

VALENCE FLUCTUATION IN Eu COMPOUNDS: ROLE OF CHARGE SCREENING⁺

by

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ABSTRACT

Observed valence state of various europium intermetallic compounds exhibit a systematic trend. They can be classified into two groups, i.e., intermetallics of strong d character at the Fermi level and s-like band intermetallics. Among the latter Eu^{2+} is the only stable configuration. The role of the d- or s-like character of band structure of the compounds is discussed with respect to the stabilization of the various Eu configurations within a one-center picture.

Charge screening plays a dominant role in this process. This discussion bears on the physics of fluctuating-valence systems, as well as on the electronic structure of various classes of intermetallic compounds.

A numerical analysis is performed considering a Moriya-like model density of states to describe the conduction states of the Eu compound. One illustrates the role of screening in the crossover between the two europium configurations in $\text{Eu}(\text{A}_{1-x}\text{B}_x)_2$ intermetallic compounds. Effects connected with temperature are also briefly discussed within our picture.

INTRODUCTION

In recent years the study of rare-earth compounds which exhibit valence fluctuations raised several interesting questions, both from experimental and theoretical points of view [1]. In particular, systematic measurements concerning europium intermetallic compounds have been performed by different experimental techniques and a number of systems which present mixed-valence configuration were discovered.

The purpose of this paper is twofold. Firstly, we want to suggest that charge screening provides a physical mechanism connecting the band structure of europium intermetallics to the stability of Eu^{2+} , Eu^{3+} configurations or to the valence-fluctuation regime. This simple picture may explain the change of excitation energy (E_{ex}) between two europium valence configurations which can be obtained from experiments [2]. The role of charge screening has been independently stressed by Halda [3] in connection with cerium-based fluctuating-valence systems. This suggests that it is of basic importance to the physics of any fluctuating-valence system.

Secondly, we intend to bring out the role of screening in the crossover between two europium valence configurations as a function of the concentration x in pseudobinary intermetallic systems like $\text{Eu}(\text{A}_{1-x}\text{B}_x)_2$. Also, for a given intermetallic compound like EuA_2 , we show the behaviour of the valence state of europium with thermal smearing of the density of states at the Fermi level.

As far as band structure is concerned, the compounds

presented in Table 1 could be classified into two groups, namely, intermetallics of expected strong d character of the electron states at the Fermi level and s-like band intermetallics. So, one expects that the left-hand side of Table 1 corresponds to transition-metal-like densities of states at the Fermi level as contrasted with the compounds on the right-hand side (e.g. EuAg_2) which are expected to have s-like conduction-electron character at E_F . Therefore, we argue that the stability of the Eu-4f^7 configuration, in these compounds, depends strongly on the character (and consequently on the values) of the density of states near the Fermi level of the metallic compound. More specifically, the Fermi level lies in a region of high density of antibonding states [13].

Another information given in by Table 1 is that compounds like EuPd , EuPd_2 , EuPd_3 , EuPd_5 show a transition from Eu^{2+} to Eu^{3+} valence state as the Pd concentration increases. Contrary to such behaviour, in Au or Ag compounds the valence state Eu^{2+} does not change with the amount of noble-metal atoms.

In Section 2 we discuss the stability criterion for various Eu valence regimes within the framework of a one-center impurity model. In Section 3 we discuss numerically some implications of the model, namely, the crossover between Eu^{3+} and Eu^{2+} configurations in Laves-phase intermetallic compounds like $\text{Eu}(\text{A}_{1-x}\text{B}_x)_2$ and temperature effects in a compound like EuA_2 . Finally, Section 4 is devoted to general discussions about the limitations of the model, its connection with Haldane's [3] one-center picture, and the further developments of the present work.

2. MODEL

We adopt here, for the sake of simplicity, a one-center impurity model. This means that one considers only one Eu atom embedded in a d- or s-like band metal. This corresponds to neglecting interactions between Eu atoms; however, as will be shown throughout, within this simple approach one obtains a qualitative explanation of the principal features in Table 1. So, we believe that on the whole the physics of the Eu valence-fluctuation phenomena in such compounds can be accounted for within a one-center picture.

In order to understand qualitatively the systematics exhibited in Table 1, we want to establish a stability criterion of the three possible Eu configurations, i.e., all Eu in the 2+ valence state, all in the 3+ state, or a mixture of valence states.

Let us start with the electronic structure of the intermetallic compound as derived from a band calculation assuming all the Eu atoms to have a $4f^7$ configuration. We now look into the stability of the assumed Eu $4f^7$ electron configuration with respect to an electron transfer to the conduction band producing a $4f^6$ configuration plus an extra conduction electron. In the light of our model this corresponds to an impurity like situation where a +1 charge is left with respect to the $4f^7$ shell and should be screened by the electron gas. This screening preserves the overall charge neutrality.

In order to ensure charge neutrality, starting from Friedel's sum rule for the one band case in tight-binding we

obtain |14|

$$\Delta Z = 1 = \frac{\alpha_\lambda}{\pi} \tan^{-1} \frac{V \rho_\lambda(E_F)}{1 - V F_\lambda(E_F)}, \quad (\lambda = s \text{ or } d) \quad (1)$$

$\rho_\lambda(\omega)$, $F_\lambda(\omega)$, and α_λ being the λ density of states (normalized to unit), its Hilbert transform, and the degeneracy of the λ band, respectively. The self-consistent screening potential V is determined from (1).

A measure of the localization of the screening is then given by the occupation of the "impurity cell"

$$\delta n_\lambda(0) = \alpha_\lambda \int_{E_{\text{bot}}}^{E_F} \left\{ \frac{1}{[1 - V F_\lambda(\omega)]^2 + \pi^2 V^2 \rho_\lambda^2(\omega)} - 1 \right\} \rho_\lambda(\omega) d\omega, \quad (2)$$

where E_{bot} is the energy of the bottom of the band.

The stability criterion for the Eu^{2+} configuration now follows. Suppose that ϵ_7 is the energy of the $4f^7$ shell Eu configurations and introduce ϵ_6 as the energy of the $4f^6$ Eu pure ionic configuration. One expects, using e.g. the simple Hirst's relation for the zero order energy of a n -electron ionic configuration, |15| .

$$\epsilon_n = - U_0 n + \frac{1}{2} F_0 n(n-1), \quad (3)$$

that ϵ_6 is larger than ϵ_7 . In (3), U_0 is an ionic-like attractive potential and F_0 is a radial Slater integral.

The Eu configuration involving seven electrons with six $4f$ electrons plus one electron transferred to the conduction band is expected to have an energy $\tilde{\epsilon}_6$ which is different from the

previous pure ionic $4f^6$ configuration energy ϵ_6 . These energies are connected by the relation [16]

$$\tilde{\epsilon}_6 = \epsilon_6 - \sum_{\lambda} \gamma_{\lambda} \delta n_{\lambda}(0) \quad (4)$$

where $\gamma_{\lambda} > 0$ is the change in energy introduced by the presence of $\delta n_{\lambda}(0)$ λ electrons ($\lambda = s$ or d) in the Wigner-Seitz cell of Eu. A more precise definition of γ_{λ} would be $\gamma_{\lambda} = \frac{\partial \epsilon_{4f^6 5d}}{\partial \delta n_{\lambda}}$, the energy $\epsilon_{4f^6 5d}$ being defined as the energy of the $4f^6$ configuration plus one electron in the $5d$ atomic orbital.

From expressions (1) and (2), specified for d and s electrons, one simultaneously insures charge screening of the extra charge and determines the amplitude of λ electrons at the "impurity cell". From (4) one sees that the piling of λ electrons at the Eu site tends to lower the energy ϵ_6 , the maximum lowering depending on electronic quantities like $\delta n_{\lambda}(0)$ and γ_{λ} . This suggests that for a strong piling of the screening charge at the "impurity center", one may obtain an $\tilde{\epsilon}_6$ comparable to ϵ_7 or even lower. A crude estimate of γ_{λ} borrowed from the case of isolated ions is provided for $\lambda = d$ by $\gamma_d = \epsilon_6 - \epsilon_7$, assuming that only d states are involved.

For a given intermetallic of s - d -like density of states, screening may be achieved in principle, by both d and s states. However, in general, owing to the character of the d states (small bandwidth and strong density of states) we expect screening to be due to d states, when the Fermi level lies in a region of available d states. On the other hand, if one considers a band structure where the Fermi level lies in a region of predominantly s -character states it may happen that local screening

cannot be achieved at all. This is because the small density of states in the broad s band sets too low a limit for the available displaced charge. This corresponds, in our picture, to the stabilization of the Eu^{2+} configuration. Therefore, one can understand qualitatively why Cu, Ag, Au compounds with several noble-metal concentrations remain always in a Eu^{2+} configuration. Note that the EuZn_2 compound situated on the right hand side of Table 1 shows a singular behavior, i.e., a fluctuation regime. We suggest that this discrepancy may be associated with a property of the density of states (presence of conduction d states). A similar behavior, showing anomalous d band character, is responsible for the peculiar magnetic properties of the ZrZn_2 compound [17].

In figure 1.(a) we show the stable $4f^7$ configuration, the valence of the Eu atoms being $2+$. We assume that the $\tilde{\epsilon}_6$ and ϵ_7 level have natural linewidths $\tilde{\Delta}_6$ and Δ_7 respectively. One obtains the stable $4f^7$ configuration when the ϵ_7 level has an energy lower than $\tilde{\epsilon}_6$ and no overlap occurs between them.

A valence-fluctuation regime is schematically drawn in figure 1.(b). This case is characterized by an overlap between the two $\tilde{\epsilon}_6$ and ϵ_7 levels. If one has a concentration y of atoms belonging to the Eu^{2+} configuration and consequently a concentration $1-y$ of atoms belonging to the Eu^{3+} configuration from our point of view a +1 charge must be self-consistently screened in such a way that the term $\sum_{\lambda} \gamma_{\lambda} \delta n_{\lambda}(\omega)$ of (4) implies that the difference $\tilde{\epsilon}_6 - \epsilon_7$ characterizes a definite mixed-valence state.

Finally in figure 1.(c) the stable $4f^6$ configuration is shown, the valence of Eu atoms being $3+$. In this case the

ε_6 level is lower than ε_7 and no overlap exists between them.

From the experimental point of view, the Eu^{3+} valence behavior is observed when, e.g. the amount of Pd in EuPd , EuPd_2 , EuPd_3 and EuPd_5 is increased. According to our picture one expects a corresponding increase in the d density of states at the Fermi level.

Another similar situation is presented by systems like $\text{Eu}(\text{Ir}_{1-x}\text{Pt}_x)_2$. Again one expects that the d density of states at the Fermi level of such compounds decreases with increasing concentration x. So, the Eu valence must change from $3+$ towards of $2+$, which is indeed observed experimentally [18]. On the other hand, it follows from Table 1 that EuT_n compounds, T being a 5d transition elements like Ir, stabilize the Eu^{3+} configuration in agreement with previous band calculations [19] which show that in Laves-phase intermetallics with Co, Rh and Ir, the d density of states increases when one goes over from 3d to 5d transition elements.

3. NUMERICAL RESULTS

In the previous Section, we have presented a one impurity center model and we have explained in a qualitative way the observed valence states of Eu ions in a quite large range of Eu intermetallic compounds, listed in Table 1.

We want now to explore numerically some features of our simple model. The details of the band structure of Eu intermetallic compounds, considered in Table 1, remain, to our knowledge, unknown. So, it is beyond the scope of this section to provide a direct check with some available experimental results starting

from a first principles calculation of the density of states. However, our numerical estimates, based on this quite naive model agree with the main tendencies observed experimentally.

In what follows we explicitly consider a simple model band structure describing Eu intermetallic compounds, namely a Moriya-like density of states [20]. Furthermore, we hope that if one considers an $\text{Eu}(\text{A}_{1-x}\text{B}_x)_2$ intermetallic system, where A and B are neighbours in the Periodic Table the rigid band approach is not so drastic.

We begin next the discussion concerning the crossover between Eu^{2+} and Eu^{3+} valence states.

Let $\text{Eu}(\text{A}_{1-x}\text{B}_x)_2$ be a pseudobinary intermetallic system, where A and B can be nd transition metals ($n=3,4,5$) and x ranges from 0 to 1. We suppose that EuA_2 has a stable Eu^{3+} configuration, EuB_2 has a stable Eu^{2+} one, whereas for values x between 0 and 1 one assumes that the $\text{Eu}(\text{A}_{1-x}\text{B}_x)_2$ compounds can exhibit a fluctuation-valence regime.

For simplicity sake the following assumptions will be made:

- i) the linewidth Δ_7 associated to the ϵ_7 level is a sharp one. This corresponds here to suppose the linewidth $\tilde{\Delta}_6$ as an effective one.
- ii) The separation between the energies of the two levels $\tilde{\epsilon}_6$ and ϵ_7 is chosen to be an half of the effective linewidth $\tilde{\Delta}_6$ associated to the $\tilde{\epsilon}_6$ level. This implies that substitution of a small concentration x of B atoms by the same amount of A atoms may modify the initially measured Eu valence state of the EuB_2 compound.

In fact, real systems can exhibit such behavior. For instance, starting from the EuPt_2 compound, if a small quantity of Pt is substituted by Ir, isomer shift measurements in $\text{Eu}(\text{Ir}_{1-x}\text{Pt}_x)_2$ [18] suddenly show a small variation of the Eu valence state. This change of Eu valence can be more rapid for a smaller range of x variation as indeed observed for $\text{Eu}(\text{Rh}_{1-x}\text{Pt}_x)_2$ [18], where a complete crossover is performed from the stable Eu^{2+} state (corresponding to $x = 0.5$) towards the Eu^{3+} state.

As discussed in the previous Section, the three possible regimes are shown in figure 1, namely:

- a) the stabilization of the Eu^{2+} state (corresponding to the EuB_2 compound).
- b) A crossover configuration where the valence goes from Eu^{3+} to Eu^{2+} (corresponding to a compound like $\text{Eu}(\text{A}_{1-x}\text{B}_x)_2$ for a given x).
- c) The stabilization of the Eu^{3+} state (corresponding to the EuA_2 compound).

Consider the two stable situations (a) and (c), where the valence fluctuation regime has not yet begun but is incipient.

From (4), one has

$$E_{\text{ex}} \tilde{\epsilon}_{6 \rightarrow 7} = \epsilon_7 - \tilde{\epsilon}_6 = \epsilon_7 - \epsilon_6 + \gamma_d \delta n_d^{3+}(0), \quad (5a)$$

$$E_{\text{ex}} \tilde{\epsilon}_{7 \rightarrow 6} = \tilde{\epsilon}_6 - \epsilon_7 = \epsilon_6 - \epsilon_7 - \gamma_d \delta n_d^{2+}(0), \quad (5b)$$

Here, E_{ex} is the excitation energy at $T=0\text{K}$, and $\delta n_d^{3+}(0)$ and $\delta n_d^{2+}(0)$ denote respectively the variation of the occupation at the impurity center associate with the Eu atom in valence states $3+$ and $2+$. We have disregarded in the above equations s-contri-

butions like $\gamma_s \delta n_s(o)$, as discussed previously.

It is to be stressed that these excitation energies represent the mean energy necessary to promote an f electron from one configuration level to another one.

Equations (5a)-(5b) yield

$$\gamma_d = \frac{E_{\text{ex } 6 \rightarrow 7}^{\sim} + E_{\text{ex } 7 \rightarrow 6}^{\sim}}{\delta n_d^{3+}(o) - \delta n_d^{2+}(o)} = \frac{\tilde{\Delta}_6}{\delta n_d^{3+}(o) - \delta n_d^{2+}(o)} \quad (6)$$

where, by using the above assumptions (i), (ii), we take $E_{\text{ex } 6 \rightarrow 7}^{\sim} = - E_{\text{ex } 7 \rightarrow 6}^{\sim} = \tilde{\Delta}_6/2$.

In the case (b) one has for the energy difference between the levels $\tilde{\epsilon}_6$ and ϵ_7 :

$$|E_{\text{ex}}(x)| = |\tilde{\epsilon}_6(x) - \epsilon_7| = |\epsilon_6 - \epsilon_7 - \gamma_d \delta n_d^x(o)| \quad (7)$$

From (6) and (7) one has

$$|E_{\text{ex}}(x)| = \frac{\tilde{\Delta}_6}{2} \left| 1 - \frac{2\delta n_d^x(o)}{\delta n_d^{3+}(o) - \delta n_d^{2+}(o)} \right| \quad (8)$$

In order to simplify our numerical estimates, one additional assumption of pure computational nature will now be made.

As mentioned before, the EuA_2 and EuB_2 compounds exhibit a Moriya-like density of states |20|

$$\rho(\omega) = C \left(1 - \frac{\omega^2}{\Delta^2} \right) \quad (9)$$

where Δ is the bandwidth and C is a normalization constant in order to ensure that

$$\int_{E_{\text{bot}}}^{E_{\text{top}}} \rho(\omega) d\omega = 1$$

One considers that the Fermi level of those model compounds are located in the Moriya band (9) in such a way that EuA_2 corresponds to a band filling $n_e = 0.9$ electrons and Eu valence state $3+$ whereas EuB_2 corresponds to a band filling $n_e = 1.0$ electron and valence state $2+$.

Consequently the term $\delta n_d^{2+}(0)$ in (8) is equal to zero. Therefore, as far as occupation numbers are concerned, the excitation energy, $E_{\text{ex}}(x)$, will depend only on the occupation $\delta n_d^{3+}(0)$ and $\delta n_d^x(0)$. Concerning the absolute value of the excitation energy, E_{ex} , one verifies a monotonic decrease until the ϵ_7 level reaches the center of the effective $\tilde{\nu}_6$ level. From this point on, the $|E_{\text{ex}}|$ increases until the value $\tilde{\nu}_6/2$ is recovered, thus corresponding to the EuB_2 compound.

The mean number of electrons as a function of the B atom concentration is

$$N_e = 0.9(1-x) + 1.0 \quad (10)$$

The estimated valence is obtained as follows. Supposing $0 < x < 1$, according to (10) and using the rigid band model, one obtains N_e . So, a definite Fermi level is calculated and consequently $\delta n_d^x(0)$ (see figure 2) and $E_{\text{ex}}(x)$ are obtained also through (2) and (8).

The situation corresponds to an overlap of the sharp ε_7 level with the $\tilde{\varepsilon}_6$ level. Since one has one electron to fill up the two basic Eu configurations, given a fraction y of the available electron which "occupy" the $\tilde{\varepsilon}_6$ level having 3+ valence state, the remaining electron fraction $1-y$ have a 2+ valence state. Then the average valence (see figure 3) is given by

$$\bar{v} = 3y + 2(1-y)$$

Bauminger et al [18] have measured the lattice parameter at room temperature of $\text{Eu}(\text{Ir}_{1-x}\text{Pt}_x)_2$ as a function of x . Assuming that the average valence of Eu varies linearly with the lattice parameters one can estimate values for the Eu valence state in such compounds. These values are also presented in figure 3 in order to get comparison between our model system with a real one.

Now a few comments concerning temperature effects. As pointed out in the Introduction, the influence of the temperature on the variation of the Eu valence state in EuA_2 intermetallic compound can be described within our model. In fact, the inclusion of temperature yields for the variation of the occupation at the impurity center

$$\delta n_d(0;T) = \alpha_d \int_{-\infty}^{+\infty} \left\{ \frac{1}{|1-VF_d(\omega)|^2 + \pi^2 V^2 \rho_d^2(\omega)} - 1 \right\} f(\omega) \rho_d(\omega) d\omega, \quad (12)$$

$f(\omega)$ being the Fermi-Dirac function. It is to be expected that the occupation $\delta n_d(0,T)$ decreases with increasing T . If one imposes a charge screening equal to one in (1), where the density of states (9)

is modified by temperature (through $f(\omega)$), the self consistent screening potential V would increase with temperature. In order to obtain physically reasonable results we make the following assumption: for a given T one considers the localized potential as being the same as obtained self-consistently at 0°K , the "additional" screening being then performed by the next neighbours. We neglect these next neighbours contributions in the calculation of $\delta n_d(0, T)$ at the impurity cell. Clearly, when the next neighbours contribution becomes important one arrives at the breakdown of the "one center impurity model".

Numerical calculations show that within our band model (9), for reasonable temperatures, the changes of $\delta n_d(0)$ with T are negligible. So, we have used also quite unrealistic values for the temperature (see figure 4), just to exhibit a notable temperature effect.

We want to show the possibility to obtain a crossover process of the Eu valence value due to temperature within our picture. The occupation number at the impurity cell as function of the band filling is plotted in fig. 4 for several values of the temperature T .

Finally some experimental remarks are in order. The effect of temperature on the excitation energy is observed to be very small in EuRh_2 [21]. This agrees qualitatively with our band model (9). In fact, our model suggests one needs a very strong value for the T parameter to obtain a change in $\delta n_d(0)$ and consequently a change on the Eu valence state. On the other hand, EuCu_2Si_2 [2] shows a strong dependence of the excitation energy with temperature. We claim that for this case, the density of states must have a high density around the Fermi level in

a region comparable with $k_B T$.

4. FINAL REMARKS

We discuss some limitations of the model described in this paper, i.e. the one-center picture. It could be argued that in intermetallic compounds such as EuA_n ($n = 1, 2, 3$, etc) or pseudo-binary $\text{Eu}(\text{A}_{1-x}\text{B}_x)_n$ compounds the Eu atom concentration would invalidate the one-center picture adopted here.

We claim that the main physical idea, namely, that of screening of charge-fluctuations is expressed by the Friedel sum rule [14] in the one-center problem and by the concept of charge transfer [16] in concentrated systems. The latter tends to determine self-consistently the best approximation for atomic charge neutrality. We believe that the picture developed above, although with the one-center limitation, brings out the main physical point, that of associating valence-fluctuations to the possibility of ensuring the charge screening.

This paper does not consider explicit time dependences for physical quantities such as, for example, the decay time which would appear in a calculation of the charge-charge correlation function. Screening is invoked to discuss the relative position of the $\tilde{\epsilon}_6$ and ϵ_7 levels. The time dependences mentioned above are phenomenologically lumped together in the f levels width $\tilde{\Delta}_6$ and Δ_7 , for which we do not present a theoretical treatment.

The results of Section 2 shows evidence that our simple model accounts qualitatively for the observed features (cf Table 1). We emphasize that a conceptual advantage of our picture is that it provides an intermediate view between opposite approaches

to the valence fluctuation problem like "ionic model" [15] or the pure one electron "band picture" of valence-fluctuation [22].

Recently, Miedema [11] noted that the Eu^{2+} configuration is unstable in alloys and compounds with heat of formation larger than 23 kcal/g-atom. This indicates that the instability of the Eu^{2+} configuration sets in when the density of states at the Fermi level lies in a region corresponding to a cohesive energy larger than (by a factor 2 or 3) for noble-metals, i.e. with a significant number of empty antibonding d band states. This agrees qualitatively with our point on the role of screening in valence-fluctuation Eu compounds.

The inclusion of the concept of charge screening in the valence-fluctuation problem has been independently developed by Haldane [3], in connection with Ce compounds. This theoretical approach is also based in a single impurity view of the problem and starts from the Anderson model. The classical non-degenerate Anderson model is complemented by the inclusion of an interaction term coupling the local f states and the conduction states, which he considers to be a degenerate d band. Using symmetry arguments, the extended Anderson model reduces to two separate sub-spaces: one responsible for charge screening and the other associated to Anderson resonance model in such a way that charge neutrality is ensured. Haldane's work [3] may be compared to ours in the following terms. The sub-space solution of the Anderson model is replaced in our work by equation (4) which is a correction of the ionic model to include the interaction γ_d between the d state amplitude at the Eu site and the remaining f electrons. In our work, similarly to Haldane's, screening is performed by a separa

te channel, but within the tight-binding version of the scattering problem (Slater-Koster problem). The charge screening condition reflects then in the valence-fluctuation problem through the determination of the local self-consistent potential which defines the "impurity occupation number" $\delta n_\lambda(0)$ (see eqn. (2) so implying in the excitation energies (5).

Finally let us comment our further improvements over the model presented here. In order to take into account the concentration of Eu atoms in the mentioned intermetallics, equations (1) and (2) are reformulated in terms of the charge transfer concept [16] of the coherent potential approximation (CPA). Again the charge neutrality is ensured by a self consistent calculation [23].

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CAPTIONS

Table 1: Some experimental results reported in the literature for the Eu valence in several intermetallic compounds.

Table 2: Values for $\delta n_d(0)$, $2E_{ex}/\Delta_6$ and \bar{v} for the x concentration in the $\text{Eu}(\text{A}_{1-x}\text{B}_x)_2$ pseudobinary intermetallic compounds.

CAPTIONS

Fig. 1: Schematic energy levels corresponding to the three possible valence configurations. The error bars indicate level widths.

Fig. 2: Plot of $\delta n_d(0)$ as a function of the band filling at $T = 0K$.

Fig. 3: Average valence values \bar{v} as a function of the concentration x of B atoms. It is also indicated the valence values for Eu in $\text{Eu}(\text{Ir}_{1-x}\text{Pt}_x)_2$ compounds obtained via lattice parameters measurements [18]. (See text).

Fig. 4: Plot of $\delta n_d(0)$ as a function of the band filling for different values of the temperature T .

EuAl₄(2⁺) |5|

EuAl₂(2⁺) |5|

	EuNi ₅ (3 ⁺) 6	EuCu ₅ (2 ⁺) 6 EuCu ₂ (2 ⁺) 6 EuCu (2 ⁺) 11	EuZn ₅ (2 ⁺) 5 EuZn ₂ (2 ⁺ 3 ⁺) 5 EuZn (2 ⁺) 5
(3 ⁺) 4 EuRh ₂ (3 ⁺ , 2 ⁺) 2	EuPd ₅ (3 ⁺) 10 EuPd ₃ (3 ⁺) 6 EuPd ₂ (2 ⁺) 4 EuPd (2 ⁺) 4	EuAg ₅ (2 ⁺) 6 EuAg ₂ (2 ⁺) 12	EuCd ₅ (2 ⁺) 5 EuCd ₂ (2 ⁺) 5 EuCd (2 ⁺) 5
(3 ⁺ , 2 ⁺) 7 EuIr ₂ (3 ⁺) 6	EuPt ₅ (3 ⁺) 6 (3 ⁺ , 2 ⁺) 9, 4 EuPt ₂ (2 ⁺) 8	EuAu ₅ (2 ⁺) 6 EuAu ₂ (2 ⁺) 12	EuHg ₅ (2 ⁺) 5 EuHg ₃ (2 ⁺) 5 EuHg ₂ (2 ⁺) 5 EuHg (2 ⁺) 5

TABLE 1

x	$\delta n_d^x(o)$	$2E_{exc}/\Delta_6$	$\langle \bar{v} \rangle$
.0	.62	1.00	3.00
.2	.53	.71	2.94
.4	.44	.42	2.80
.6	.33	.06	2.54
.8	.19	.39	2.22
1.0	.00	-1.00	2.00

TABLE 2

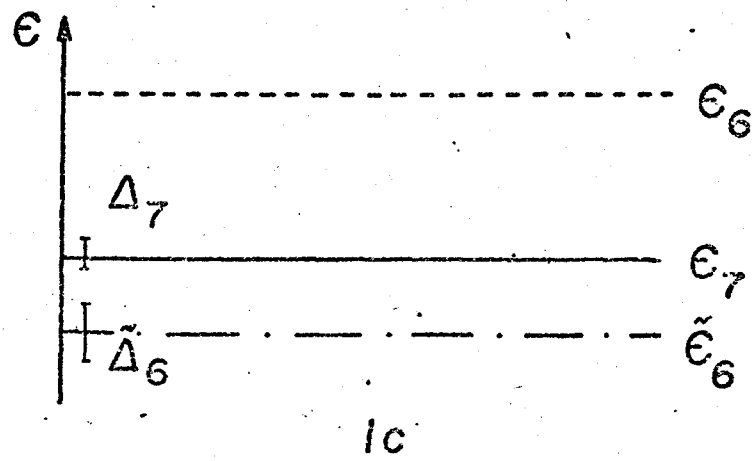
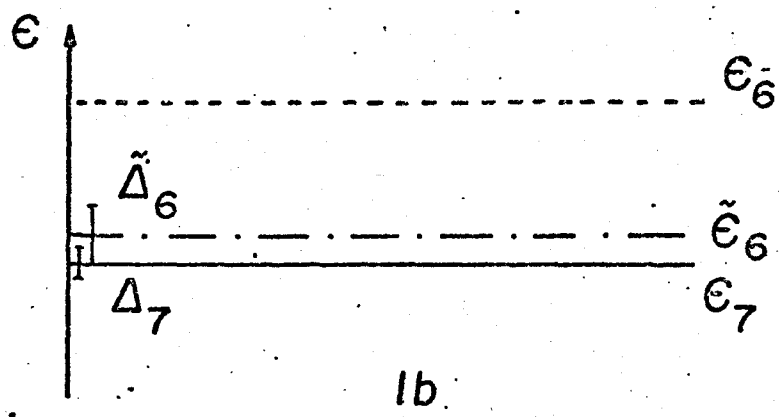
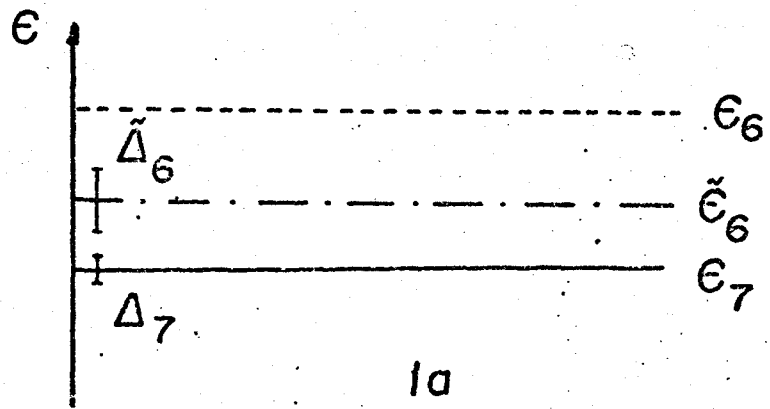


FIG. 1

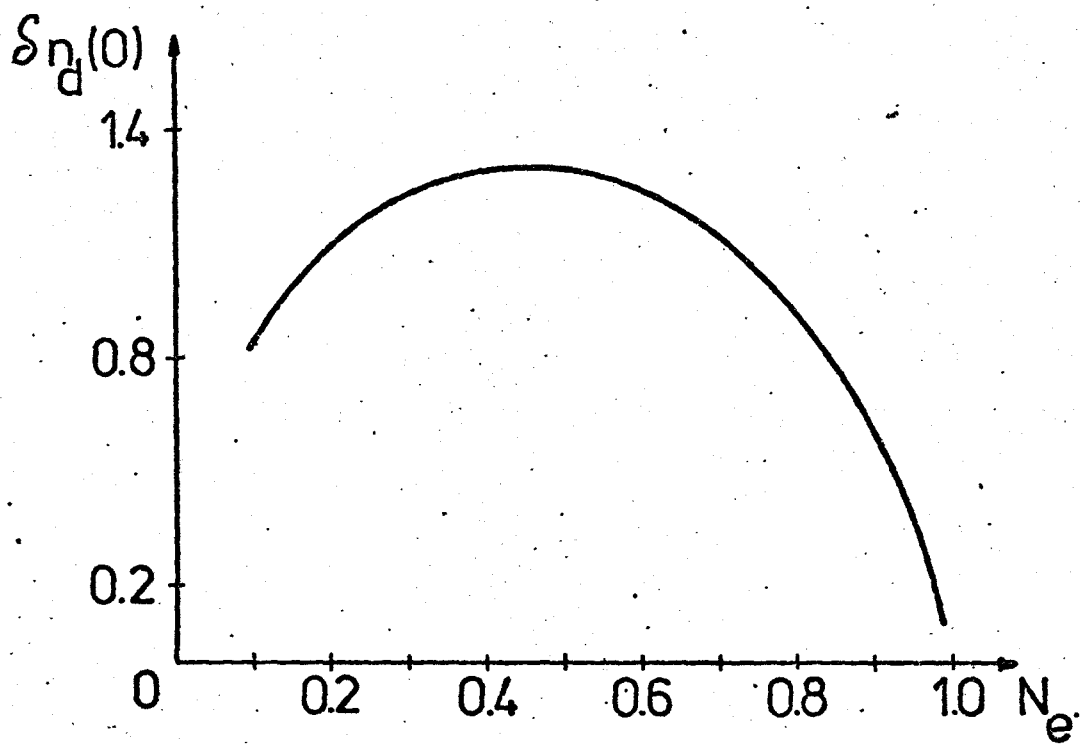


FIG.2

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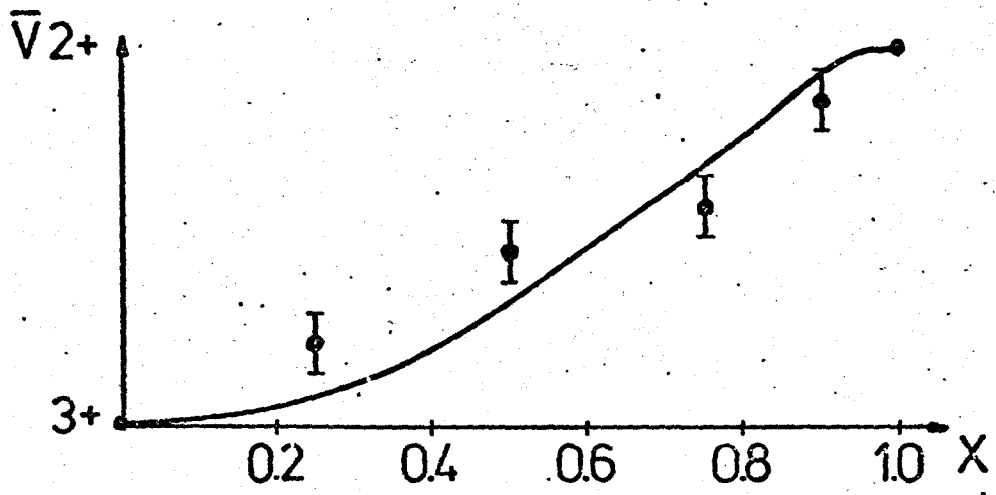


FIG.3

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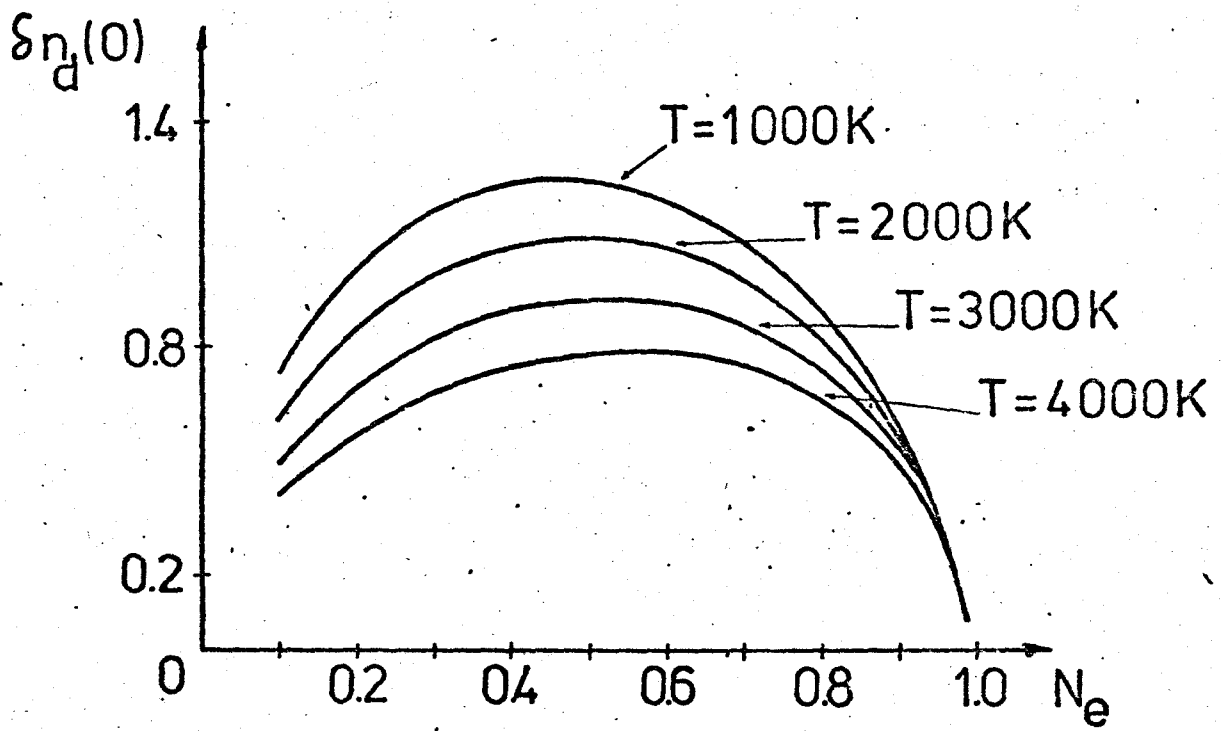


FIG.4