

A0045/77

NOV, 1977

VALENCE FLUCTUATION IN Eu-TRANSITION METAL COMPOUNDS ^{**}

O. L. T. de Menezes, A. Troper, and A.A. Gomes
Centro Brasileiro de Pesquisas Físicas
Av. Wenceslau Braz, 71, Rio de Janeiro, RJ, Brazil

and

P. Lederer^{*}
W. W. Hansen Laboratories of Physics
Stanford University
Stanford, California 94305

^{**} To appear in the Proceedings of the International Conference of Transition Metals (PTM), Toronto 1977.

^{*} On leave of absence from Laboratoire de Physique des Solides Université Paris Sud, 91405 - Orsay, France.

VALENCE FLUCTUATION IN Eu-TRANSITION METAL COMPOUNDS

O. L. T. de Menezes, A. Troper, and A. A. Gomes
Centro Brasileiro de Pesquisas Físicas, RJ, Brazil

and

P. Lederer*
W.W. Hansen Laboratories of Physics, Stanford University

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. In the latter, Eu^{++} 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.

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

* On leave of absence from Laboratoire de Physique des Solides - Université Paris Sud, 91405 - Orsay, France.

In the recent years, the study of rare-earth compounds which exhibit valence fluctuations raised several interesting questions, both experimental (see Table 1) and theoretical (Varma 1976).

The purpose of this note is to suggest a simple physical mechanism connecting the band structure of Europium intermetallics to the stability of the Eu^{2+} , Eu^{3+} configurations or the valence fluctuation regime.

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_5), which are expected to be of s-like conduction electrons at E_F . In this work, we intend to argue that the stability of the $\text{Eu} 4f$ 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 (Friedel 1969).

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

The picture, we want to suggest goes as follows: start

with the electronic structure of the intermetallic compound as derived from a band calculation assuming all the Eu atoms in the $4f^7$ configuration. We now ask the question of the stability of the assumed Eu $4f$ electron configuration with respect to an electron transfer to the conduction band, thus producing $4f^6$ configuration plus an extra conduction electron.

We analyse this question, for simplicity sake, as one center picture, i.e. we consider only one Eu center. This corresponds to an impurity like situation, where a +1 charge is left with respect to $4f^7$ shell, and should be screened by the electron gas. This screening preserves the overall charge neutrality.

The concept of charge screening has also been independently introduced by Haldane (Haldane 1977) in the description of valence fluctuations.

We want to discuss here, 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. Note that we do not deal here with dynamic effects.

In order to ensure charge neutrality, we start from Friedel's sum rule for one band case, in tight-binding form (Friedel et al. 1966),

$$\Delta Z = 1 = \frac{1}{\pi} \operatorname{tg}^{-1} \frac{\pi V \rho(E_F)}{1 - VF(E_F)} \quad (1)$$

$\rho(\omega)$ and $F(\omega)$ being the density of states and its Hilbert transform, respectively. The self-consistent screening potential V is determined from equ.(1). A measure of the localiza-

tion of the screening is then given by the change in the occupation of the "impurity cell" δn , obtained through the usual Koster-Slater problem (Koster and Slater 1954), using V determined from (1).

The stability criterion for Eu^{2+} configuration goes now as follows. Suppose that ϵ_7 is the energy of the $4f^7$ shell Eu configuration and introduce ϵ_6 as the energy of the $4f^6$ Eu pure ionic configuration. One expects, using, say the simple Hirst's relation for the zero order energy of a n -electron ionic configuration (Hirst 1970) that ϵ_6 is larger than ϵ_7 .

The Eu configuration involving 7 electrons (6f electrons plus the electrons transferred to the conduction band) is expected to have an energy (Gellat and Ehrenreich 1974):

$$\tilde{\epsilon}_6 = \epsilon_6 - \gamma_\lambda \delta n_\lambda + O(n_\lambda^2) \quad (2)$$

where $\gamma_\lambda > 0$, is the change in energy introduced by the presence of δn_λ , λ -electrons ($\lambda = s$ or d) in the Wigner-Seitz cell of Eu. In the following, one assumes equ.(2) to be valid, even for $\delta n \sim 1$. From equ.(2) 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 δn_λ and γ_λ . A crude estimate of γ_λ borrowed from isolated ions is provided for $\lambda = d$ by $\gamma_d = \epsilon_6 - \epsilon_7$. This suggests that for a strong piling of the screening charge at the "impurity center", one may produce ϵ_6 comparable to ϵ_7 or even lower. Incidentally, let us not that for s -like conduction states, one expects that, due to the large radial extension of these states, γ_s

is small and consequently $\tilde{\epsilon}_6$ is to be much higher than ϵ_7 , so stabilizing the Eu^{2+} configuration. We emphasize that perfect screening of the extra charge is assumed, the stability of Eu^{2+} configuration being associated to the weak coupling constant γ_S .

This remark enables us to understand qualitatively why Cu, Ag, Au compounds with several noble metal concentrations remain always in a Eu^{2+} configuration.

The situation corresponding to d-like Eu intermetallic compounds is now discussed, using equ.(4). Suppose that the levels ϵ_7 and $\tilde{\epsilon}_6$ exhibit natural linewidths Δ_7 , $\tilde{\Delta}_6$. In figure 1 the possible regimes are quoted, according to equ.(2). The valence fluctuation regime corresponds to a situation with overlapping width, the Eu^{3+} configuration corresponding to a state $\tilde{\epsilon}_6$ lower than the ϵ_7 level. This lowering is mainly ascribed to δn_d , which may increase if the Fermi level lies in a region of high d-density of states. At the equilibrium value x of the fluctuation valence compound, the quantity γ_λ appearing in equ.(2) is to be understood as determined from the electronic structure of the fluctuating medium. The relative positions of the $\tilde{\epsilon}_6$ and ϵ_7 levels at the Eu "impurity site" are self consistently determined by the requirement that the total excess charge be 1 while a fraction x of Eu atoms is in the $\tilde{\epsilon}_6$ state. The Eu^{3+} behavior is observed, when, say the amount of Pd in EuPd , EuPd_2 , EuPd_3 , EuPd_5 is increased where one expects a corresponding increase in the d-density of states. On the other hand, it follows from Table 1, that EuT_n compounds, T being 5d-transition elements, like Ir, stabilize the Eu^{3+} configuration, in a perfect agreement with previous band calculations (Carvalho 1974), which

show that in Laves-phase intermetallics with Co, Rh, and Ir, the d-density of states increases where one goes over from 3d to 5d transition elements.

So far the model discussed is essentially a one center picture. Real systems perform physically, when a fluctuation regime is stable, a time average of configurations with concentration x of Eu^{3+} and $(1-x)$ for Eu^{2+} . In such situation one expects, as in concentrated alloys, the screening sum rule (equ. 1) to be replaced within the CPA frame work (Gellat and Ehrenreich 1972) by a charge transfer calculation (Menezes et al.).

Acknowledgements:

The authors would like to thank Prof. J. Friedel for a critical reading of the manuscript and comments.

REFERENCES

- Carvalho J A B 1974 M.Sc. Thesis (unpublished), Pontifícia Universidade Católica, Rio de Janeiro.
- Friedel J, Gautier F, Gomes A A and Lenglard P 1966, in Quantum Theory of Atoms, Molecules and the Solid State, Academic Press, New York pp 445.
- Friedel J 1969, The Physics of Metals, I. Electrons, edited by Ziman Z M, Cambridge University Press, pp 340-408.
- Gellat Jr C D and Ehrenreich H 1974, Phys. Rev. B10 398-415.
- Haldane F D M 1977, Phys. Rev. 15 2477-2484.
- Hirst L L 1970, Phys. Kondens. Materie, 11 225-78.
- Koster G F and Slater J C 1954 Phys. Rev. 95 1167-76.
- Menezes O L T, Troper A, Magalhães A N, Lederer P, Gomes A A (to be published).
- Varma C M 1976 Rev. Modern Phys. 48 219-38.

FIGURE CAPTIONS

Table 1: Some experimental results reported in the literature for the Eu valence in several intermetallic compounds. The star indicates a valence fluctuation regime.

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

				EuAl ₄ (2 ⁺) 1
				EuAl ₂ (2 ⁺) 1
	EuNi ₅ (3 ⁺) 4	EuCu ₅ (2 ⁺) 4	EuZn ₅ (2 ⁺) 1	
		EuCu ₂ (2 ⁺) 4	EuZn ₂ (2 ⁺ 3 ⁺) 1	
		EuCu (2 ⁺) 9	EuZn (2 ⁺) 1	
	EuPd ₅ (3 ⁺) 7	EuAg ₅ (2 ⁺) 4	EuCd ₅ (2 ⁺) 1	
(3 ⁺) 2	EuPd ₃ (3 ⁺) 4			
EuRh ₂ (3 ⁺ , 2 ⁺) 3	EuPd ₂ (2 ⁺) 2	EuAg ₂ (2 ⁺) 8	EuCd ₂ (2 ⁺) 1	
	EuPd(2 ⁺) 7		EuCd (2 ⁺) 1	
	EuPt ₅ (3 ⁺) 4	EuAu ₅ (2 ⁺) 4	EuHg ₅ (2 ⁺) 1	
			EuHg ₃ (2 ⁺) 1	
	(3 ⁺ , 2 ⁺) 6, 2			
EuIr ₂ (3 ⁺) 4	EuPt ₂ (2 ⁺) 5	EuAu ₂ (2 ⁺) 8	EuHg ₂ (2 ⁺) 1	
			EuHg (2 ⁺) 1	

TABLE 1

- (1) Wallace W E 1973 Rare Earth Intermetallics, Academic Press, New York.
- (2) Wickman H H, Wernick J H, Sherwood R D and Wagner C F 1968 J. Phys. Chem. Solids 29 181-182.
- (3) Bauminger E R, Felner I, Froindlich D, Levron D, Nowik I, Ofer S and Yanovsky R 1974 J. Physique C6 61-70.
- (4) Gschneider K A 1969 J. Less-Common Met. 17 1.
- (5) Moser J, Klein U F, Wortman G and Kalvius G M 1977 Physica 86-88B 243-245.
- (6) Erdman B and Keller C 1973 J. Solid State Chem. 7 40.
- (7) Longworth G and Harris I R 1973 J. Less-Common Met. 33 83.
- (8) van Steenwijk F J 1976, Thesis, Rijks Universiteit, Leiden.
- (9) Mildema A R 1976 J. Less-Common Met. 167-173.

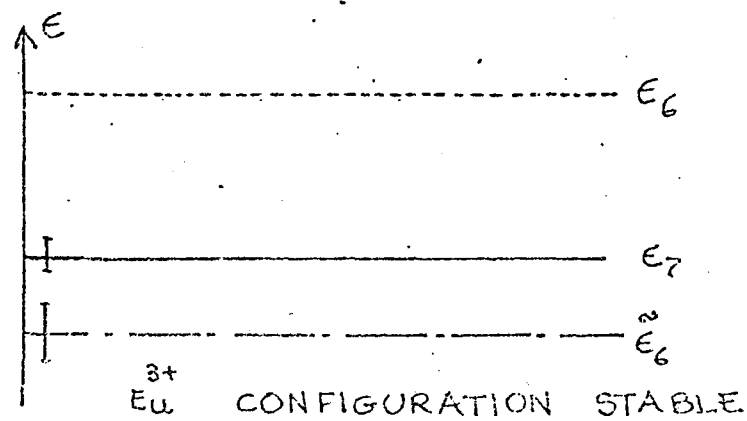
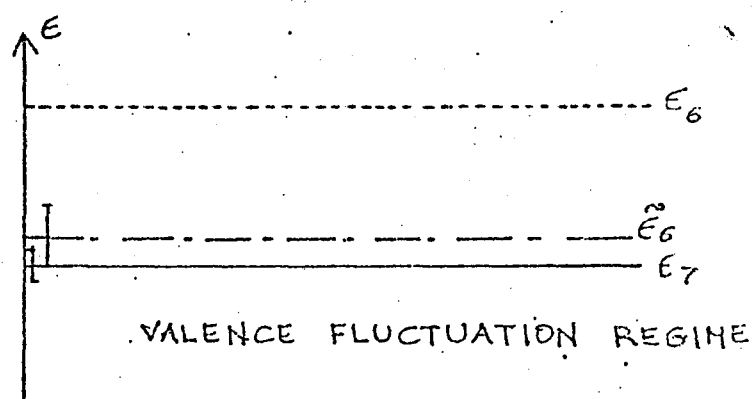
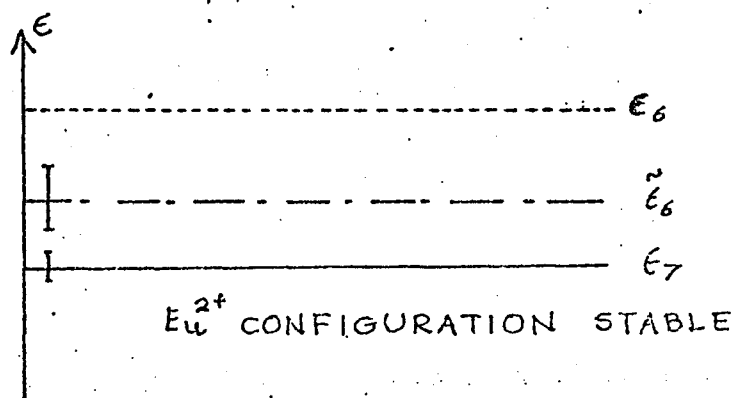


FIG. 1