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Boron-induced valence change of cerium in $CePd_3$

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It is found that boron can be added to $CePd_3$ to form compounds having the formula $CePd_3B_x$ where x typically lies between 0 and 1. Addition of boron causes an expansion in cell volume without a change in the structure. The increase in cell volume as a function of boron concentration is much larger in $CePd_3B_x$ compounds compared with that in $LaPd_3B_x$ or $GdPd_3B_x$ compounds. While $CePd_3$ is a well-known mixed-valent system, susceptibility and lattice-parameter measurements show that the addition of boron to $CePd_3$ causes a change in the valence state of cerium from a mixed-valent to an almost trivalent state. The change is striking in going from $CePd_3$ to $CePd_3B_{0.12}$.

Over the recent years there has been a great deal of interest in the phenomenon of valence fluctuation in rare-earth-containing systems.[1] Ordinarily the rare-earth ions exist in a trivalent state. However, Ce, Sm, Eu, Yb, and Tm and possibly some others are capable of showing two valence states. In suitable systems, these rare-earth ions fluctuate between two integrally occupied valence states, $4f^n$ and $4f^{n-1}$, at a very rapid rate (10^{12} cps). A characteristic feature of valence fluctuation systems is the demagnetization of the $4f$ shell at low temperatures. (There has been one exception, namely, TmSe and systems derived from it.[2]) Thus the susceptibility tends to a temperature-independent value at low temperatures.

An anomaly in the unit-cell volume of the rare-earth-containing compound in relation to the usual lanthanide contraction for trivalent ions is the first obvious indication that the rare earth exists in an abnormal valence state. In the quadrivalent state there is a decrease in the $4f$ ionic radius, which results in a decrease in unit-cell volume. Likewise, when the rare-earth ion is in a divalent state, there is an increase in the $4f$ ionic radius and the cell volume. It is therefore possible to change the valence state of rare-earth ions by application of pressure. The pressure may be applied externally, in which case there is a contraction in cell volume, which is likely to cause a change towards the higher valence state. In some cases the pressure can be generated internally, by replacing one or more constituents with others having different ionic radii. In this case the valence change is in the direction determined by whether the cell volume increases or decreases. Such valence changes have been observed, for instance, in rare-earth-doped SmS.[3,4]

During the course of investigating the magnetic behavior of rare-earth ternary borides such as RT_3B_2 (R = rare earth, T = Rh, Ru, etc.), in particular $CeRh_3B_2$,[5] we noted that compounds having the general formula $CeRh_3B_x$, $CePd_3B_x$, etc., can be prepared with x typically lying between 0 and 1. The compound $CePd_3$ is a well-known mixed-valent system.[6] In this Communication we present results of lattice parameter and susceptibility measurements on $CePd_3B_x$ alloys and show, what we believe to be the first observation, that addition of boron causes a change of valence state of cerium in $CePd_3$.

Master alloys of the formula $CePd_3$ and $CePd_3B$ (and similarly for the La and Gd analogs) were prepared by arc melting stoichiometric amounts of the constituent elements. The alloys RPd_3B_x (R = La, Ce, and Gd) were then made by melting together appropriate amounts of the corresponding RPd_3 and RPd_3B alloys. For the purpose of this Communication we confine to $0 < x \leq 1$. The purity of the starting materials was as follows: Rare earth 99.9%, Pd 99.95%, and B 99.99%. The alloy buttons were melted several times to ensure homogeneity. Powder x-ray-diffraction patterns were obtained from as cast materials at room temperature using Philips diffractometer with Cu $K\alpha$ radiation. These showed that the compounds are single phase materials for $0 < x \leq 1$ and have the cubic $AuCu_3$-type structure (space group $Pm3m$). The rare earth occupies ($1a$) site and Pd occupies ($3c$) sites. The most likely position for boron is the octahedral ($1b$) position. This will give a limiting composition of RPd_3B_x at $x = 1$. However, we do find single-phase-cubic materials even for $x > 1$ in the case of $CePd_3B_x$, the only one examined so far. Therefore, it is likely that some other positions are also occupied by boron.

Figure 1 shows a comparison of the lattice parameter of RPd_3 and RPd_3B compounds for R = La, Ce, Pr, Nd, Sm, and Gd. It has been well established that cerium in $CePd_3$ is in a mixed valent state. Its lattice parameter, therefore, shows an anomalous decrease when referred to the usual lanthanide contraction. Introduction of boron seems to restore the lat-

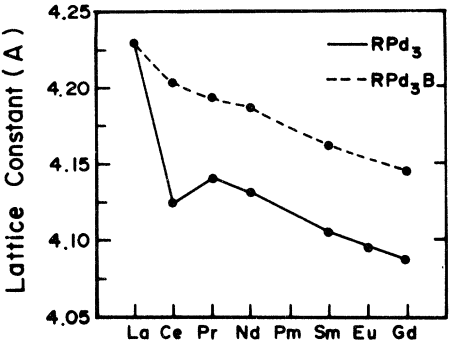

FIG. 1. Lattice parameter of RPd$_3$ and RPd$_3$B compounds for R = La, Ce, Pr, Nd, Sm, and Gd.

tice parameter of CePd$_3$B back to the value which fits nicely the lanthanide contraction. This provides us with the first indication that the addition of boron has caused a change in the valence state of cerium in going from CePd$_3$ to CePd$_3$B.

Figure 2 shows the variation of lattice parameter in LaPd$_3$B$_x$, GdPd$_3$B$_x$, and CePd$_3$B$_x$ systems as a function of x. It is seen that, with increasing boron concentration, the lattice parameter of CePd$_3$B$_x$ increases substantially; the increase is dramatic even for $x = 0.12$. Beyond $x = 0.5$ the lattice parameter is essentially independent of the boron concentration. On the other hand, the LaPd$_3$B$_x$ system shows little or no change in the lattice parameter with increasing boron concentration. In other RPd$_3$B$_x$ compounds, for instance, with R = Gd, we do find expansion in lattice with increasing x, but the percentage expansion in CePd$_3$B$_x$ for the same x is always larger. Thus we take the results in Figs. 1 and 2 to imply that cerium has changed from mixed valent in CePd$_3$ to essentially a trivalent state in CePdP$_x$ alloys even for very low boron concentration. This is corroborated by the susceptibility measurements.

Figure 3 shows the temperature dependence of the susceptibility of CePd$_3$B$_x$ alloys in the temperature range 77 to 400 K. In the case of CePd$_3$ the susceptibility on lowering the temperature flattens out below about 120 K. This behavior is characteristic of valence fluctuation systems. However, on adding boron, a striking difference in the temperature dependence of susceptibility is observed. Even for small addition of boron, e.g., $x = 0.12$, the susceptibility starts following Curie-Weiss behavior in the temperature range investigated with effective magnetic moment $\mu_{\rm eff} = 2.24\mu_B$ and $\Theta_P = \sim -64$ K (the $\mu_{\rm eff}$ value for free Ce^{3+} ion is $2.56\mu_B$). With further increase of boron ($x = 0.25$, 0.5, and 1.0) the Curie-Weiss behavior is present with $\mu_{\rm eff}$ becoming closer to the free-ion value. The paramagnetic Curie temperature shows an interesting behavior. For $x = 0.12$ it is negative and relatively large, becomes almost zero for $x = 0.25$ and 0.5, and again attains large negative value for $x = 1.0$. Though this behavior is not understood, it is likely that the initial negative value of Θ_P is due to the mixed valent character of the system, while for $x = 1.0$ the large Θ_P value may be an artifact of crystal fields or exchange interaction between Ce^{3+} ion. Thus, the susceptibility measurements clearly demonstrate that boron has caused a valence change in cerium from a mixed valent to a largely trivalent state. The results of lattice parameter and susceptibility measurements are largely summarized in Table I.

To our knowledge this is the first observation of boron-induced valence change in a rare-earth alloy. Since in alloys with small x values, all the boron sites are not occupied, it is possible that environment effects become important in the sense that Ce^{3+} to

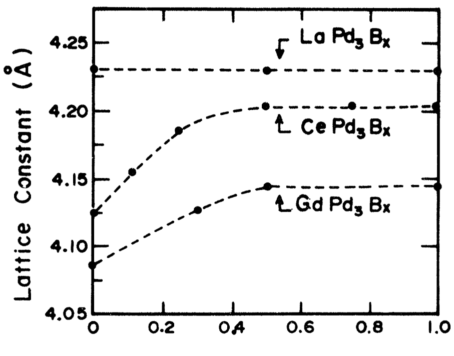

FIG. 2. Variation of lattice parameter of RPd$_3$B$_x$ compounds (R = La, Ce, and Gd) with boron concentration x.

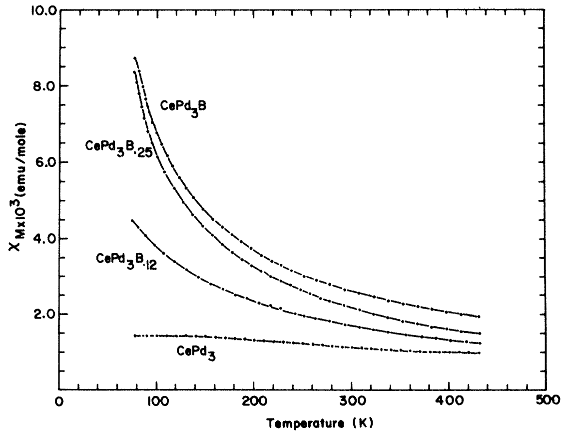

FIG. 3. Temperature dependence of the susceptibility of CePd$_3$B$_x$ compounds (x = 0, 0.12, 0.25, and 1.0).

TABLE I. The lattice constant, μ_{eff} per formula unit and paramagnetic Curie temperature Θ_P of $CePd_3B_x$ compounds ($x = 0.12$, 0.25, 0.5, and 1.0).

Compound	Lattice constant a (Å)	μ_{eff} (μ_B)	Θ_P (K)
$CePd_3$	4.124		
$CePd_3B_{0.12}$	4.156	2.24	−64.6
$CePd_3B_{0.25}$	4.186	2.30	−2.2
$CePd_3B_{0.5}$	4.203	2.36	−3.6
$CePd_3B$	4.203	2.69	−43.0

Ce^{4+} change may require a minimum number of near-neighbor borons. Therefore for small x values, some cerium ions may continue to be in a mixed valent state, while some others might have fully become trivalent. Of course, it should not be taken to imply that the addition of boron merely acts like a negative pressure, causes lattice expansion and hence a valence change in cerium. This may represent only one type of influence which boron brings about, but it also contributes electrons to the conduction band which in turn can contribute to a variety of other phenomena, such as changes in s-f interaction, changes in electron phonon interaction, etc. The observed changes in Θ_P values in $CePd_3B_x$ alloys may represent one such manifestation. Boron NMR and other related studies are in progress to understand the electronic behavior of these compounds.

To summarize, it has been shown from susceptibility and differential change in lattice parameter measurements that boron when alloyed with $CePd_3$, causes a change in the valence state of cerium from mixed valent to nearly trivalent ions. The crystal structure remains unchanged. This study may open further avenues of research where magnetic, electronic, and other physical properties may be changed or controlled by adding boron to the system. In particular, in mixed valent systems such as $CePd_3$ the amount of mixed valent character may be controllable. In some cases, it is also possible that a small addition of boron may stabilize compounds which are otherwise unstable at ambient conditions. Several rare-earth ternary boride systems are already known to show exotic behavior.[7] The present observation adds one more facet to such studies.

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[7] See, for instance, M. B. Maple, in *Science and Technology of Rare Earth Materials,* edited by E. C. Subbarao and W. E. Wallace (Academic, New York, 1980), p. 267.