Negative pressure driven valence instability of Eu in cubic $Eu_{0.4}La_{0.6}Pd_3$

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Abstract
We report the change in the valency of Eu-ions in the binary intermetallic cubic compound
$EuPd_3$ induced by La doping at rare-earth sites. Doping of La generates negative chemical
pressure in the lattice, resulting in a significant increase of the lattice parameter without altering
the simple-cubic structure of the compound. Results of dc-magnetic measurements suggest that
this increase in the lattice parameter is associated with the valence transition of Eu-ions from
Eu^{3+} to a mixed-valent state. As Eu^{2+}-ions possess a large magnetic moment, this valence
transition significantly modifies the magnetic behavior of the compound. In contrast to
introducing boron at the vacant body center site of the unit cell to change the valency of
Eu-ions, as in the case of $EuPd_3B$, our results suggest it can also be altered by doping a
rare-earth ion of larger size at the lattice site of Eu in $EuPd_3$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Although metallic perovskite compounds have received less attention than their oxygen-based variants, more attention is now being paid due to the many interesting properties exhibited by this family of compounds both from fundamental as well as application points of view [1–10]. In particular, attention is being paid to rare-earth and transition-metal based metallic perovskite compounds. $RT_3B_xC_{1-x}$ (R: rare-earth element, T: transition-metal) is one such series of present interest [4–10]. Palladium based (T = Pd) members of this series crystallize with $Pm\bar{3}m$ space-group symmetry, in both perovskite (RPd_3B) as well as a similar cubic phase (RPd_3) with the vacant body center position [6–13]. Cubic lattice parameters (a) of RPd_3 compounds follow the usual lanthanide contraction except in the case of $CePd_3$ [11–13], where the measured value of a is significantly smaller than that expected under the normal lanthanide contraction effect. This discrepancy in the value of a has been mainly attributed to the anomalous mixed-valent ($3+ < \nu < 4+$) state of Ce-ions in this compound in comparison with the stable $3+$ valency of rare-earth ions in other RPd_3 compounds [13]. The addition

of boron manifests itself in a significant increase in the value of a of the resulting RPd_3B in comparison with that of RPd_3. Similar to RPd_3, the values of a of boron-doped RPd_3B also follow the normal lanthanide contraction, except for $EuPd_3B$ which exhibits a relatively larger value of a [11, 12]. As in the case of $CePd_3$, the anomalous and high value of a in $EuPd_3B$ is a manifestation of the valency change of Eu-ions from normal $3+$ to an intermediate valence state ($2+ < \nu < 3+$) [11, 12]. Valence transition of Eu-ions from a stable Eu^{3+} in $EuPd_3$ to a predominantly Eu^{2+} state in $EuPd_3B$ brings substantial modifications in magnetic behavior [12]. $EuPd_3$ exhibits nearly temperature independent susceptibility [12]. In contrast, the divalent-state of Eu^{2+} ($^8S_{7/2}$) possesses a fairly large paramagnetic moment of 7.94 μ_B and results in a Curie–Weiss (CW) behavior in $EuPd_3B$ [12]. The underlying reason for the valence change of the Eu-ions from $3+$ in $EuPd_3$ to predominantly $2+$ in $EuPd_3B$ has been mainly attributed to the change in the crystal environment around Eu-ions and (or) the increment in the value of a upon boron addition [12, 14].

In the present paper, we demonstrate that the valency of Eu-ions present in $EuPd_3$ can also be altered by exerting negative chemical pressure by doping with the non-magnetic

rare-earth element La in the compound. The ionic radii of La^{3+} is more than that of Eu^{3+} and hence its introduction in the lattice leads to lattice expansion. To achieve sufficient increase in the unit cell volume as well as to maintain enough stoichiometry of Eu to get adequate magnetic signal, we have selected the composition $Eu_{0.4}La_{0.6}Pd_3$ for the present study. In this paper, we report the study of magnetic and electrical-transport properties of this doped compound.

2. Experimental details

The compound was prepared by argon arc-melting the stoichiometric amount of europium, lanthanum (both 99.9% pure) and palladium (>99.95% pure). The sample chamber of the arc-furnace was first evacuated and flushed several times using argon gas before the start of melting. The sample was then melted six to seven times after flipping each time to ensure proper homogeneity. The as-cast compound was then wrapped in a molybdenum foil and sealed in a quartz tube under vacuum and annealed for 240 h at 1000 °C to homogenize the phase. Structural characterization was performed by powder x-ray diffraction (XRD) measurement using Cu $K\alpha$ radiation in a Phillips-PW diffractometer. DC-magnetic measurements were performed using a SQUID magnetometer (MPMS-7, Quantum design Inc., USA) in the temperature range 2–300 K. Electrical resistivity measurements were performed by the conventional four-probe method in the temperature range 4–300 K in a home-built setup.

3. Results and discussions

Powder-XRD data suggest the formation of the single phase compound $Eu_{0.4}La_{0.6}Pd_3$ with $Pm\bar{3}m$ space-group symmetry, similar to that of $LaPd_3$ and $EuPd_3$ [15]. As expected, Rietveld analysis of powder-XRD data suggests that both La and Eu occupy the cube corner site $(0, 0, 0)$ of the cubic unit cell. The value of the cubic lattice parameter obtained from the refinement of powder-XRD data of $Eu_{0.4}La_{0.6}Pd_3$ is $a = 4.170$ Å. The reported value of the lattice parameter of $EuPd_3$ is $a = 4.102$ Å and that of B doped $EuPd_3B$ is $a = 4.196$ Å [16].

Figure 1 shows the temperature dependence of the magnetic susceptibility (χ) of $Eu_{0.4}La_{0.6}Pd_3$. The observed $\chi(T)$ of $Eu_{0.4}La_{0.6}Pd_3$ clearly deviates from the behavior observed in the case of $EuPd_3$, where the Eu-ions are in the trivalent-state [10]. Instead of a nearly temperature independent variation in $EuPd_3$, $\chi(T)$ exhibits a higher value and exhibits an upturn below $T \sim 25$ K. The observed $\chi(T)$ also deviates from a CW behavior observed in the case of $EuPd_3B$ [10], where the Eu-ions are in divalent-state. Hence, the observed $\chi(T)$ behavior of $Eu_{0.4}La_{0.6}Pd_3$ suggests that Eu-ions are neither in a purely trivalent and nor in a divalent-state in this compound. The $\chi(T)$ data also exhibit a broad hump near $T \sim 125$ K, which is often considered as the signature of the presence of ions having temperature dependent valency [17, 18]. This broad hump in $\chi(T)$ occurs due to the competition between two effects; an increase in the χ with decrease in temperature
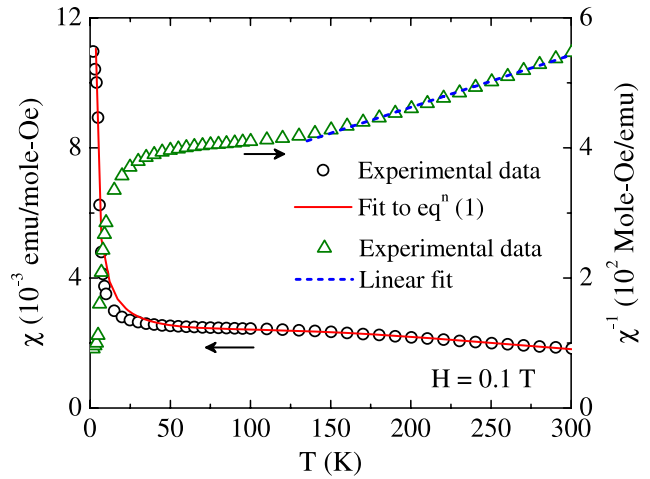

Figure 1. Temperature variation of the molar susceptibility (χ) and inverse molar susceptibility (χ^{-1}) of $Eu_{0.4}La_{0.6}Pd_3$. The continuous line is the fit to $\chi(T)$ data using the $\chi(T)$ expression given by equation (1) in the text. The dashed line is the linear-fit of $\chi^{-1}(T)$ data in the range of 150–300 K.

and a decrease in the population of excited magnetic states of unstable valence ions with decrease in temperature. The $\chi(T)$ of $Eu_{0.4}La_{0.6}Pd_3$ follows CW behavior above 150 K, as evident from the linear variation of inverse-susceptibility (χ^{-1}) in the temperature range 150–300 K (figure 1). The values of effective paramagnetic moment (μ_{eff}) and paramagnetic Curie temperature (θ_P) derived from the linear part of the $\chi^{-1}(T)$ plot are 3.15 μ_B/f.u. and −378 K, respectively. Although, the value of μ_{eff} suggests that a large fraction of Eu-ions present in the lattice is in the magnetic Eu^{2+} state near room temperature, the large and negative value of θ_P suggests the presence of valence fluctuating ions in the compound [17, 18].

We have analyzed the $\chi(T)$ data of $Eu_{0.4}La_{0.6}Pd_3$ using the interconfiguration fluctuation (ICF) model [19, 20], which is often used for explaining the observed hump in the $\chi(T)$ of the compounds containing valence fluctuating ions. In the ICF model, the valency of the unstable valence ions is a function of temperature and depends on basically two parameters; the energy difference (E_{ex}) between the ground state $(Eu^{3+}$, non-magnetic in the present case) and the excited state $(Eu^{2+}$, magnetic in the present case) and the characteristic spin-fluctuation temperature (T_{sf}) that describes the internal dynamics of the fluctuations. It is worth mentioning that in the ICF model we consider that E_{ex} is relatively small compared to all the multiplet-splittings. Hence, thermal excitation of only Hund's ground states of each configuration should be taken into account [19]. However, in the case of Eu^{3+}, due to the similar values of orbital and spin-angular-momenta, the multiplet-splittings of the ground level are small in energy and comparable to thermal excitations. Hence consideration of only the non-magnetic ground state $(^7F_0$, $Eu^{3+})$ and the magnetic excited state $(^8S_{7/2}$, $Eu^{2+})$ will not present the complete picture. However, as a first approximation one can neglect the effect of multiplets as it will only marginally modify the relative populations of Eu^{3+} and Eu^{2+}-ions, particularly at low temperatures. It may also
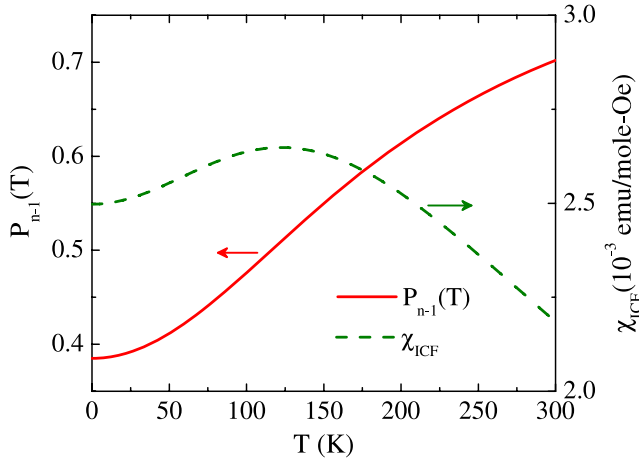
Figure 2. Temperature dependence of the fractional occupation, $P_{n-1}(T)$, of the Eu excited state (Eu^{2+}) and molar susceptibility resulting from interconfigurational fluctuations of Eu-ions (χ_{ICF}), plotted along the left and the right vertical axis, respectively.

Figure 3. Electrical resistivity (ρ) as a function of temperature. The solid line is the fit using the parallel-resistor model given by equation (3) in the text.

be mentioned here that normally average fractional valency of valence fluctuating ions (e.g. Eu in this case) is a temperature dependent quantity. However, in contrast to this Dhar *et al* have shown that the average valency of Eu-ions is temperature independent for $T > 160$ K in $EuPd_3B$ [9]. The Eu-ions with such a temperature independent population would effectively exhibit a CW behavior with a lower value of μ_{eff} originating (<7.94 μ_B) from the fraction of Eu-ions in the Eu^{2+} valence state [10]. To include the effect of such Eu-ions with temperature independent valency, an additional CW term is needed in the $\chi(T)$ expression. Hence, the $\chi(T)$ of the present compound can be described by equation (1), where the temperature dependence of magnetic susceptibility of valence fluctuating ions (χ_{ICF}) is described by the first term of equation (1), while the second term represents CW susceptibility.

$$\chi(T) = (1-f)\left(\frac{N}{3k_B}\right)\left[\frac{\mu_n^2 P_n(T) + \mu_{n-1}^2 P_{n-1}(T)}{\sqrt{T^2 + T_{sf}^2}}\right]$$
$$+ \frac{fC}{T} + \chi_0. \tag{1}$$

Here, μ_n, μ_{n-1} and P_n, P_{n-1} are the effective paramagnetic moments and fractional populations of the non-magnetic ground state and magnetic excited state respectively, f is the fraction of Eu-ions with a temperature independent valence state that exhibits CW behavior and χ_0 is temperature independent susceptibility.

The fractional population of the ground state can be described as

$$P_n(T) = \frac{(2J_n + 1)}{(2J_n + 1) + (2J_{n-1} + 1)\exp(-E_{ex}/\sqrt{T^2 + T_{sf}^2})} \tag{2}$$

where J_n and J_{n-1} are the total angular momentum of the ground and the excited states respectively. P_n and P_{n-1} hold the probability relation, $P_n + P_{n-1} = 1$.
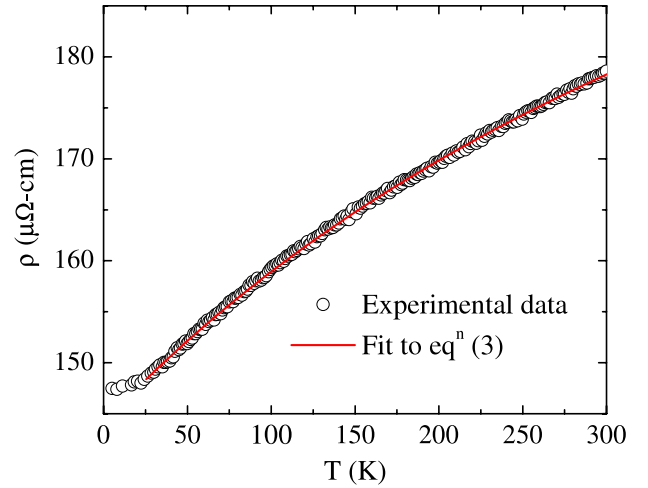
As mentioned above, we have considered non-magnetic Eu^{3+} as the ground state (E_n) and the magnetic Eu^{2+} state as the excited state (E_{n-1}). Hence, we have taken the effective paramagnetic moments of the ground state (μ_n) and excited state (μ_{n-1}) as 0 and 7.94 μ_B, respectively. The angular momentum values J_n and J_{n-1} have been taken as 0 and $\frac{7}{2}$, respectively. We have fitted the $\chi(T)$ data to equation (1) and the result is shown by the continuous solid line in figure 1. The resulting fit satisfactorily describes the temperature dependence of $\chi(T)$ of $Eu_{0.4}La_{0.6}Pd_3$ over the whole temperature range. The values of various fitting parameters are as follows; $f = 0.66$, $T_{sf} = 164$ K, $E_{ex} = 418$ K and $\chi_0 = -0.00045$ emu mol^{-1} Oe^{-1}. The high value of f suggests that a large fraction of Eu-ions is in the magnetic state Eu^{2+}. The value of μ_{eff} for $EuPd_3B$ calculated by Dhar *et al* is 6.77 μ_B [10]. Considering the moment value of Eu^{2+}-ions (7.94 μ_B), the time-averaged fraction of Eu^{2+}-ions present in $EuPd_3B$ can be estimated as 0.85. The value of $f = 0.66$ obtained in the present work for $Eu_{0.4}La_{0.6}Pd_3$ is slightly smaller than that in $EuPd_3B$. Figure 2 represents the variation of χ_{ICF} and P_{n-1} with temperature. One can see from this figure that the value of P_{n-1} that represents the fractional population of the magnetic Eu^{2+} state increases with increase in temperature due to thermal excitation. As mentioned earlier, the value of χ_{ICF} exhibits a broad maxima centered around $T = 125$ K.

We have also investigated the electrical resistivity (ρ) behavior of the compound (figure 3). The $\rho(T)$ exhibits a normal tendency of saturation at low temperatures, however they exhibits a nonlinear temperature dependence for $T > 25$ K. This kind of behavior has been observed in many high-resistivity materials whose resistivity approaches $\rho \sim 150$ $\mu\Omega$ cm [21–23]. This occurs when the electronic mean-free-path becomes very short (of the order of a few atomic spacings). Such nonlinear temperature variation of ρ exhibits a negative curvature ($d^2\rho/dT^2 < 0$) and can be interpreted using the parallel-resistance model, first proposed by Wiesmann *et al* [24]. In this model, the temperature dependence of ρ can be

expressed as

$$\frac{1}{\rho(T)} = \frac{1}{\rho_{id}(T)} + \frac{1}{\rho_{max}} \qquad (3)$$

where

$$\rho_{id}(T) = \rho_{id}(0) + C_1 \left(\frac{T}{\theta_D}\right)^n \int_0^{\theta_D/T} \frac{x^n \, dx}{(1 - e^{-x})(e^x - 1)} \qquad (4)$$

where $\rho_{id}(0)$ is the residual resistivity, θ_D is the Debye temperature and C_1 is the numerical constant. ρ_{max} basically plays the role of a shunt resistance. The actual residual resistivity is given by

$$\rho_0 = \frac{\rho_{id}(0)\rho_{max}}{\rho_{id}(0) + \rho_{max}}. \qquad (5)$$

$\rho_{id}(T)$ given in equation (4) represents the ideal temperature dependence of ρ under the Bloch–Grüneisen model, where the dominant scattering mechanism is of electron–phonon nature. Since $\rho_{id}(T)$ varies linearly with temperature at sufficiently high temperatures, we have approximated the temperature variation of ρ_{id} as, $\rho_{id}(T) = \rho_{id}(0) + \alpha T$. Figure 3 shows that the fit is quite good in the temperature range 25 K $< T <$ 300 K. The values of fitting parameters are; $\rho_{id}(0) = 354.4 \, \mu\Omega$ cm, $\alpha = 1.05 \, \mu\Omega$ cm K^{-1} and $\rho_{max} = 243.1 \, \mu\Omega$ cm. The value of the actual residual resistivity obtained using the expression given in equation (5) is $\rho_0 = 144.2 \, \mu\Omega$ cm, which is very close to the value obtained by extrapolating the $\rho(T)$ data to $T = 0$ K.

4. Conclusions

We have shown that the valency of Eu-ions, which is trivalent in binary EuPd$_3$, can be altered by doping with non-magnetic rare-earth La-ions in the lattice. Although, the resulting compound Eu$_{0.4}$La$_{0.6}$Pd$_3$ preserves the cubic symmetry, a larger than expected increase in the unit cell volume has been noticed. The result of $\chi(T)$ has been interpreted in terms of the ICF model and an additional CW term originated from the fraction of Eu-ions in the temperature independent valence state. The analysis suggests that at high temperature a large fraction of Eu-ions present in the doped compound Eu$_{0.4}$La$_{0.6}$Pd$_3$ is in the magnetic Eu^{2+} state. The variation of ρ with temperature has been analyzed using the parallel-resistance model. Our work suggests that the observed valence transition is due to negative-pressure-driven lattice parameter enhancement. This work also demonstrate that the valency of Eu-ions present in the cubic lattice of EuPd$_3$ can be altered without filling the body center site of the cubic unit cell.

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