy the positions at the centre of the edges. Consequently the occupancy probability for one of these sites is

$$p_n(T) = n/3N$$

and thus, for the probability that K of the six first neighbours of europium and boron atoms, one obtains

$$P_K(n) = \binom{6}{K} p_n^K (1 - p_n)^{6-K}.$$

As a consequence the probability $p_K(T)$ that at the temperature T a Eu ion has K boron atoms as first neighbours takes the form

$$P_K(T) = \sum_n p_n(T) P_K(n).$$

Since we are dealing with very large numbers, the peak of $p_n(T)$ in the neighbourhood of its maximum value \bar{n} is extremely sharp. Therefore the average value of $P_K(n)$ corresponds to the value in the most probable configuration. Thus one has

$$P_K(T) = \binom{6}{K} p^K (1 - p)^{6-K}$$

with $p = \bar{n}/3N$. The probability that at the temperature T a Eu ion has H boron atoms as second neighbours can be evaluated following the same procedure; one obtains

$$P_H(T) = \binom{8}{H} p'^H (1 - p')^{8-H}$$

where, as in our case, $M = N$:

$$p' = (N - \bar{n})/N = 1 - 3p.$$

In order to evaluate \bar{n} let us denote by Δ the energy required to remove a boron atom from the centre of the edge to the centre of the cell. Then, if there are K atoms at the centres of the edges, the energy of the systems will be $(M - n)\Delta$ above its ground state. The number of ways that one can arrange n boron atoms in the $3N$ edge centres and the remaining $M - n$ in the centres of the cells are

$$\binom{3N}{n}$$

and

$$\binom{N}{M - n}$$

respectively. The weight of the configuration is thus the product of these numbers. The free energy F of the crystal can thus be evaluated.

Putting $p = n/3N$, $M/3N = a$, $x = \exp(-\Delta/T)$, from the equilibrium condition $\partial F/\partial n = 0$ one has

$$\bar{n} = 3N\{1 + \alpha + x(\frac{1}{3} - \alpha) \pm \sqrt{[1 + \alpha + x(\frac{1}{3} - \alpha)]^2 - 4\alpha(1 - x)}\}/2(1 - x).$$

The probability that a europium ion assumes the 2+ valence can now be written in the form

$$P(\text{Eu}^{2+}) = \sum_{K \geq K_0} \sum_{H \geq H_0} P_K(T) P_H(T).$$

3. Conclusions

These expressions have been used to fit the experimental data in order to determine Δ , K_0 and H_0 . Figure 1 shows the fitting of the intensity ratio on the basis of the above theory. In the low-temperature range ($T \leq 120$ K), one finds that $\Delta \approx 60$ K while, for higher temperatures, greater values of Δ (≈ 150 K) seem better. For high temperatures (above 120 K) the fitting is less satisfactory. This can be attributed to a variety of reasons. First of all we must recall that the intensity ratio diminishes as T increases and that as a consequence the effects of inhomogeneities become more important. Moreover, in high-temperature ranges the spectra collapse into a single line because of the rapid fluctuation between the states $|2+\rangle$ and $|3+\rangle$. As a consequence the information contained in these spectra with regard to the number of europium ions in the two states is less than at low temperatures. Finally it should be recalled that the effect of boron atoms beyond the second neighbours and any correlation between the probabilities of first and second neighbours were disregarded.

For the threshold values K_0 and H_0 it was discovered that the transition from Eu^{3+} to Eu^{2+} is determined for all the temperatures by at least two first neighbours, while the

number of second neighbours must be at least five up to 110 K, gradually decreasing to one between 110 and 160 K. Such behaviour, i.e. a dependence on T of the number of neighbours necessary to stabilize a given valence for the rare-earth ion, has already been detected for lanthanide compounds (Bauminger *et al* 1974).

A possible explanation of the influence of the boron atoms on the valence of europium could be as follows: in a metallic complex the valence of europium depends on the energy position with respect to the Fermi level ε_F of the localized 4f level, which an electron from the conduction band occupies. For our compound the conduction band consists of the 5d states of palladium and the 6s states of europium. The interaction with the band is reasonably greater for boron atoms placed at the middle points of the edges of the cube than for those placed at the centre of the cube. This interaction could for example consist of transfer of electrons to the band or of a reduction in the space available to the band states, or both; anyway the final effect is that the Fermi level rises in energy. This favours the overlap of the occupied band states with the localized 4f level and thus the valence fluctuation.

Moreover, as the Fermi distribution becomes smooth when T increases, the overlap probability increases too, and it is reasonable to suppose that the number of boron atoms necessary to determine a good overlap is less at high temperatures than at low temperatures.

Finally one can see that the two states obtained in our previous work (Cianchi *et al* 1989) can now be identified as follows: one corresponds to a number of first neighbours below the threshold K_0 and the other to a number of first neighbours above it. The change in the europium valence from Eu^{3+} to Eu^{2+} involves an energy variation which will certainly be of the order of the energy required when a boron atom moves from the centre of the cell to the centre of the edge. The probability of this valence change is thus determined by the energy gap between the above two positions and not by T . The inverse process is of course temperature dependent. This agrees with the fitting of the experimental data.

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