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# METAL-NON METAL TRANSITIONS IN RARE EARTH COMPOUNDS. EXPERIMENT AND THEORY. —

## VALENCE INSTABILITIES IN RARE EARTH SYSTEMS

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**Résumé.** — On discute le comportement anormal des composés des terres rares ayant une valence intermédiaire avec une attention spéciale sur le concept du temps de vie des deux configurations 4f voisins.

**Abstract.** — The anomalous behaviour of intermediate valence rare earth compounds is discussed with special emphasis on the concept of the life time of two adjacent 4f shell Hund's rule configurations.

**1. Introduction.** — The purpose of this introductory contribution of the session on valence instabilities in 4f systems is to first survey the basic features of this relatively new topic and then to report two recent results of our group in Köln and Jülich. The survey can only be brief. More extensive reviews are found in ref. [1-3].

In certain intermetallic rare earth (RE) compounds or concentrated RE alloys there exists an anomalous so-called intermediate valence (IV) phase which is separated from the normal stable valence phases by more or less sharp boundaries in the p-T, p-V, x-T, x-V or T-H phase planes. In this IV phase a rich variety of anomalies is observed in whatever quantity one cares to investigate experimentally, e. g. in all transport properties, in susceptibility and specific heat, in thermal expansion, in Mössbauer-, photoemission-, X-ray and optical absorption spectra, in the neutron scattering cross-sections, etc. Many of the anomalies are apparently giant relatives of better known corresponding effects in actinide and transition metals. Their common origin is the delocalization of a partially filled electron shell in the metal. Phenomenologically the delocalizing 4f state results in «bands» at the Fermi level which are much narrower than bands formed from 5f and d shells in actinides and transition metals; hence the larger anomalies.

The study of valence instabilities in RE metals touches on quite a few active branches of solid state physics, e. g. the local moment problem, Kondo effect, itinerant magnetism, metal-insulator and other phase-transitions, superconductivity, electron-phonon and band theory, to name a few.

**2. Properties of normal rare earth metals.** — Before discussing rare earth valence instabilities, three relevant general features of rare earth metals with stable 4f shell should be mentioned by way of contrast :

**2.1 INTEGRAL 4f OCCUPATION NUMBER.** — In the high temperature static susceptibility (far above any magnetic ordering temperature or crystal field splitting) one normally observes Curie Weiss behaviour  $\chi = C/(T + \theta)$  with  $C = N\mu_B^2 g_J^2 J(J + 1)/3 k_B$ . Within a few percent  $C$  is consistent with  $J$  and  $g_J$  as calculated from the Hund's rules groundstate of the  $n$  fold occupied 4f shell. Here  $n$  runs from 1 to 13 between Ce and Yb, minus plus one. Note that  $J$  contains orbital as well as spin angular momentum. In those cases where  $n$  can take on several values for the same element (Ce, Sm, Eu, Tm, Yb) the observed Curie constant is associated with only one or the other, i. e. it identifies  $n$  unambiguously. Therefore  $n$  appears to be integral to first order.

In the 4f shell of Sm and Eu ( $n = 5$  or  $6$ ) the first excited multiplet states are only a few hundred degrees K above the Hund's rules ground state. This leads to the well known Van Vleck anomalies of the susceptibility at ambient temperatures. The multiplet structure is a consequence of the central symmetry of the potential seen by the 4f electrons, plus strong Hund's rule correlations and spin orbit coupling in the 4f shell *alone*. Even weak mixing with other types of electron states, especially conduction electrons, should strongly modify or even wipe out this characteristic low energy structure. The fact that the Van Vleck anomalies appear usually on Sm and Eu in metals just as they do in insulators is a strong indication for the absence of mixing, i. e. again for integral  $n$  on these 4f shells in metals.

Finally, the same integral  $n$  state is pointed to by the frequently observed weak metallic crystal field splittings of the Hund's rule ground state. Crystal field splitting leaves the integral occupation number of the shell untouched, or reversely, weak crystal field splitting of the Hund's rule ground state could not possibly survive strong mixing with conduction electrons.

In short, it appears that in normal rare earth metals the 4f shell behaves as it does in insulators ; its occu-

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pation number is integral for all practical purposes, as it is in the lower lying completed rare gas shells. The eigenstates of the 4f system are then products of eigenstates of the local 4f shells. Mixing with conduction electrons at the Fermi level, which would make  $n$  nonintegral and introduce an energy width to the correlated local shell state, is not observed. In dilute RE solutions, low temperature susceptibility and EPR measurements put an upper limit of  $10^{-6}$  eV on the mixing width of integral  $n$  states of the 4f shell in some cases. We call *stable* such RE shells which show integral occupation of a single configuration in a metal

**2.2 RKKY POLARIZATION.** — The conduction electrons of the metal do of course penetrate the 4f shell. Although the resulting interaction does not cause observable mixing, it leads to phase shifts of the conduction electrons, i. e. to charge and spin density oscillations. The latter cause the well known RKKY effects : a small deviation of the effective 4f magnetic moments from the Hund's rule value, spin disorder resistivity, a several order of magnitude increase of the magnetic 4f interaction temperatures compared with insulators and a drastic depression of the transition temperature of superconductors with dilute rare earth impurities.  $T_m$ , the magnetic ordering temperature of compounds and  $xdT_c/dx$ , the depression of the superconducting transition temperature  $T_c$  of alloys with RE concentration  $x$ , both scale approximately with a single energy parameter across the entire RE series through the de Gennes factor, i. e. they are both  $\Lambda \cdot (g_J - 1)^2 J(J + 1)$ , where  $\Lambda \approx 10^{-3}$  eV is a constant, to first order independent of  $n$ , and  $J$  and  $g_J$  are the Hund's rule values for given  $n$ . With common values of the conduction electron density of states at the Fermi level,  $\Lambda$  indicates a 4f-conduction electron exchange integral of order 0.1 to 0.2 eV [4]. The direct Coulomb integral is of course larger, and it is somewhat of a puzzle why such strong interaction does not normally lead to observable mixing.

**2.3 THE IONIC RADIUS.** — The third remarkable feature of normal RE metals is the apparent existence of a definite volume of the RE cell, which depends very strongly on the RE valence, but very little on the environment, e. g. on the partners in a compound or on the state of an alloy, whether concentrated or dilute. The valence is here defined by  $V \equiv Z - 54 - n$ , where  $Z$  is the atomic number ; it can be determined experimentally through the dependence of the magnetic properties on the 4f occupation number  $n$ , as outlined above. In figure 1, due to Jandelli [5], the lattice constants of six series of RE compounds (the monochalcogenides and monpnictides) are plotted against an empirical quantity, the so-called ionic radius. For  $V = 3$  one obtains six nearly straight lines with the same slopes. Similar dependencies seem to exist for  $V = 2$ , although they are less clearly documented for

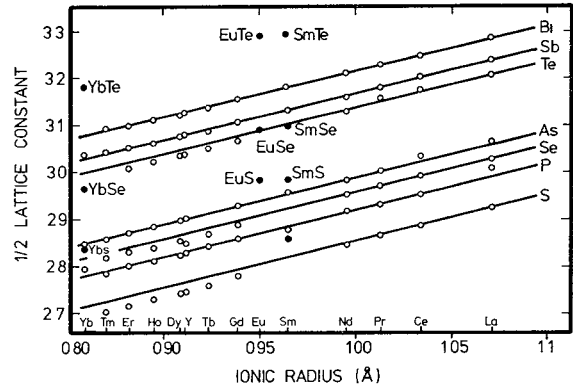


FIG. 1. — Lattice constant plotted against the empirical RE ionic radius for RE-monochalcogenides and RE monopnictides at 300 K (Ref. [5]). The structure is NaCl. Open circles correspond to trivalent, solid dots to divalent configurations according to the magnetic data. The solid dot at Sm between P and S lines is the SmS lattice constant in the high pressure IV phase (Ref. [6]).

lack of points. The strong dependence of the lattice constant of metals with RE components on the RE valence can be understood as a simple consequence of *atomic screening* : The volume of a RE atom in the lattice is determined by the radius of the 6s 5d shell. The radius of the 6s and 5d shells is about the same and ten times larger than that of the 4f shell. Thus the nuclear charge  $Z'$  seen by the 6s 5d shell is to a good approximation equal to the valence. A decrease of the 4f occupation number  $n$  by one (transition of a 4f electron to the 5d shell) will increase  $Z'$  by one ; the 6s 5d shell will contract abruptly, with a concomitant decrease of the average lattice constant of the metal host. This effect persists even when the sd electrons are partially delocalized (form bands).

Table I gives those 4f 5d 6s configurations of several RE elements which are relevant in metals.

TABLE I

*Configurations of ambivalent rare earths in metals*

RE	Configuration	Valence
Ce	$6s^2 5d^1 4f^1$	3
	$6s^2 5d^2$	4
Sm	$6s^2 4f^6$	2
	$6s^2 5d^1 4f^5$	3
Eu	$6s^2 4f^7$	2
	$6s^2 5d^1 4f^6$	3
Tm	$6s^2 4f^{13}$	2
	$6s^2 5d^1 4f^{12}$	3
Yb	$6s^2 4f^{14}$	2
	$6s^2 5d^1 4f^{13}$	3

**3. Identification of intermediate valence systems.** — We shall call  $E_n$  the energy of a lattice cell containing a RE atom with 4f occupation number  $n$ . According to table I in compounds Sm can be observed with either

6 or 5 4f electrons, Eu with either 7 or 6, etc. This means that for Sm either  $E_5$  or  $E_6$  can be the configurational ground state energy, depending on the metallic environment. Thus  $E_5$  and  $E_6$  cannot be very far from each other. Obviously, for a given RE compound increasing pressure favors the state with smaller  $n$ , since it is associated with a smaller volume. The intensive interest in IV systems developed after several insulator metal transitions were discovered by resistivity measurements under increasing pressure [6] in the RE monochalcogenides. These transitions were associated with 4f valence transitions; i. e. with delocalization of one electron of the 4f shell (4f to 5d transition, the 5d's form bands). This discovery put the long known pressure induced  $\gamma \rightarrow \alpha$  transition of metallic Ce [7] into a more general context. Table II lists the

TABLE II  
Isostructural valence transitions induced  
by hydrostatic pressure

System	$P_c$ kbar	Order	Character
Ce	8	I	mm
SmS	6.5	I	nm
SmSe	30	II	nm
SmTe	50	II	nm
TmTe	20	II	nm
YbTe	150	II	nm
CeP	100	?	mm
EuO	300	I	nm

$P_c$  is the critical pressure at 300 K, the third column gives the order of the transition, and the last indicates non metal-metal or metal-metal character.

most important pressure induced 4f valence transitions known today, their critical pressure and whether they are first or second order, metal-metal or non metal-metal. Similar transitions can be induced by lattice pressure, i. e. by alloying at atmospheric pressure. In this procedure, any partner of a given compound can be replaced by a chemically similar element with smaller volume with slowly increasing concentration  $x$ . The resultant reduction of the overall lattice constant reduces the volume available to the ambivalent 4f element and leads eventually to a valence transition at a critical concentration  $x_c$ . Table III lists some such systems. A third possibility to induce valence transitions is the variation of temperature. The best known case is again the  $\gamma \rightarrow \alpha$  transition in Ce [8]. More recently such temperature driven transitions have been studied in  $\text{Sm}_{1-x}\text{Gd}_x\text{S}$  [9] and in  $\text{Ce}_{1-x}\text{Th}_x$  [10].

It was soon realized that such transitions, whether induced by hydrostatic or lattice pressure or by temperature, never went all the way from one to the next state of integral 4f occupation number. This is quite apparent from the susceptibility and the lattice

TABLE III  
Valence transitions induced by alloying

System	$x_c$	Order	Character
$\text{La}_{1-x}\text{Ce}_x\text{Pd}_3$	0.5	I	mm
$\text{Ce}(\text{Rh}_{1-x}\text{Pd}_x)_3$	0.78	II	mm
$\text{Sm}_{1-x}\text{Gd}_x\text{S}$			nm
$\text{SmS}_{1-x}\text{Se}_x$		both	nm
$\text{Sm}_{1-x}\text{Y}_x\text{S}$	0.15	I	mm
$\text{SmS}_{1-x}\text{As}_x$	0.15	I	mm
$\text{Sm}_{1-x}\text{Th}_x\text{S}$	0.18	I	mm
$\text{Ce}_{1-x}\text{Th}_x$		both	mm

$x_c$  is the critical concentration at 300 K, the third and fourth columns have the same meaning as in table II.

constant, both of which are found to be intermediate between their expected values at the adjacent integral valence states,  $n$  and  $n - 1$ . Figures 2 and 3 show as examples the susceptibility of SmS [11] and TmTe [12] under pressure. The transition starts from  $\text{Sm}^{2+}$  and  $\text{Tm}^{2+}$ , respectively. In SmS it is first order (hysteretic) and in TmTe second order (reversible). The expected range of values for fully trivalent  $\text{Sm}^{3+}$  and  $\text{Tm}^{3+}$  is indicated in the high pressure phase (dotted lines for figure 2, marks on the right hand ordinate for each temperature in figure 3). The lattice constant anomaly of the high pressure phase of SmS can be read off from figure 1 (full dot at Sm ionic radius between P and S lines). If one assumes that the average valence is to first order a linear function of the lattice constant, one finds  $\bar{V} = 2.7$ . More recent work on SmS films with carefully controlled stoichiometry indicates  $\bar{V} \approx 2.9$  [13]. The existence of a mixed valence phase is also a necessary implication of the second order nature of some of the transitions (SmSe, SmTe, TmTe under pressure, etc.). The intermediate valence state cannot

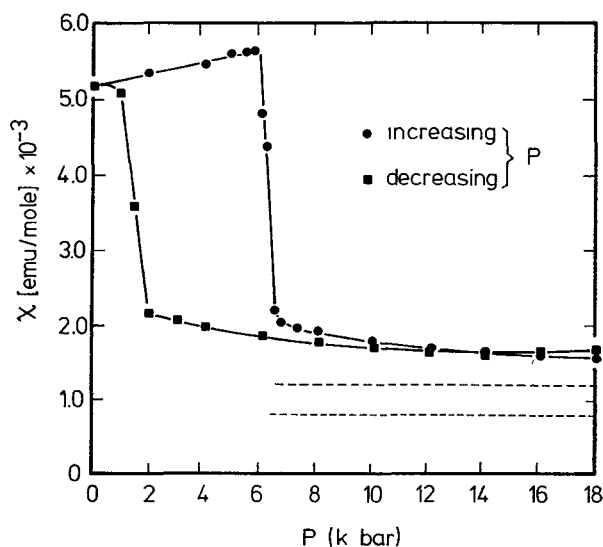


FIG. 2. — Susceptibility of SmS as function of hydrostatic pressure at 300 K (Ref. [11]). The expected range of susceptibility for trivalent SmS is indicated by dotted lines.

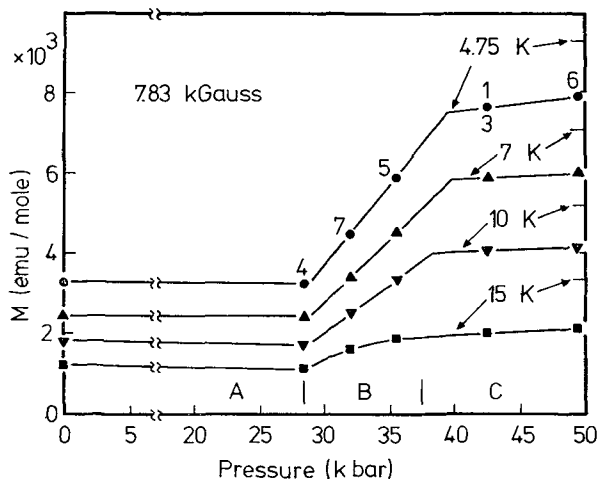


FIG. 3. — Susceptibility of TmTe as function of hydrostatic pressure at various temperatures (Ref. [12]). Pressure was varied in 8 steps, as indicated by numbers ( $p = 0$  at step 2 and 8). Note reversibility. Susceptibility expected of trivalent TmTe is indicated on right hand ordinate for each temperature. Two IV phases (B and C) can be distinguished.

be avoided in a valence transition, nor does any experiment so far indicate clearly a complete traversing of the intermediate valence phase from one integral valence state to the next, i. e. from a state of stable 4f shell behaviour with occupation  $n$  to the next with stable valence behaviour associated with  $n - 1$ . The case which comes closest to this ideal is the double series of substitutionary alloys  $\text{La}_{1-x}\text{Ce}_x\text{Pd}_3$  [14] and  $\text{Ce}(\text{Pd}_{1-y}\text{Rh}_y)_3$  [15]. In the first one has a first order transition at  $x = 0.5$  from  $4f^1$  to  $4f^0$  ( $0 < \epsilon < 1$ ) and in the second a second order transition from  $4f^2$  to  $4f^0$  with a noteworthy sharp phase boundary at  $y = 0.22$ . Unfortunately arrival at the integral valence state  $4f^0$  is not very exciting.

Although the phase boundaries of valence transitions are quite interesting, it seems of greater urgency to learn more about the mixed or intermediate valence state itself. With this goal in mind, one course of action is to work preferably in easily accessible ranges of the field parameters  $p$  and  $T$  and to avoid the complications of interpretation of the experimental results which arise from the variety of local environments in alloys. In other words, one may look for intermetallic

TABLE IV

RE intermediate valence compounds stable at atmospheric pressure

Ce ( $T < 100$ K)		YbAl <sub>2</sub>
CePd <sub>3</sub>	SmB <sub>6</sub>	YbAl <sub>3</sub>
CeN	EuCu <sub>2</sub> Si <sub>2</sub>	YbCu <sub>2</sub> Si <sub>2</sub>
CeSn <sub>3</sub>	EuRh <sub>2</sub>	YbC <sub>2</sub>
CeAl <sub>3</sub>	TmSe	YbB <sub>4</sub>
CeCu <sub>2</sub> Si <sub>2</sub>		YbCuAl
		YbCu <sub>2</sub>
		YbIn <sub>3</sub>

RE compounds which are in the IV phase at atmospheric pressure, all the way down to  $T \rightarrow 0$ . Such compounds do exist and can e. g. be identified by searching for lattice constant anomalies in the voluminous literature on RE compounds [16]. Table IV lists the more prominent cases. They involve so far five of the thirteen RE elements with partially occupied 4f shell, mostly Ce and Yb.

4. **Static vs. dynamic mixture.** — The intermediate or mixed valence phase can be visualized as a static or a dynamic mixture of the two configurations in question. In the static mixture the two configurations exist on different distinct sites for infinite time. In the dynamic mixture each RE site looks identical in time average, while the local state is best described by  $n$  at one time and by  $n - 1$  at another. One then must associate a characteristic time scale  $\tau$  with the temporal motion between the two configurations.

In general the experimental evidence overwhelmingly favors the dynamic mixture. An unequivocal tool to decide between static or dynamic mixture is a measurement of the Mössbauer isomer shift. This method is very well applicable in Eu compounds [17] and has been quite useful in the case of Sm as well [18, 19]. The isomer shift depends on the electronic charge density at the nucleus and reacts as distinctly to a change of occupation of the 4f shell as the radius of the 6s 5d shell, primarily because of the associated change of the 6s density at the nucleus. If the time scale  $\tau$  of the transitions between the two RE configurations is long compared with the lifetime of the excited state of the Mössbauer nucleus ( $2 \times 10^{-8}$  s in  $^{149}\text{Sm}$  and in  $^{151}\text{Eu}$ ), there will be two isomer shifts, one at frequency  $\nu_n$ , the other at  $\nu_{n-1}$  with relative intensity  $I_n/I_{n-1} = (V_{n-1} - \bar{V})/(\bar{V} - V_n)$ . If, on the other hand, the timescale is short compared to the Mössbauer lifetime, the two lines are pulled together due to motional narrowing to one line at position

$$\bar{\nu} = \nu_n(\bar{V} - V_n) + \nu_{n-1}(V_{n-1} - \bar{V}).$$

(The frequencies  $\nu_n$  and  $\nu_{n-1}$  must be calibrated with suitable integral valence compounds.) This single line Mössbauer spectrum is indeed observed in SmB<sub>6</sub> [18] EuCu<sub>2</sub>Si<sub>2</sub> [17] and SmS [19]. Its existence asserts the dynamic mixture in these compounds and puts an upper limit of about  $10^{-11}$  s on the lifetime of the individual configurations. It should be emphasized that the physical origin of this single line spectrum is a fast charge (not spin) fluctuation. Also, the single line spectrum has been observed at Helium temperatures [17-19]. Therefore the dynamic mixture cannot be primarily driven by thermal excitations; it is a property of the groundstate of these compounds.

The existence of the dynamic mixture immediately raises the following question: While Hund's rule behaviour indicates the validity of the concept of a single configuration for a stable RE shell in a metal, i. e. of a state of the 4f shell with integral occupation

number  $n$  and practically infinite lifetime, now that the shell lifetime definitely has become finite and indeed short, how much validity remains there to the concept of a configuration characterized by  $n$ , or  $n - 1$ ? Does it make any practical sense to talk of a mixture of only *two* configurations as suggested by intermediate lattice constant and susceptibility of the IV phase? Or is the mixing process so violent that many more configurations of different  $n$  need to be considered as suitable basis of local states to describe what is really happening? The latter picture was adopted for  $d$  shells in dilute solution in the early history of the treatment of delocalizing shells by Friedel [20] and Anderson [21].

For rare earth IV compounds, however, experiment shows quite clearly, that the set of only two configurational states  $n$  and  $n - 1$  is sufficient. This is for example demonstrated very convincingly by the photoemission technique called ESCA. Figure 4 shows the ESCA spectrum of  $\text{SmB}_6$  [22], the same compound in which a single line Mössbauer spectrum asserts a dynamic process [18]. For a suitable range of energy of the exciting photons, the great majority of the photoemitted electrons originates in the  $4f$  shell, and each initial  $4f$  configuration creates a unique spectrum of photo electrons. In figure 4 one observes

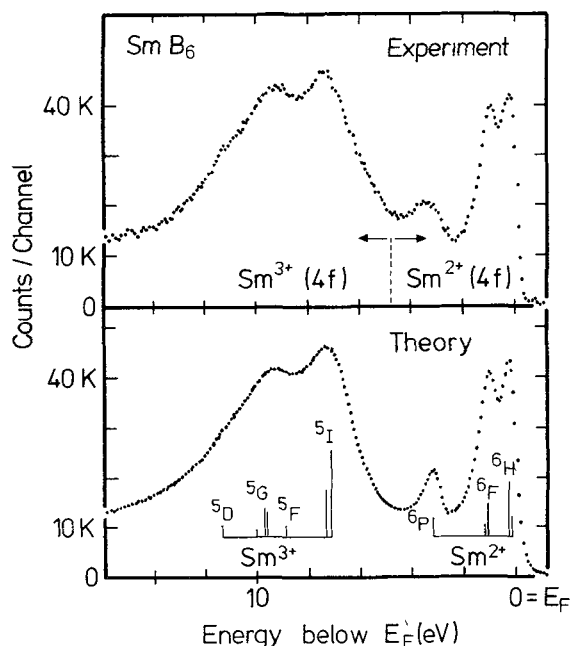


FIG. 4. — Experimental and theoretical XPS spectrum of  $\text{SmB}_6$  (Ref. [22]). Two initial configurations are distinguishable. The resolution is limited by the lifetime of the final XPS state. Ratio of initial  $\text{Sm}^{3+}$  to  $\text{Sm}^{2+}$  is 6 : 4.

two and only two such spectra, characteristic for  $4f$  photoelectrons from the initial  $4f^5$  and  $4f^6$  configurations. The intensity ratio is very close to that expected from  $\bar{V}$  as measured by the intermediate lattice cons-

tant, by the position of the Mössbauer line [18], and by the intermediate value of the susceptibility [23].

If the photoemission process is sufficiently fast compared to the lifetimes  $\tau_n$  and  $\tau_{n-1}$  of the states  $n$  and  $n - 1$  and if the Hund's rule correlation energy is large enough to ensure rearrangement of all electrons in one or the other configurational ground state in a time short compared to  $\tau_n$  and  $\tau_{n-1}$ , then one expects exactly what one sees: A spectrum of two configurations side by side. Of course because of the finite lifetimes, each configurational spectrum cannot have better energy resolution than  $h/\tau_n$  or  $h/\tau_{n-1}$ . The resolution of the spectrum in figure 4 is given by instrumental conditions and by the lifetime of the excited configuration left behind in the photoemission process, which is short compared to  $\tau_n$  and  $\tau_{n-1}$ . Thus, the ESCA experiment cannot measure  $\tau_n$  either, but it puts a *lower* limit on the configurational lifetimes, namely  $\tau_n, \tau_{n-1} > 10^{-15}$  s.

For  $\text{SmB}_6$ , Mössbauer and ESCA experiment together then put the configurational lifetimes into the range  $10^{-15}$  s  $< \tau_n, \tau_{n-1} < 10^{-11}$  s. They turn out to be of order  $10^{-12}$  to  $10^{-13}$  s.

#### 5. Lifetimes from anomalous temperature dependence of local properties. —

Is there a way to measure lifetimes more directly? If they are indeed of order  $10^{-13}$  s or longer, various physical properties should show anomalies below a few 100 K, as the temperature moves through  $T_n = h/\tau_n k_B$ . This is indeed the case. In order to interpret the behaviour of anomalies of a certain class of properties it is useful to reflect on the statistical mechanics of IV compounds.

In the configuration  $n - 1$  there exists an extra  $s$  or  $d$  electron with lifetime  $\tau_{n-1}$ . In compounds where the outer  $sd$  shells of the RE atoms form bands, this electron becomes a conduction electron if  $\tau_{n-1}$  is long compared to the inverse  $sd$  band width. For  $\tau_{n-1} \approx 10^{-13}$  s one estimates ten to one hundred lattice sites for the average distance which this electron travels before being reabsorbed. Obviously with this conduction electron the groundstate of the entire  $4f$  metal can no longer be regarded as the  $N$  fold product of the configurational groundstate of a single lattice cell, as it can be in the case of stable  $4f$  shells. The proper representation of the groundstate of the metal must now involve states which are extended over many lattice cells, i. e. delocalized wave functions. At present theoreticians are struggling with the problem of constructing such delocalized states which incorporate two highly correlated  $4f$  shell states per cell [24-28]. A complete solution to this problem lies in the far future. In order to have a guideline for experimental progress one is forced to look for phenomenological models.

In the groundstate of the dynamic mixture the energy of an individual  $4f$  shell is no longer well defined. However, if one can be sure that one evaluates local

properties, the state of the metal might still be usefully regarded as the  $N$  fold product of one individual cell state, albeit not an energy eigenstate. One such local property is the static susceptibility, since the susceptibility of the conduction electrons is negligible compared with that of the incompletely filled 4f shells. Another is the volume (lattice constant) which is dominated by the above atomic screening effect. One condition on the single cell approach is that in the time average all cells behave identically. This excludes any complicated magnetic order at  $T \rightarrow 0$ . Since one characteristic property of IV compounds is apparently just the absence of magnetic order as  $T \rightarrow 0$ , the single cell state basis looks promising. Another condition is that there be no significant correlations between the motions of individual cells. Under these conditions if only two configurations occur during the motion of each cell, and if the lifetimes are sufficiently long, the energy spectrum of the single cell state at  $T = 0$  should be representable by two broadened peaks centered at  $E_n$  and  $E_{n-1}$  with widths  $\Delta_n = h/\tau_n$  and  $\Delta_{n-1} = h/\tau_{n-1}$ . We define  $E_{\text{ex}} \equiv E_{n-1} - E_n$  and discuss specifically  $E_{\text{ex}} > 0$ . The ratio of the spectral weight integrated separately over each peak must be given by the observed fractional occupation (valence  $\bar{V}$ )

$$A_n/A_{n-1} = \varepsilon_n/(1 - \varepsilon_n). \quad (1)$$

These peaks are the remnants of two  $\delta$  functions at  $E_n$  and  $E_{n-1}$  which describe the positions in energy of the two configurational ground states without mixing [29]. We call the mixing rate  $\Delta = \rho(E_{\text{f}}) v_{\text{kf}}^2$ . It is assumed to be the width of the single virtual bound 4f state which would exist if no configurational correlation energies would block mixing of 4f with conduction electron states through  $v_{\text{kf}}$  [20, 21]. Not much can be said about the actual mixing rates with this block except that  $\tau_{n-1}/\tau_n \rightarrow 0$  for  $E_{\text{ex}}/\Delta \rightarrow \infty$ , and  $\tau_{n-1}/\tau_n \rightarrow 1$  for  $E_{\text{ex}}/\Delta \rightarrow 0$ . In the latter case  $\tau_{n-1}$  and  $\tau_n$  must be of order  $h/\Delta$ .

If there are degeneracies  $g_n$  and  $g_{n-1}$  in the original configurational ground states, furthermore, if all excited intraconfigurational states lie far above these states (compared with  $E_{\text{ex}}$  and  $\Delta$ , [29]) and finally, if  $\Delta$  does not depend on the states  $\alpha$  within  $g_n$  and  $g_{n-1}$ , then each peak in the IV single cell energy spectrum is a superposition of  $g_n$  and  $g_{n-1}$  peaks with equal areas  $a_{\alpha,n} = a_n$  and  $a_{\alpha,n-1} = a_{n-1}$  respectively, and

$$g_n a_n/g_{n-1} a_{n-1} = \varepsilon_n/(1 - \varepsilon_n). \quad (2)$$

The areas  $a_\alpha$  are proportional to  $P_\alpha$ , the probability of occupation of a given state  $\alpha$  of the original manifolds  $g_n$  and  $g_{n-1}$  in the IV state. At  $T \rightarrow 0$  they are also proportional to the respective lifetimes :

$$\varepsilon_n(T \rightarrow 0) = g_n \tau_n / (g_n \tau_n + g_{n-1} \tau_{n-1}). \quad (3)$$

The probability  $P_\alpha$  of occupation of the state  $\alpha$  in  $g_n$  may be written for two extreme temperatures as follows

$$P_\alpha(T) \sim \begin{cases} \exp(-E_\alpha/\Delta_\alpha) & (T \rightarrow 0) \\ \exp(-E_\alpha/k_B T) & (T \gg T_\alpha \equiv \Delta_\alpha/k_B). \end{cases} \quad (4)$$

These expressions are acceptable if  $E_\alpha$  and  $\Delta_\alpha$  do not depend on temperature. One obtains a smooth interpolation for intermediate temperatures if one writes simply

$$P_\alpha(T) \sim \exp(-E_\alpha/k_B(T_\alpha + T)). \quad (5)$$

At this time there is no justification for this interpolation other than that good fits to experiment are obtained if one uses eq. (5) in a quasipartition function

$$Z^* \equiv \sum_\alpha P_\alpha(T)$$

to calculate thermal averages,

$$\langle A \rangle = \sum_\alpha A_\alpha P_\alpha(T)/Z^*. \quad (6)$$

For the susceptibility one obtains in the limit  $\mu_B H \ll k_B T, E_{\text{ex}}$  [30]

$$\chi(T) = (N/3 k_B) [\varepsilon_n(T) \mu_n^2/(T_n + T) + (1 - \varepsilon_n(T)) \mu_{n-1}^2/(T_{n-1} + T)] \quad (7)$$

$$(\mu_n^2 \equiv \mu_B^2 g_n^2 J_n(J_n + 1))$$

$$\varepsilon_n^{-1}(T) = 1 + [(2J_{n-1} + 1)/(2J_n + 1)] \times \exp[-E_{n-1}/k_B(T + T_{n-1}) + E_n/k_B(T + T_n)]. \quad (8)$$

Clearly with the assumption of three temperature independent parameters ( $E_{\text{ex}}$ ,  $T_n$  and  $T_{n-1}$ ) the above strange kind of statistical mechanics makes rather precise predictions on the temperature dependence of the susceptibility and the valence, since the degeneracies  $2J + 1$  and the Lande  $g_J$  factors cannot be tampered with. Similar expressions can be written down for other macroscopic observables which are dominated by local properties, e. g. for the temperature dependence of the volume (lattice constant), the magnetostriction, pressure dependence of the susceptibility, Mössbauer isomershift [17], relative weight of the two 4f ESCA spectra and the like.

In the case of IV compounds with Ce and Yb, one of the configurations has  $J = 0$  ( $4f^0$  in Ce,  $4f^{14}$  in Yb). In such simple cases a fit of eq. (7) and eq. (8) requires only two parameters ( $E_{\text{ex}}$  and  $T_{n-1}$ ), which makes the test of these expressions still more stringent. Figure 5 shows two examples for Yb compounds, which prove that constant  $E_{\text{ex}}$  and  $T_{n-1}$  make physical sense at least in some compounds [31]. In the next section we shall show that  $T_{13}$  for YbCu<sub>2</sub>Si<sub>2</sub> can also be seen in the transport properties. The relatively small errors of  $E_{\text{ex}}$  and  $T_{13}$  show good sensitivity of the fit to the parameters. The positive curvature of the  $\chi^{-1}(T)$  plots is tied to  $E(J \neq 0) > E(J = 0)$ , i. e.  $E_{13} > E_{14}$ . The successful fit of the maximum of the susceptibility of YbAl<sub>3</sub> is particularly intriguing, since such maxima occur quite often in IV compounds and also in all non-magnetic transition metals at the beginning and at the end of the d series (Sc, Y, Lu, La, Pd, Pt).



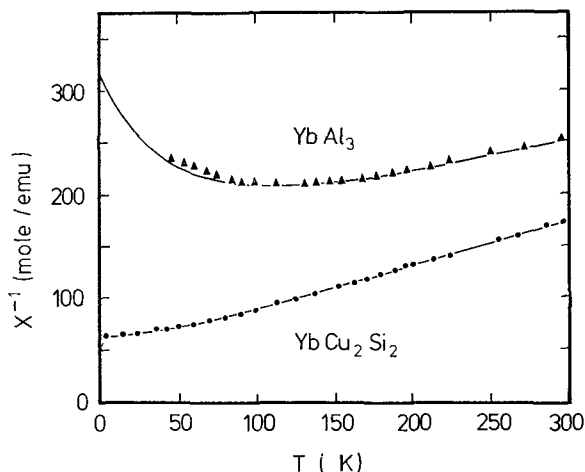


FIG. 5. — Temperature dependence of inverse susceptibility of  $\text{YbCu}_2\text{Si}_2$  and  $\text{YbAl}_3$  (Ref. [31]). Solid lines are fits of eq. (7) with following values of  $E_{\text{ex}} = E_{13} - E_{14} > 0$  and  $T_{13}$ :  $\text{YbCu}_2\text{Si}_2$ :  $E_{\text{ex}}/k_B = (170 \pm 5)$  K and  $T_{13} = (75 \pm 5)$  K;  $\text{YbAl}_3$ :  $E_{\text{ex}}/k_B = (560 \pm 25)$  K and  $T_{13} = (160 \pm 10)$  K.

There are other IV compounds where fits with temperature independent  $E_{\text{ex}}$  and  $T_n$ ,  $T_{n-1}$  are not so successful, especially at low temperatures ( $\text{EuCu}_2\text{Si}_2$ ,  $\text{SmB}_6$ ). Fits with temperature dependent  $E_{\text{ex}}$  and  $T_n$ ,  $T_{n-1}$  can then of course be enforced, but do not seem justified until independent measurements of the temperature dependence of these quantities are available.

**6. Lifetimes from transport properties.** — The above single cell representation is not appropriate for a description of transport properties, for which one needs an extended states representation. Hirst has recently discussed the low energy excitation spectrum of IV compounds [25]. He finds a very large density of quasi-particle excitations at the Fermi level. This spectrum is relevant for the specific heat. One indeed finds exceedingly large linear specific heat coefficients in all IV compounds, e. g.  $\gamma = 145$  mJoule/atom  $\text{K}^2$  in the high pressure IV phase of  $\text{SmS}$  [32]. Unfortunately, although this spectrum is presumably a fermion spectrum in a metal, it is not necessarily one of conduction electrons alone. At this time it seems premature to exploit it for quantitative discussion of transport. It is clear, however, that the width of the anomaly at the Fermi level must reflect the configuration lifetime, and that therefore transport properties should show anomalies as the temperature moves through  $T_n$  and  $T_{n-1}$ . There is one further drawback: The quasi-particle excitation spectrum is a function of the valence, i. e. the ratio of the population of the two configurations. Since the valence is a function of temperature, so is the excitation spectrum. Therefore one cannot expect IV compounds to show « rigid band » behaviour [25], and anomalies which occur while running the temperature through the width of the spectrum can only give a coarse estimate of an average  $T_n$ .

Figure 6 gives the temperature dependence of the electrical resistivity and the thermopower of  $\text{YbCu}_2\text{Si}_2$  [30]. Both show dramatic anomalies, namely a maximum of  $d\rho(T)/dT$  near 40 K (there is no extremum in this quantity for a normal metal) and a maximum of the thermopower at 60 K, with a value about two orders of magnitude above that of normal metals in this temperature range. Both characteristic temperatures are close to  $T_{13} = 75$  K determined from the susceptibility fit of this compound [31] (Fig. 5). The transport properties therefore seem sensitive to the lifetime  $\mathcal{T}_{13} = h/k_B T_{13}$ , but not to  $E_{\text{ex}}$  as expected.

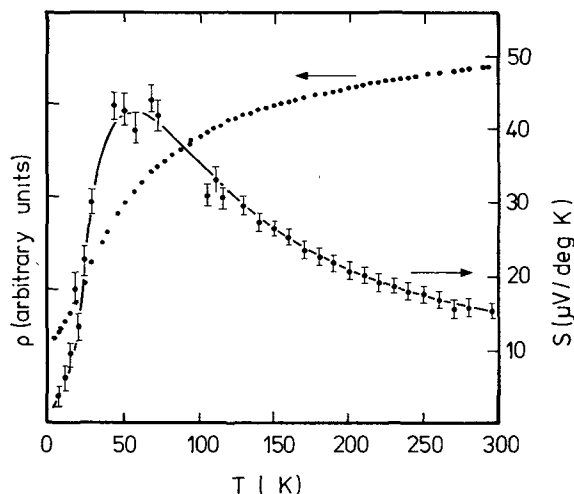


FIG. 6. — Electrical resistivity and thermopower of  $\text{YbCu}_2\text{Si}_2$  (Ref. [30]). Anomalies appear near  $T_{13} = 75$  K found in figure 5.

Because of the expected temperature dependence of the excitation spectrum it seems worthwhile to look for a method which can measure this spectrum near  $T = 0$  ( $T \ll T_n$ ). With this goal in mind we have begun a program to study the tunnel spectrum of diodes containing an IV compound on one side of the junction at helium temperature [33].

Figure 7 shows the differential conductance of Mo-Oxide- $\text{YbCu}_2\text{Si}_2$  at 1.6 K. Again, there is a big anomaly. The curve can be decomposed into a zero bias anomaly (ZBA) with logarithmic bias dependence between 2 and 35 meV and an asymmetric rest, as shown in figure 7. The ZBA is enormous in magnitude (77 % of the conductance at large negative bias) as well as in half width (about 7.5 meV). Literature values in other systems [34] have a maximum magnitude of 18 % of background and a half width of less than 1 meV. Between 1.6 and 20 K the ZBA is found to decrease with increasing temperature in the familiar manner [34]. However, at all temperatures it is insensitive to magnetic fields up to 5 T within the accuracy of the measurement, in contrast to behaviour in the literature where the peak splits in two with increasing field [34]. ZBA's have been previously discussed on the basis of the Kondo effect [35, 36]. If the present ZBA is



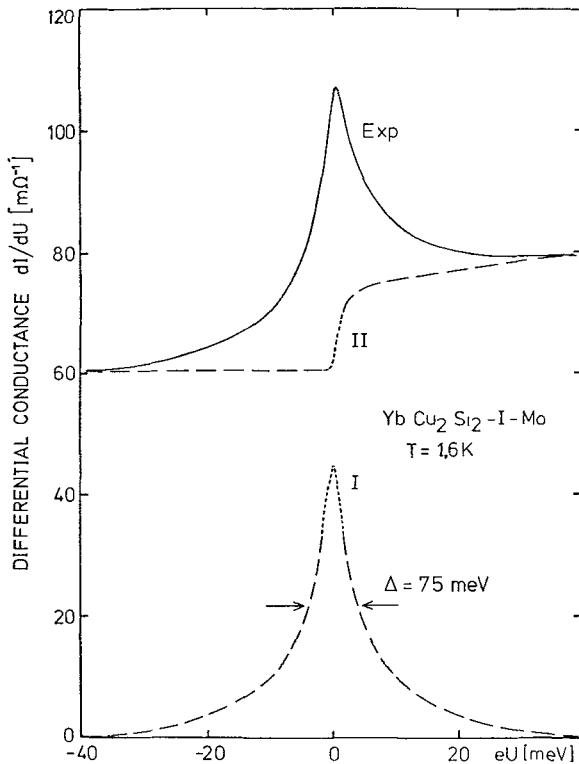


FIG. 7. — Differential conductance of tunnel diode of  $\text{YbCu}_2\text{Si}_2$  against Mo (barrier is Mo-Oxyde). Dashed lines: Decomposition of curve into zero bias anomaly (I) with logarithmic voltage dependence between 2 and 35 meV and asymmetric rest (II). Sign of  $U$  refers to  $\text{YbCu}_2\text{Si}_2$ .

due to the same mechanism, the absence of a magnetic field effect can be explained by the high characteristic temperature  $T_K$  which we extract from the half width ( $T_K \approx 80$  K). This temperature again is very close to  $T_{13} \approx 75$  K from the susceptibility fit of the same compound (Fig. 5). The asymmetry of the conductance background is presumably due to strong dissimilarities of the quasiparticle density of states and mobility at both sides of the barrier. In the IV compounds  $\text{CeCu}_2\text{Si}_2$  and  $\text{CePd}_3$  there are similar asymmetries in the conductance, but the ZBA is missing. No such anomalies of the conductance are found in  $\text{LuCu}_2\text{Si}_2$  (stable  $4f^{14}$ ) and  $\text{GdCu}_2\text{Si}_2$  (stable  $4f^7$ ).

#### 7. Lifetimes from direct linewidth measurements. —

The characteristic temperatures  $T_n$  and  $T_{n-1}$  which are identified with the inverse lifetimes of the Zeeman levels of the two configurations of a given cell do not seem to depend on temperature in certain compounds ( $\text{YbCu}_2\text{Si}_2$ ,  $\text{YbAl}_3$ , Fig. 5). This must not be true in general, and it seems desirable to have a direct measurement of linewidths as function of temperature which could then be used in eq. (6) to better calculate certain thermal averages. We have therefore begun a study of the energy width of the quasielastic diffuse neutron scattering cross-section of  $\text{CePd}_3$  [37]. Magnetic diffuse neutron scattering measures the susceptibility  $\chi(\mathbf{q}, \omega$ ,

$T$ ) where  $\hbar\mathbf{q}$  is the momentum and  $\hbar\omega$  the energy transfer in the scattering process. The linewidths  $\Delta_n$  of the  $4f$  Zeeman levels are thought to be due to cell motions which are uncorrelated in time from one cell to the next, presumably because a conduction electron is involved, which can be emitted and absorbed at random times.

The time dependent susceptibility is obtained from  $\chi(\mathbf{q}, \omega, T)$  via a Fourier transform. For this quantity, one can make a relaxation ansatz to describe the random motion:

$$\text{Im } \chi(\mathbf{q}, t, T) \sim \chi(\mathbf{q}, 0, T) \cdot \exp(-t/\tau(T)). \quad (9)$$

Then the double differential diffuse magnetic scattering cross-section is

$$\frac{\partial^2 \sigma}{\partial \omega \partial q} = C(k_f/k_i) F_J^2(q) [n(\omega) \pm \frac{1}{2} + \frac{1}{2}] \times \chi(\mathbf{q}, 0) \frac{\pm \hbar\omega/\tau}{(\hbar\omega)^2 + (\hbar/\tau)^2}. \quad (10)$$

Here  $C$  is a known constant,  $k_i$  and  $k_f$  are the initial and final momenta,  $F_J(q)$  is the magnetic form factor of the  $4f$  shell in the Hund's rule ground state  $J$ ,  $n(\omega) = [\exp(\beta\hbar\omega) - 1]^{-1}$  is the Bose factor and  $\pm$  refers to energy loss or gain. In other words, the line is expected to have Lorentzian shape.

After having assured that the  $q$  dependence of the form factor is indeed consistent with  $4f$  scattering in  $\text{CePd}_3$ , the measured time of flight (TOF) cross-section was fitted with eq. (10) using  $\chi(\mathbf{q}, 0, T)$  and  $\tau(T)$  as adjustable parameters.  $\chi(\mathbf{q}, 0, T)$  has the same abnormal IV temperature dependence as the static susceptibility  $\chi(0, 0, T)$  [38]; also its absolute value is reduced with respect to the Curie-Weiss law expected from the  $4f^1$  configuration by the same amount (about  $1/2$  at room temperature). The most interesting feature however is the linewidth which can be read off directly from the TOF spectra and is shown in figure 8 as function of

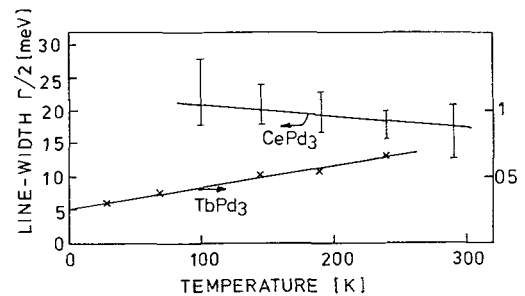


FIG. 8. — Temperature dependence of energy linewidth of diffuse magnetic neutron cross-section for  $\text{CePd}_3$  and  $\text{TbPd}_3$ .

temperature.  $\Gamma$  is about 40 meV and nearly temperature independent between 300 and 100 K. This value is nearly two orders of magnitude above that of  $\Gamma$  for

TbPd<sub>3</sub>, a stable 4f<sup>8</sup> compound whose linewidth shows the normal Korringa relaxation behaviour  $\Gamma \sim T$  (the extrapolated value at  $T = 0$  in figure 8 is the instrumental resolution). If Ce in CePd<sub>3</sub> had stable 4f<sup>1</sup> configuration, its line width should also follow Korringa behaviour with much smaller absolute values than for TbPd<sub>3</sub> and there should be a crystal field excitation spectrum. The crystal field spectrum is absent [39], apparently wiped out by the violent relaxation.

Thus the neutron cross-section strongly supports the idea of short temperature independent lifetimes of the Zeeman levels due to spontaneous interconfiguration fluctuations.

The fit of the static susceptibility [38] to eq. (7) gives  $\Delta_1 = 14$  meV, i. e. the linewidth at finite momentum transfer ( $q \approx 1.5 \text{ \AA}^{-1}$ ) is about three times larger than that measured at zero momentum transfer. This suggests that the decay of the magnetization is faster within a single cell than over the entire sample. A reason for this might be a residual correlation between the jumping times of neighbouring cells to minimize the strain energy which must be large because of the large difference in ionic radii of both configurations. This line narrowing for  $q \rightarrow 0$  cannot be due to magnetic interaction, which can at most be 0.2 K in this compound. If the linewidth of CePd<sub>3</sub> should turn out to be as large at  $T \rightarrow 0$  as it is between 300 and 100 K,

one cannot be surprised by the absence of magnetic order. Generally, as long as  $\Delta_n/k_B$  is larger than the ordering temperature  $\Lambda.(g_J - 1)^2 J(J + 1)$  of an IV compound expected by interpolation from related compounds (see section 2.2), the metal must remain nonmagnetic.

**8. Conclusion.** — The study of valence instabilities in metallic RE systems is just at its beginning. The large anomalies known so far certainly do not yet comprise the full spectrum. Particularly interesting should be the effect of valence fluctuations on the phonon spectrum. Almost nothing is known about this experimentally, while there exists already some theoretical work [40, 41, 42]. A very interesting question is the connection between the valence instability of a RE ion in a compound with the Kondo anomalies exhibited by the same ion in dilute solution. Obviously RE valence instabilities will give work to experimentalists and theoreticians for many years to come. A thorough understanding of this phenomenon will surely improve our grasp on actinide and transition metal physics as well.

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