PHYSICAL REVIEW B VOLUME 17, NUMBER 10 15 MAY 1978

# Temperature effects in the valence fluctuation of europium intermetallic compounds

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(Received 4 January 1978)

A previously reported model for valence fluctuations in europium compounds is extended in order to account for thermal-occupation effects. Experimental results are critically discussed and new experiments are suggested.

The problem of valence-fluctuation in europium intermetallic compounds in the framework of a one-center picture was discussed in a recent work.[1] It was suggested that the charge screening can provide a physical mechanism connecting the band structure of europium intermetallic compounds to the stability of $Eu^{2+}$, $Eu^{3+}$ configurations or the valence-fluctuation regime. The model may explain the change of the excitation energy ($E_{ex}$) between two europium valence configurations, namely, $4f^6 5d^1$ for $Eu^{3+}$ and $4f^7$ for $Eu^{2+}$. The main ideas of the model are as follows: the transfer of one electron from the $4f^7$ configuration to the conduction band introduces a +1 charge that must be screened by the electron gas to preserve the overall charge neutrality. The configuration with 6 localized $f$ electrons plus one in the conduction band has an energy $\tilde{\epsilon}_6$, and is connected with $\epsilon_6$, the energy of the pure ionic $4f^6$ configuration, by the approximate relationship

$$\tilde{\epsilon}_6 = \epsilon_6 - \gamma_d \delta n_d(0) , \qquad (1)$$

where $\gamma_d$ is the change in energy introduced by the presence of $\delta n_d(0)$ electrons at the impurity center. Because of $\gamma_d \delta n_d(0)$, $\tilde{\epsilon}_6$ may be of the same order than $\epsilon_7$ (the energy of the $4f^7$ configuration) or lower. The model does not include dynamic effects. One has taken phenomenological linewidths $\tilde{\Delta}_6$ and $\Delta_7$, for each level,[1] so that the overlap of these broadened levels could describe a valence-fluctuation regime.

In order to check the model against some available experimental data, we have performed[1] simple numerical calculations. We considered a $Eu(A_{1-x}B_x)_2$ pseudobinary intermetallic system, $A$ and $B$ being transition metals (e.g., Ir, Pt). This disordered system was described in the simplest way, taking disorder into account through the virtual crystal approximation. The europium valence in $EuA_2$ and $EuB_2$ compounds were taken as 3+ and 2+, respectively. The crossover between the two valence states is achieved when $x$ ranges from 0 to 1.

We have also analyzed the role of temperature on the calculation of electronic quantities like $\delta n_d(0)$ and from (1) on the $E_{ex}$ for a given compound. For a parabolic $d$-band shape[1] such effects become relevant only at high temperatures (~1000 K), when the change of $\delta n_d(0)$ is appreciable. This result supports a previous study of the Eu isomer shift in $EuRh_2$.[2] based on a temperature-independent excitation energy.

In this communication we want to extend the model of Ref. 1 in order to discuss temperature and concentration effects on the europium valence in compounds like $Eu(A_{1-x}B_x)_2$. The discussion is restricted to situations where, for a given concentration, the electronic contribution to $E_{ex}$ is roughly temperature independent. Then, temperature effects arise from the thermal occupation of the $\tilde{\epsilon}_6$ and $\epsilon_7$ level, which should be described by the appropriate statistics. In this study, degeneracy effects will be briefly discussed. Again, since this extended model does not include dynamics, the level widths will be treated phenomenologically.

Consider an intermetallic compound $EuA_2$ exhibiting a strong $d$-character conduction band. The local change $\delta n_d(0)$ is governed by the screening condition in the $Eu^{3+}$ configuration.[1] For a simple band shape (parabolic) the temperature dependence of $\delta n_d(0)$ is almost negligible.[1] Then, in order to discuss temperature effects, let us start with some remarks on the appropriate statistics for this problem.

Hirst[3] emphasized that the conduction states obey the Fermi-Dirac statistics, whereas the rare-earth ionic states obey the Boltzmann statistics. This point of view was adopted in different experimental works[2,4] to obtain values of $E_{ex}$ and the effective linewidth of the $4f^7$ level. On the contrary, the theoretical approaches starting from an Anderson Hamiltonian incorporate *ab initio* the Fermi-Dirac statistics.[5,6]

The use of the Boltzmann statistics for the $4f$ levels introduces difficulties in the description of the fluctuations at very low temperature, since only one level will be occupied. To avoid this problem Sales and Wohlleben[5] have assumed a "quasi-Boltzmann" partition function by inserting a phenomenological fluctuation temperature $T_{sf}$, associated by Sales and Visvanathan[7] to the linewidth of the $4f$ level.

Klaase *et al.*[8] have observed that this formulation is in conflict with Nernst's law. Indeed, Sales[9] recently assumed that the temperature-dependent occupation of the broadened $4f$ configuration is to be described within the Fermi-Dirac statistics. In that work some experimental results were fitted starting from this assumption.

A few remarks about the choice of the Fermi statistics may be added. Usual microscopic models[5,6] describe valence fluctuation in terms of fermion excitations. In Alascio's work,[5] which is closest to our phenomenological formulation, the valence fluctuations are described by the usual conduction-band fermion excitations together with ionic excitations (from a $|n,J\rangle$ to a $|n-1,\ J'\rangle$ many electron state) defined by fermion-like operators. $J$ and $J'$ are the angular momentum of the $n$, $n-1$ configurations. Hybridization between conduction and localized states is introduced and an approximate Green's function treatment is presented.[5] Although our model[1] does not include hybridization and consequently does not account for levels widths we still keep the fermion-like character of the excitations.

The normalized occupation of the two europium configurations, with $n-1$ and $n$ electrons for a given temperature $T$, is

$$P_{(n-1)}+P_{(n)}=1\ , \tag{2a}$$

$$P_{(n-1)}=\int_{\infty} f(\epsilon)\frac{\tilde{\Delta}_6}{\tilde{\Delta}_6^2+(\epsilon-\tilde{\epsilon}_6)^2}\,d\epsilon\ , \tag{2b}$$

$$P_{(n)}=\int^{\infty} f(\epsilon)\frac{\Delta_7}{\Delta_7^2+(\epsilon-\epsilon_7)^2}\,d\epsilon\ , \tag{2c}$$

where $f(\epsilon)$ is the Fermi function and a Lorentzian shape for the broadened $4f$ level was assumed. The terms $P_{(n-1)}$ and $P_{(n)}$ in (2a) are assumed to contain implicitly degeneracy effects. In fact, since we are not calculating susceptibilities, the external magnetic field is set equal to zero. Within the manifold $\{M\}$ of states associated to the angular momentum $J$, the occupation probability is identical for each state. In order to get the probability per degenerate level $M$ one should divide $P_{(n-1)}$ and $P_{(n)}$ respectively by $2J+1$ and $2J'+1$. The total probability of occupation for each configuration is given by the sum over the manifold and (2) follows.

The mean valence extracted from Mössbauer and lattice parameter measurements depends on the occupation of each configuration and is given by

$$\bar{V}=3P_{(n-1)}+2P_{(n)}\ . \tag{3}$$

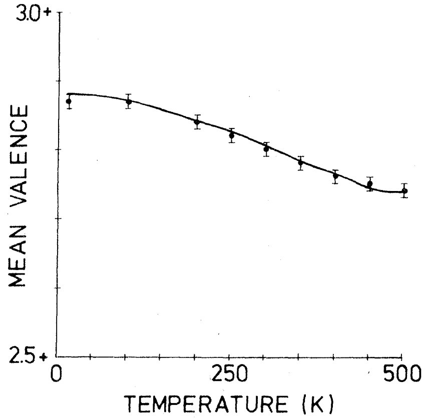

FIG. 1. Theoretical curve of the mean valence of Eu in $EuRh_2$ as a function of temperature. The experimental points are taken from isomer-shift measurements (Ref. 2).

We further assume $\tilde{\Delta}_6\sim\Delta_7\sim\Delta$. This is expected to be true for a compound which exhibits fast fluctuation between the two europium configurations. This assumption is not necessarily valid for values of $x$ near 0 and 1, where only one configuration is almost completely stable.[9]

We obtain a simple relation between $E_{ex}$ and $\Delta$ from (2) at $T=0$ K:

$$\bar{V}=2.5+(1/\pi)\arctan(E_{ex}/\Delta)\ . \tag{4}$$

The experimental value for $\bar{V}$ at $T=0$ K and at another temperature (e.g., room temperature) allows determination of $E_{ex}$ and $\Delta$.

Figure 1 shows an application of the above considerations. Isomer shift measurements of $EuRh_2$ as a function of temperature were reported in Ref. 2. In order to check the model defined by Eqs. (2) one adopts the following procedure: using the values of the isomer shift in extreme temperature limits, the $T=0$ K extrapolation and $T=500$ K, from (2)–(4) one gets $E_{ex}$ (assumed to be temperature independent) and the linewidth $\Delta$. These results inserted back in (2) and (3) generate the intermediate temperature values, which agree with the experimental results. This analysis yields $E_{ex}\sim 1250$ K and $\Delta\sim 270$ K. This is to be compared to the results of Bauminger *et al.*[2] who obtain the values of 1550 and 615 K, respectively. This difference in the linewidth is to be ascribed to the different starting assumptions.

Up to here one has analyzed only "pure" compounds; now we turn our attention to compounds of the form $Eu(A_{1-x}B_x)_2$. The above discussion provides a mechanism to study the temperature dependence for a compound of a given concentration.

The existence of two physical quantities (concentration and temperature) suggests the construction

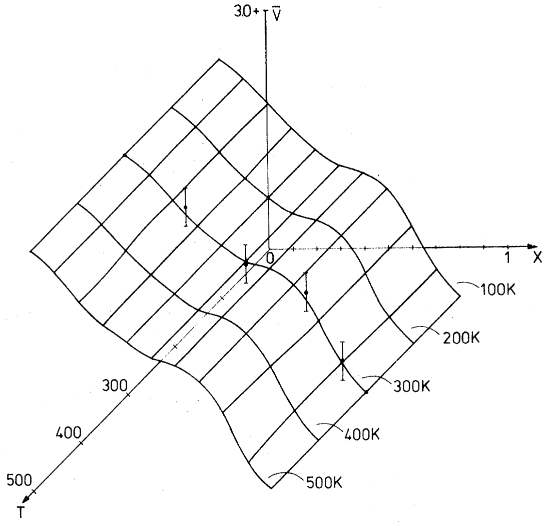

FIG. 2. Mean valence as a function of temperature and $x$ concentration of $\mathrm{Eu}(A_{1-x}B_x)_2$ intermetallic compounds (see text).

of the surface obtained by plotting the valence as a function of $x$ and $T$. Firstly, we describe how this surface may be constructed using the model of Ref. 1. The possibility of obtaining the surface from experimental data independently of some assumptions of the model will be mentioned later on.

The construction of Fig. 2 goes as follows: the excitation energy $E_{\mathrm{ex}}$ changes because $\delta n_d(0)$ varies with concentration and we calculate this using the virtual crystal approximation of Ref. 1. The linewidth for each concentration, is assumed to be the same for both europium configurations. In the absence of dynamics in our picture we associate a fluctuation time of $10^{-11}$ sec at the extreme concentrations ($x = 0$ and $x = 1$).[9] For the intermediate concentration $x = 0.5$ we adopt a linewidth compatible with fast fluctuations, namely, a fluctuation time of the order of $10^{-15}$ sec,[9] in between we adopt a linear interpolation. The results are shown in Fig. 2, where we present also for room temperature, the valence observed in the compound $\mathrm{Eu}(\mathrm{Ir}_{1-x}\mathrm{Pt}_x)_2$ as a function of $x$. This enables a comparison between the model results and the experimental ones. We emphasize that Fig. 2 was constructed under a simplified theoretical model. If systematic experimental investigations were available for the Isomer shift, these results could be plotted in a surface. The method outlined for the construction of Fig. 1 would then free us from the phenomenological linewidth assumptions.

The information provided by the surface constructed directly from experiment can be summarized as follows. For a given concentration $x$, using data from low temperatures and following the method used in the construction of Fig. 1 one derives the quantities $E_{\mathrm{ex}}(x)$ and $\Delta(x)$. Repeating this procedure for several values of $x$ one gets $E_{\mathrm{ex}}$ vs $x$. This plot contains the required information concerning the electronic contributions involved. In fact, assuming Eq. (1), one derives the electronic correction $\gamma_d \delta n_d(0)$. In this quantity are incorporated both the charge screening condition and the alloying $(A_{1-x}B_x)$ effects, in particular the neighbor correction invoked by Bauminger *et al.*[2] Indeed, a detailed theoretical computation of $\delta n_d(0)$ could involve an extended coherent potential approximation (CPA) calculation of the disordered $d$ band of the $\mathrm{Eu}(A_{1-x}B_x)_2$ compound including neighbor corrections,[10] together with the local screening hypothesis discussed in Ref. 1. Thus, the advantage of this method with respect to the empirical formula of Bauminger *et al.*[2] is to separate clearly statistical effects from the pure electronic ones, and could provide an estimate of the neighbor effects as compared to the simple virtual crystal approach adopted here through the more realistic CPA.

To conclude, let us emphasize our main points. First of all, the model developed in Ref. 1 suitably extended by the use of Fermi statistics to include thermal effects, account under simple approximations for the available data (cf. Fig. 2). Secondly, we suggest a way to extract the excitation energy from the experimental temperature-dependent valence (cf. Fig. 1) which is free from model dependent assumptions for the electronic effects. This enables a direct test of the predictions of the model developed in Ref. 1.

## ACKNOWLEDGMENTS

The authors would like to thank Dr. P. Lederer for many useful discussions during this work.

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