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THE EFFECT OF THE ELECTRONIC AND STRUCTURAL ENVIRONMENT ON THE VALENCE OF CERIUM

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Summary

By means of a semiempirical analysis the electrostatic energy E_ψ of a charge immersed in the screened Coulomb potential of the total charge distribution of the metal was selected as the most appropriate parameter for correlating different cerium environments. The choice was made by determining the smallest dispersion in plots of various physicochemical parameters *versus* the rate of depression α of the superconducting transition temperature T_c of thorium-based alloys containing cerium impurities. The magnetic moment of cerium, which depends on the environment, was found to have the greatest effect on the depression of T_c. E_ψ was found to be proportional to $\alpha^{-1/2}$.

The analysis was extended to some AB_j compounds (A ≡ elements of groups II - V including cerium and thorium; $B_j \equiv N$, Sn_3, Tl_3, Rh_3, Co_2, Ir_2, B_6 and Be_{13}). An empirical relationship between E_ψ and the volume contraction $\Delta V/V$ due to the formation of the compound was found. The cerium valence for any CeB_j compound is deduced from the E_ψ(Ce) value compatible with the curve of $\Delta V/V$ *versus* E_ψ(A), taking into account the fact that the valence and atomic radius of cerium are related.

1. Introduction

The valence Z^* of cerium in different alloys and compounds depends mainly on parameters such as pressure, temperature and the electronic and structural environment. The external variables pressure and temperature are able to shift Z^* over some tenths of its total possible range ($3 \leqslant Z^* \leqslant 4$), except in those cases (*e.g.* pure cerium) in which the system undergoes a first-order transition. Variation of the environment by alloying can enable the cerium ion to exhibit all of its possible valence values in which it retains, on average, anything from one to zero electrons in its 4f shell [1].

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Microscopic models that attempt to describe the mechanism by which the cerium f electron delocalizes (or fluctuates between two consecutive electronic configurations) usually take as a starting point the fact that the localized 4f state E_{4f} and the Fermi level E_F are energetically very close [2], *i.e.*

$$E_{ex} = E_{4f} - E_F \approx \Delta \text{ or } k_B T$$

where Δ is the hybridization energy and $k_B T$ is the thermal energy. This procedure does not require an understanding of the reason for this quasi-degeneracy which depends strongly on the chemical environment.

The changes in energy of the electronic configuration associated with alloying are related, among other things, to changes in the chemical potential μ ($\mu = E_F$). In general it is not possible to calculate changes in μ because it depends on a large number of unknown parameters. It is also difficult to select a parameter that can be used to compare quantitatively different environments. However, a physicochemical parameter that relates all the elements that are able to form a particular environment (*i.e.* all the A elements that form the same AB_j compound with a specific partner B) can be sought.

A comparison between different environments by examination of their A elements is shown in Fig. 1 in which families of isostructural AB_j compounds are ordered as a function of the magnetic contribution of cerium to the CeB_j phase normalized to the expected contribution from a trivalent cerium ion at 300 K. The A elements on the ordinate are ordered according to the value of the parameter $\log E_\psi(A)$ which will be discussed later. The vertical line for each family extends over the range of A elements for which a particular AB_j is formed. The valence regime and the magnetic behaviour of cerium in the phases given in the lower part of the figure are shown in the upper part of the figure.

The concept of electronegativity ϵ, introduced by Pauling [3] to explain the tendency of atoms to attract electrons to themselves, is qualitatively useful in this work. Gordy and Orville Thomas [4] and Phillips [5] have proposed formulae to calculate ϵ, but generally it is taken as a trend shown by the elements. Other parameters that can be used for comparing different environments are the work function Φ, the electron density n_{ws} in the Wigner–Seitz cell and the screening length λ. n_{ws} and λ appear to be more appropriate quantities if the system is a metal ($\lambda = f(n_{ws})$). The function Φ can be obtained experimentally; however, it shows a great deal of variability in compounds and no simple expression for its calculation has been derived [6].

Another parameter which can be considered is the energy E_ψ of a charge q immersed in the screened Coulomb potential of the total charge distribution of the metal which is given by $E_\psi = q\psi$ [7]. A simple approximation, useful for our correlation work, is the usual screened potential

$$\psi \propto \frac{Ze}{r} \exp(-\lambda r) \tag{1}$$

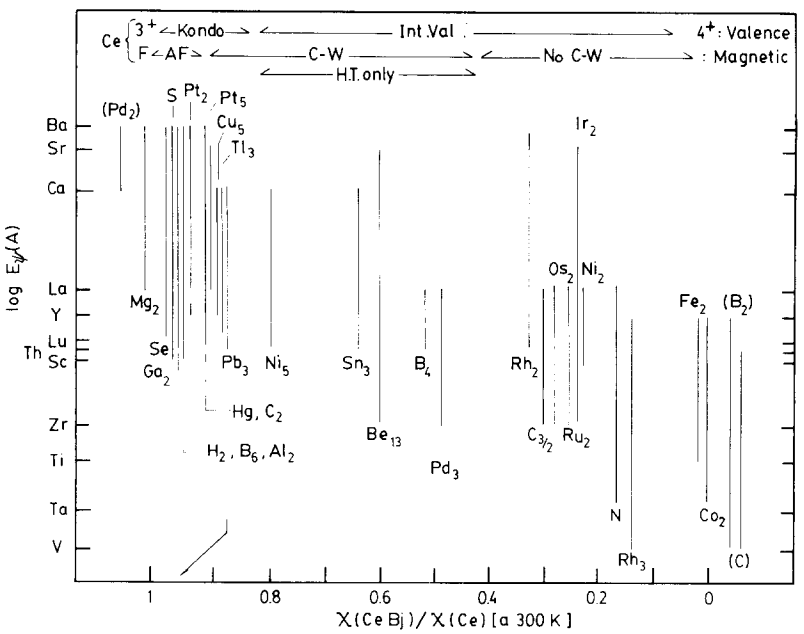

Fig. 1. Families of isostructural AB_j compounds ordered as a function of the normalized magnetic contribution of cerium to the CeB_j phases. The A elements on the ordinate are ordered according to the value of log E_ψ(A) (see text) and the vertical line includes all the A elements for which a particular AB_j is formed. The valence regime and the magnetic behaviour of cerium in the phases given in the lower part of the figure are shown in the upper part of the figure. The B_j in parentheses do not form compounds with cerium.

where Z is the valence of the metal, e is the electronic charge, r is the Goldschmit 12-fold coordination atomic radius and $\exp(-\lambda r)$ is the Thomas–Fermi screening factor. The correlations derived justify the use of this approximation. In the case of cerium the trivalent and tetravalent atomic radii (r_3 = 1.846 Å and r_4 = 1.688 Å) are taken from ref. 8. The screening length λ is obtained from macroscopic parameters:

$$\lambda \propto (Z/V_{at})^{1/6}$$

where V_{at} is the atomic volume. If the charge q is an electron lying in the outermost orbital of an atom, it still sees a screened potential because $r > 4\lambda^{-1}$ in the elements under study. It is probable that ψ represents only the nearest-neighbour contribution because the potential due to the second-nearest neighbours was estimated to be about an order of magnitude smaller. In Fig. 2 we show the relative values of all the parameters discussed above for A elements from groups II - V of the periodic table including thorium and trivalent and tetravalent cerium (Ce^{3+} and Ce^{4+} respectively). In the case of pure elements $q = Z$. The E_ψ(A) values are listed in Table 1.

We now need a physically measurable property, sensitive to the chemical environment, which allows us to select the most appropriate parameter from those proposed above. The valence of an element (such as cerium, ytterbium,

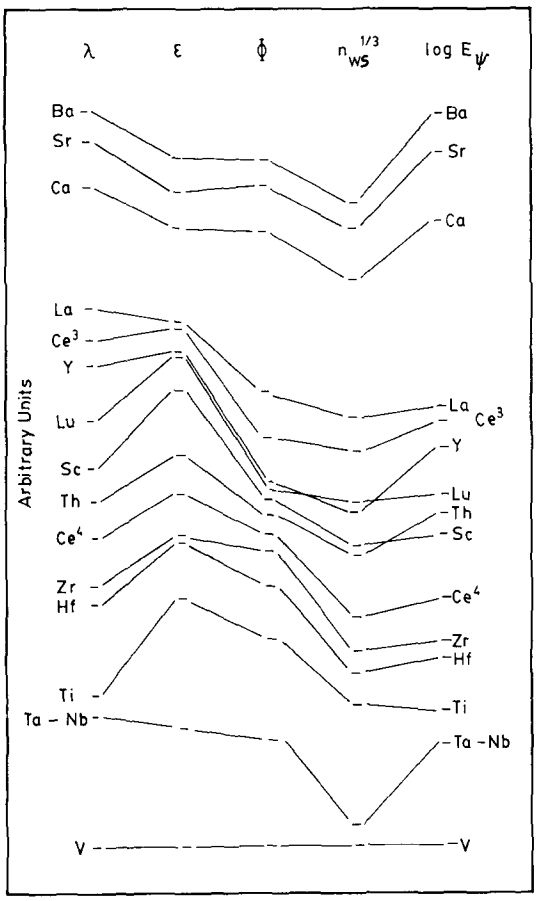

Fig. 2. Comparison of the values of environment-dependent parameters for elements in groups II - V including thorium and trivalent and tetravalent cerium (Φ and $n_{ws}^{1/3}$ were taken from ref. 9).

uranium etc.) that precisely depends on the chemical environment is a suitable parameter for this application.

2. Alloys

When a paramagnetic impurity is introduced into a superconducting matrix, the transition temperature T_{c0} is strongly affected by the magnetic moment of the impurity [10]. Therefore cerium impurities can be used as a probe for comparing the chemical environment in superconducting thorium-based alloys in the system Th_iX_j with $i + j = 1$ and X ≡ La, Y, Sc, Lu, Zr or Hf [11]. The magnetic moment of the cerium impurities in these matrices is weakened because of the strong admixture between the localized and conduction electron states. In this case the depression of T_{c0} to the reduced

TABLE 1

Parameters used to calculate $E_\psi(A)$ for A elements from groups II - V including thorium and trivalent and tetravalent cerium

Element A	*Valence Z*	*Goldschmit radius r* (Å)	*Atomic volume* V_{at} (Å^3)	$E_\psi(A)$ (eV)
Ba	2	2.24	65.2	0.113
Sr	2	2.15	57.2	0.130
Ca	2	1.97	42.8	0.168
La	3	1.87	37.4	0.335
Ce^{3+}	3	1.846[a]	35.6	0.347
Y	3	1.790	32.9	0.388
Gd	3	1.795	33.0	0.383
Lu	3	1.72	29.6	0.446
Sc	3	1.63	25.0	0.527
Th	4	1.81	32.8	0.512
Ce^{4+}	4	1.688[a]	27.2	0.663
Zr	4	1.59	23.4	0.826
Hf	4	1.58	22.6	0.829
Ti	4	1.47	17.7	1.029
Ta	5	1.46	18.1	1.480
Nb	5	1.45	17.9	1.484
V	5	1.34	13.9	1.881

[a]Values taken from ref. 8.

value T_c can be fitted by a modified exponential function first proposed by Kaiser [12]:

$$\frac{T_c}{T_{c0}} = \exp\left(-\frac{\alpha n_i}{1-\delta n_i}\right)$$

where n_i is the number of impurity atoms present.

In Fig. 3 we show the relationship between E_ψ and the initial rate of depression α of T_c given by

$$\alpha = \frac{1}{n_i} \ln\left(\frac{T_c}{T_{c0}}\right) \qquad (n_i \to 0)$$

We found that, of all the parameters discussed above, E_ψ plotted against the measured value of $\alpha^{-1/2}$ showed the smallest dispersion. The standard deviations S for the various parameters plotted *versus* $\alpha^{-1/2}$ (in arbitrary units) are $S(\epsilon) = 0.22$, $S(\Phi) = 0.27$, $S(n_{ws}^{1/3}) = 0.31$, $S(\lambda) = 0.16$ and $S(E_\psi) = 0.09$. The value of E_ψ for any Th_iX_j alloy is estimated as the weighted average of the values for the components:

$$E_\psi(Th_iX_j) = iE_\psi(Th) + jE_\psi(X) \qquad (2)$$

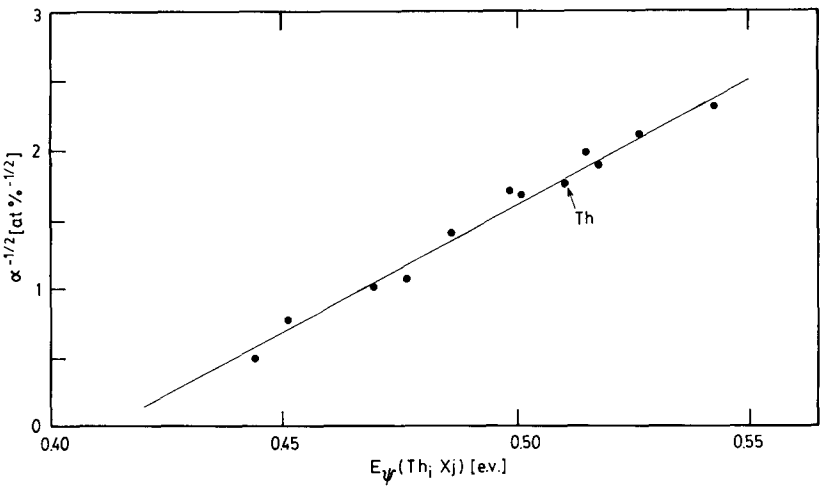

Fig. 3. Relationship between the initial rate of depression α of T_c α and the electrostatic energy E_ψ of an atom immersed in the screened Coulomb potential due to the rest of the metal calculated for Th_iX_j matrices ($X_j \equiv La_{0.35}$, $La_{0.20}$, $Y_{0.56}$, $Y_{0.35}$, $Lu_{0.20}$, $Y_{0.10}$, $Sc_{0.10}$, $Sc_{0.35}$, $Sc_{0.20}$, $Zr_{0.10}$, $Hf_{0.05}$) and pure thorium using eqn. (2). The values of α were obtained from ref. 11.

This assumption is justified because in a metal (a) the valence electrons are not localized at individual atoms and (b) the interatomic distances are homogeneously distributed.

The valence of cerium in the Th_iX_j alloys can be deduced by assuming that a cerium atom in the matrix will adapt its valence Z^* and volume such that its energy in the electrostatic field ($E_\psi(\mathrm{Ce}) = Z^*\psi$) will be equal to that of an average matrix atom ($E_\psi(\mathrm{Ce}) = E_\psi(\mathrm{M})$). In the evaluation of ψ using eqn. (1), Z and λ are taken to have the matrix values because these depend on the valence and the electron density of the entire alloy. The interatomic distance d may, however, be locally distorted because the cerium volume in that environment may differ from the average volume of a matrix atom. We therefore use the value

$$d = r^*(\mathrm{Ce}) + r(\mathrm{M})$$

where $r(\mathrm{M})$ is the average atomic radius of the matrix and $r^*(\mathrm{Ce})$ is a function of Z^* that can be evaluated by using the Gschneidner relationship [13]:

$$Z^* = 13.61 - 5.75r^*(\mathrm{Ce})$$

The equation for Z^* can thus be written

$$Z^* = \frac{E_\psi(\mathrm{M})}{14.4}\,\frac{d}{Ze^2}\,\exp\left(\frac{\lambda d}{2}\right) \qquad (3)$$

In the case of the ThCe alloy we obtain $Z^* = 3.6$ which is in agreement with the value obtained from the magnetic moment of cerium in that alloy at room temperature [14].

We emphasize that the equilibrium condition assumed here is the invariance of E_ψ when a matrix atom is replaced by cerium atom. This is equivalent to taking E_ψ as the primary determinant of the total energy.

3. Compounds

Having verified E_ψ as the most appropriate parameter for comparing the chemical environments of cerium in alloys, we can now attempt to extrapolate this analysis to a family of compounds that includes a cerium compound. We consider compounds of general formula AB_j in which A is an element of groups II - V including cerium and thorium and B is fixed.

In most cases it is impossible to determine precisely the valence which the partner B assumes in the compound. The B elements considered here do not usually show a simple relationship between valence and metallic radius as is the case for elements lower in the periodic table. Therefore we cannot estimate E_ψ directly from eqn. (1). None the less, although absolute values for $E_\psi(AB_j)$ may not be available, we can compare the $E_\psi(Ce)$ value with the values of $E_\psi(A)$ for the other A elements in the same family of compounds. We assume that the unknown value of $E_\psi(B_j)$ is constant for a single family of compounds. In terms of eqn. (2) we can express this as

$$E_\psi(A_1B_j) - E_\psi(A_2B_j) = E_\psi(A_1) - E_\psi(A_2)$$

Different partners will simply shift the scale.

We can calculate $E_\psi(Ce)$ for a given AB_j family if we assume that the cerium is in the trivalent or tetravalent state where we know Z^*. However, if the cerium has an intermediate valence we cannot calculate $E_\psi(Ce)$ and we have to seek a measurable parameter $\beta(AB_j)$ which, when related to $E_\psi(A)$, will allow us to estimate $E_\psi(Ce)$ from the measured value of $\beta(CeB_j)$. We first check this procedure by taking β as the standard heat of formation ΔH_f of the nitride family AN.

$\Delta H_f(AN)$ (values taken from ref. 15) is plotted against $\log E_\psi(A)$ in Fig. 4(a) where the full curve represents the relationship between these parameters, *i.e.* $\Delta H_f(AN) = f\{E_\psi(A)\}$. This relationship can be used to estimate $E_\psi(Ce)$ in CeN from the point where the $\Delta H_f(AN)$ curve reaches the $\Delta H_f(CeN)$ value. The valences $Z^*(Ce)$ of cerium corresponding to the $\log E_\psi(A)$ values on the abscissa are also included.

Because ΔH_f values are not known for other families of compounds, we must replace ΔH_f by a parameter that can be estimated for all compounds under investigation. Such a parameter is the percentage volume contraction due to the formation of the compound which is defined by

$$\beta = \frac{\Delta V(AB_j)}{V} = 100\left(\frac{V_{AB}}{V_A + V_B} - 1\right)\% \qquad (4)$$

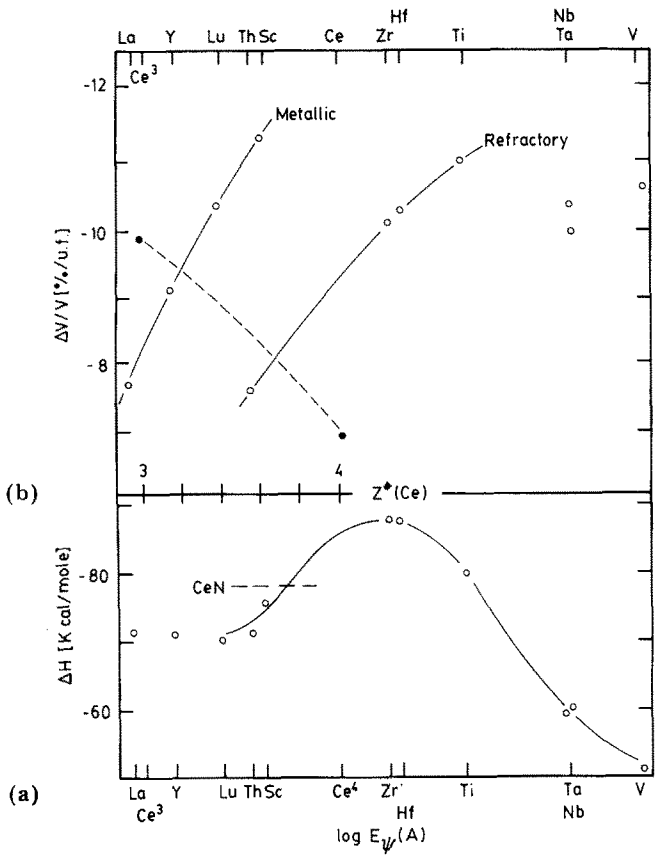

Fig. 4. (a) ΔH_f *vs.* log E_ψ(A) for the nitrides AN (○) (– – –, ΔH_f for CeN; Z^*(Ce) is the cerium valence corresponding to the values of log E_ψ(A) on the abscissa); (b) $\Delta V/V$ for AN *vs.* log E_ψ(A) (——) and $\Delta V/V$ for CeN *vs.* log E_ψ(Ce) calculated as a function of Z^*(Ce) (– – –) (the crossing points of these curves give two possible values for the cerium valence in this compound (see text for details)).

and is related to the magnitude of ΔH_f [16]. In some cases it is easier to use the atomic contraction $\Delta d/d$ (*i.e.* the reduction in the interatomic distance d). Then eqn. (4) becomes

$$\frac{\Delta d(\mathrm{AB})}{d} = 100\left(\frac{2d_{\mathrm{AB}}}{d_{\mathrm{A}} + d_{\mathrm{B}}} - 1\right)\%$$

Figure 4(b) shows the application of the procedure using $\Delta V/V$ to the nitride family. The curve of volume contraction $\Delta V/V$ *versus* E_ψ(A) reaches a maximum at E_ψ(Sc); at higher values of E_ψ(A) a second branch corresponding to the refractory nitrides appears [17]. In the figure $\Delta V/V$ for CeN is plotted against log E_ψ(Ce) as the locus of points for which the coordinates are varied continuously between their values for trivalent and tetravalent cerium. An effective value for $E_\psi{}^*$(Ce) is obtained from the point where the locus crosses the log E_ψ(AN) *versus* $\Delta V/V$ curve. In the AN family the two

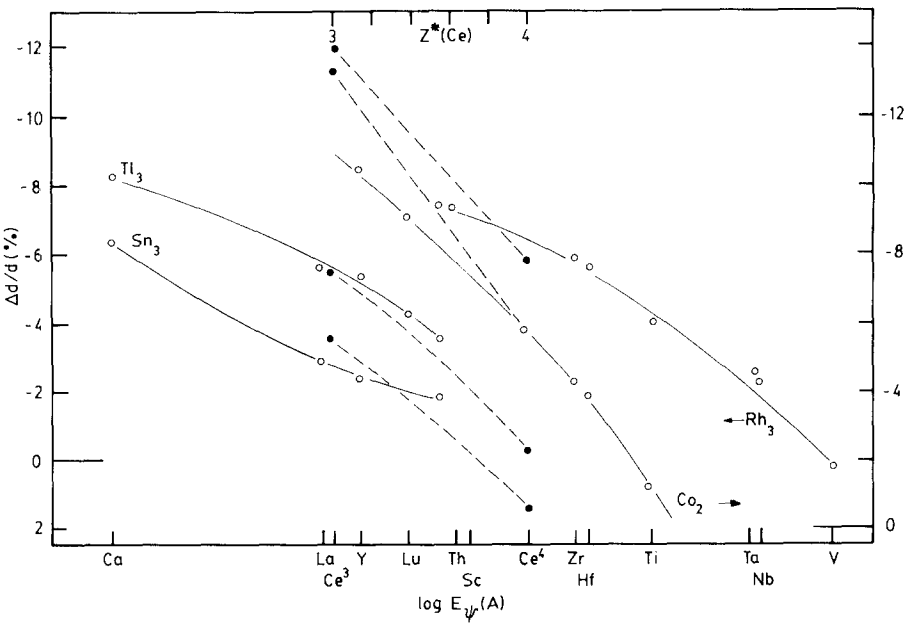

Fig. 5. $\Delta d/d$ *vs.* log E_ψ(A) (——) and $\Delta d/d$ *vs.* log E_ψ(Ce) calculated as a function of Z^*(Ce) (– – –) for ASn_3, ATl_3, ARh_3 and ACo_2. The crossing points of the two sets of curves give the cerium valence in each group of compounds.

branches give two possible values for E_ψ*(Ce); we chose the value corresponding to $Z^* = 3.67$ which is closer to the value of 3.70 obtained from ΔH_f. The cerium valence determined from magnetic measurements using the model of Alascio *et al.* [18] is 3.65 for $E_{ex} = 2100$ K and $\Delta \approx 1000$ K. It should be noted that the difference between the E_ψ values at the two crossing points is about 0.16 eV (about 1800 K).

Figure 5 shows $\Delta d/d$ *versus* log E_ψ(A) for the cubic compounds ASn_3, ATl_3, ARh_3 and ACo_2. In this case $\Delta d/d$ is used instead of $\Delta V/V$ because this parameter shows a significantly smaller dispersion in the relationship with log E_ψ(A). The cerium valences in ASn_3, ATl_3, ARh_3 and ACo_2 are estimated to be 3.3, 3.0, 3.8 and 4.0 respectively, in agreement with the literature values. As expected the contraction of d is never greater than 10%.

Figure 6 shows the analysis of the AB_6, AIr_2 and ABe_{13} compounds in which the cerium valences are 3.0, 3.5 and 3.4 respectively. The plot of $\Delta V/V$ *versus* log E_ψ(A) shows two branches for the ABe_{13} family, one for the elements A′ ≡ La and Th and the other for the elements A″ ≡ Y, Gd, Lu, Sc and Zr. This behaviour suggests that the electronic band structure of the $A'Be_{13}$ group is different from that of the $A''Be_{13}$ group. Kappler [19] observed similar behaviour for the Curie temperature θ of the systems $(Ce_xM_{1-x})Be_{13}$. In the limit of dilute cerium in non-magnetic matrices (M ≡ La, Th, Lu and Y) he obtained $\theta \approx -140$ K for A″ ≡ Lu and Y and $\theta \approx -70$ K for A′ ≡ La and Th.

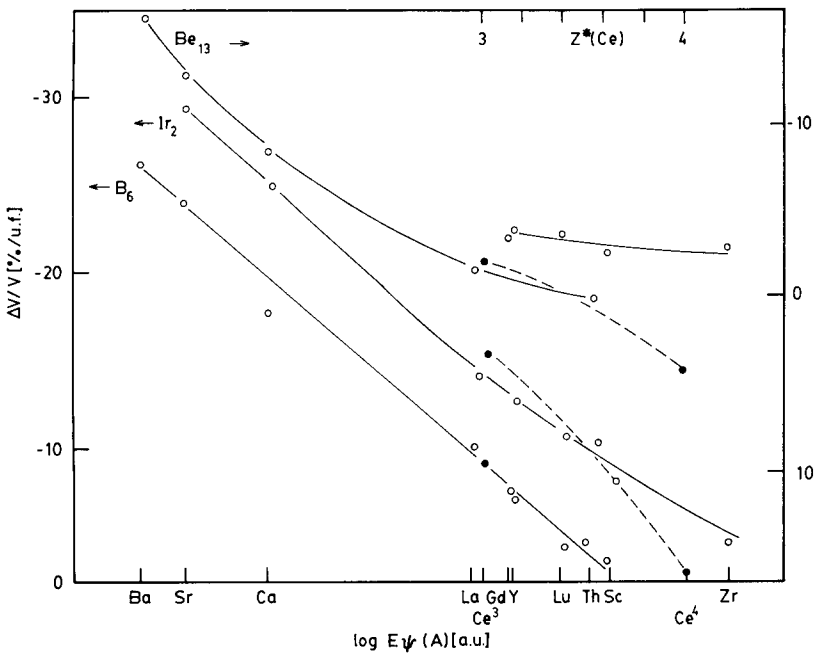

Fig. 6. $\Delta V/V$ *vs.* log E_ψ(A) (——) and $\Delta V/V$ *vs.* log E_ψ(Ce) calculated as a function of Z^*(Ce) (– – –) for AB_6, AIr_2 and ABe_{13}. The crossing points of the two sets of curves give the cerium valence in each group of compounds. In the case of the CeB_6 compound only the trivalent cerium point is shown.

4. Conclusions

We have shown by means of a semiempirical analysis that there is a parameter E_ψ, which can be estimated quantitatively, that allows the elements of groups II - V including cerium and thorium to be correlated. This parameter is a simple approximation for the electrostatic energy of a charge immersed in the screened Coulomb potential of the total charge distribution of the metal. Its interpretation in terms of microscopic parameters is not yet understood. It was selected from a number of other parameters because it showed the smallest dispersion with respect to its functional dependence on a measurable property depending strongly on the environment. This property is the initial rate of depression α of the superconducting transition temperature and the functional dependence is given by

$$\alpha^{-1/2} = a + bE_\psi(\mathrm{Th}_i\mathrm{X}_j)$$

where a and b are constants.

It was also shown that the volume contraction $\Delta V/V$ and the atomic separation contraction $\Delta d/d$ were appropriate for relating the energies involved in the formation of compounds belonging to the same family. However, the opposite slopes obtained for $\Delta V/V$ *versus* log E_ψ(A) and $\Delta d/d$

versus $\log E_{\psi}(A)$ cannot be explained by our empirical systematics. This relationship between valence and environment can be used either to analyse the valence changes in elements with fluctuating valences or to compare different environments.

The evaluation of the valence of cerium in a given compound is affected by different inaccuracies that are characteristic of each experimental technique [20]. The interpretation of magnetic measurements depends among other things on the theoretical models used to fit the experimental data and the possibility of subtracting the band (or matrix) contribution. Volumetric measurements depend on the appropriate choice of the trivalent and tetravalent reference systems (see refs. 20 and 21). Similar difficulties exist in the determination of bulk and surface properties by means of X-ray analysis and X-ray photoelectron spectroscopy techniques [22]. The use of physicochemical parameters, which are independent of those discussed above, allows new information to be obtained which can be used to check different results.

The present study, in which "alloying" is introduced as the primary parameter in the analysis, can be extended to all cerium compounds belonging to well-characterized families. A similar analysis can be applied to other elements with fluctuating valences such as ytterbium, uranium and plutonium provided that their atomic radii can be determined with sufficient accuracy at an integral value of the valence.

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