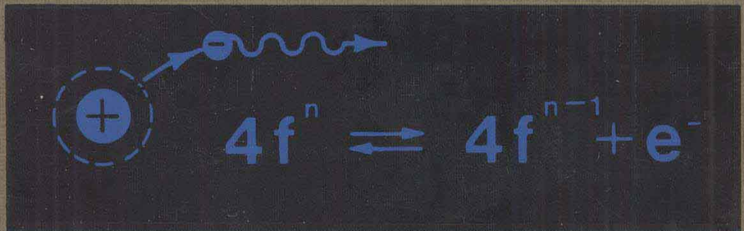
SANTA BARBARA INSTITUTE FOR THEORETICAL PHYSICS CONFERENCE

VALENCE FLUCTUATIONS IN SOLIDS

L.M. FALICOV, W. HANKE, M.P. MAPLE
EDITORS



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VALENCE FLUCTUATIONS IN SOLIDS

Santa Barbara Institute for Theoretical Physics Conference,
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VALENCE FLUCTUATIONS IN SOLIDS

FOREWORD

The International Conference on Valence Fluctuations in Solids was held in Santa Barbara, California, USA between January 27 and 30, 1981. It was the closing event of a six-month workshop on the same subject which, coordinated by the three Conference Co-Chairmen, took place at the Institute for Theoretical Physics of the University of California, Santa Barbara, between July and December, 1980.

The Conference consisted of four morning and three evening sessions of oral invited presentations and two afternoon meetings of poster contributed papers. The present volume contains all these.

The state of the art in the rapidly developing field of Fluctuating Valence is well represented by the contributions to the Conference. A strong interaction between theory and experiment and a confluence of widely varying experimental and theoretical techniques have been the landmarks of this area of research ever since its inception in the early 1970s. This was clearly in evidence in the first and groundbreaking conference which took place in Rochester, New York, USA in 1976 and whose proceedings, Valence Instabilities and Related Narrow-Band Phenomena, edited by R.D. Parks (Plenum, New York, 1977) are by now one of the standard references in the field. The pattern established in Rochester was once again in evidence in Santa Barbara, and the vigor and variety of the research presented in January 1981 augurs well for continuing activity at the same level.

The Conference was made possible by the financial support of the U. S. National Science Foundation and a generous grant from the IBM Corporation.

The organization of the Conference and the publication of these Proceedings could not have been possible without the skillful and gracious help of the staff of the Institute for Theoretical Physics in general, and of Ms. Lois Sellers in particular. Her patience, organization ability and sense of humor and opportunity are gratefully acknowledged.

The presence and advice of Miss Nancy McLaughlin of the University of California, San Diego, contributed in no small amount to the success of the meeting.

Special thanks are due to Professor Walter Kohn, who as Director of the Institute for Theoretical Physics, provided the warm hospitality and congenial environment which made the Workshop and the Conference great successes.

L. M. Falicov
W. Hanke
M. B. Maple
Conference Co-Chairmen

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SYSTEMATICS OF VALENCE FLUCTUATION SYSTEMS

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Knowledge of the fractional valence as function of ionic species, temperature, pressure and other parameters is essential for a quantitative and often even a qualitative understanding of the anomalies associated with the fluctuating valence state. According to available experimental data the valence in compounds as well as dilute alloys behaves in a fashion much more characteristic of the individual rare earth species than of the matrix. There is a high temperature limit of the valence of Ce, (Pr), Tm and Yb determined solely by Hunds rules and a characteristic high temperature dependence in Eu associated with intraionic multiplet structure of $4f^6$. The valence of dilute Eu can change by nearly 40% between 0 and 300 K. The valence transition of Ce (and Pr) remains fractional (tetravalent Ce compounds seemingly do not exist). The temperature dependence of the valence of Ce and Yb fluctuating valence compounds is characterized by a shift from the nonmagnetic towards the trivalent, magnetic configuration with increasing temperature. This causes an abnormal expansion in Ce and an abnormal contraction in Yb compounds. Thermal expansion of the matrix accelerates the valence change in Ce and decelerates it in Yb compounds. The pressure dependence of the excitation energy is discussed.

1. INTRODUCTION

The subject of this introductory experimental talk is of course too voluminous to be treated exhaustively in the given time and space. I shall therefore discuss only stochiometric compounds and some dilute alloys and will focus on the actual value of the fractional valence. Why is that value so important? For quantitative and, even at this time, for qualitative reasons. For one thing, it is by now well known that temperature, pressure and other parameters can change the valence appreciably. For transport this implies a change of the number of conduction electrons and a shift of the concentration of one type of scatterer (say the $4f^{n+1}$ ions) in favor of another (the $4f^n$ ions). Anybody interested e.g. in explaining transport anomalies as function of temperature even qualitatively must know the rate of valence change with temperature. The same is true for specific heat, susceptibility, neutron inelastic magnetic line width etc. Secondly, while compounds and concentrated alloys of Rare Earth (RE) ions in the fluctuating valence state show macroscopic anomalies in transport, specific heat, susceptibility etc , which are very similar to anomalies of the same physical properties due to the same RE species in dilute alloys, the latter are usually explained with Kondo type models, which imply nearly integral valence. Kondo type theories are also often applied to compounds by one school of thought which may be put into the fluctuating valence class by another. Clearly one needs a microscopic measurement of the valence to find out which procedure is justified. Moreover, if it turns out that the valence of dilute impurities can be strongly nonintegral (it does!), then the stability of the fluctuating valence state cannot depend much on the Fermi energy of the conduction electrons. The emphasis of the search for a stability criterion must then shift to local properties like Hund's rule degeneracies, ionic volume, lattice pressure etc. Thirdly, there are now theories being formulated (1), which predict magnetization and charge relaxation rates from the valence as decisive input parameter. They should be checked! Finally, when shifting from qualitative to quantitative experiments, one must expect surprizes. One of them happened in the case of tetravelant Cerium compounds.

In short, valence measurements seem very timely at the present stage of maturity of the field. The available evidence already shows clearly that the valence and its rate of change with temperature, pressure and other parameters is characteristic of the RE species rather than of the host material, and that for a given species it is very similar in compounds and dilute alloys.

Unfortunately to this day accurate numbers of the valence are hard to come by. Nobody claims to know any valence to better than ±10% absolutely. This is mainly due to uncertainty with respect to systematic errors in the extraction of a number from experimental data. Some measurements (e.g. thermal expansion) carry the promise of several orders of magnitude better precision, but to fully exploit their potential we need to greatly improve our understanding of some aspects of the physics of the fluctuating valence state, especially of the effect of pressure.

From an experimentalist's point of view the parameters which control the valence are, in order of decreasing energy scale
1. lattice pressure
2. Hund's rule degeneracies
3. intraionic multiplett splittings

4. crystal field splittings
5. magnetization and charge relaxation rates.

Of these parameters only the relaxation rates and maybe the size of the crystal field parameters are intrinsically connected with the fluctuating valence; the rest comes from general crystal chemistry and atomic physics. The intrinsic parameters can be measured to some extend and/or treated phenomenologically. It is encouraging to see that the relaxation rates and their trends as function of fractional valence can actually again be classified theoretically with the aid of Hund's rules (and hopefully in the future with the aid of crystal field symmetries) by a relatively straightforward but appropriate perturbation theory (1). Given these parameters, the valence can be obtained from thermodynamics.

In the following we shall first critically examine the experimental methods to measure the valence. Then we shall lay down the thermodynamical tools by which the valence can be predicted from the above parameters. We shall then focus on the thermodynamic predicition of the high temperature limit of the valence in comparison with experiment. Next we shall demonstrate the importance of measurements of the valence on two examples: the valence of impurities and of tetravalent Cerium compounds. After discussing the behavior of the valence at lower temperature a few words will finally be said about trends of valence changes with intraionic and external pressure and with thermal expansion of the matrix.

2. VALENCE MEASUREMENTS

Table I lists the experimental methods to measure the valence which are in use at this time. The first two lines show applicability to the six potentially IV RE species and to distinguishing dynamic from static mixture at $T \to 0$. The next two lines give the limits of temperature and pressure range achieved so far in at least one published experiment. (These ranges are not necessarily common or easy to cover.) Asterisks indicate room for larger pressure and temperature ranges. The fifth line gives the limit of relative accuracy achieved so far, again in at least one experiment. Relative accuracy is defined here as the limit of detection of a valence change driven e.g. by temperature or pressure, under otherwise unchanged experimental conditions, on the same sample of a compound. The relative accuracy for dilute alloys can be roughly estimated by dividing the listed values through the RE concentration (except for Moessbauer (ME) measurements where the relative accuracy is a much slower function of concentration). This shows why we know so little about the valence of dilute alloys. The list also shows how difficult it is to ascertain experimentally homogeneous (dynamic) mixture. This can be done directly (microscopically on the RE site) only by ME measurements in IV Eu and Sm. The next best methods are low temperature susceptibility or low temperature neutron diffraction (absence of magnetic order), of course only in the vast majority of IV systems which do not order magnetically. In questionable cases capacitive thermal expansion could detect any phase transition and would prove homogeneous mixture by their absence. In magnetically ordering IV compounds, homogeneous mixture can so far only be assumed on the basis of circumstantial evidence (e.g. TmSe).

From the point of view of general applicability, relative accuracy (and last but not least, ease of handling), x-ray lattice constant and -absorption measurements are the clear frontrunners. ME is singular in its applicability only to Eu, but at all temperatures, pressures and concentrations. Capacitive thermal expansion is singular with respect to relative accuracy. It can be generally applied to all systems (even dilute alloys) over a large temperature range (especially to very low temperatures) but of course only at zero pressure.

Method	x-ray diffraction	capacitive thermal expansion	Moessbauer	L_{III} x-ray absorption	XPS UPS	static susceptibility
Ionic species	all	all	Eu(Sm)	all	all	all
dynamic or static mixture?	no	possibly	yes	no	possibly	yes
pressure range [kbar]	0-300^x	0	0-50^x	0^x	0	0-45^x
Temperature range [K]	1-1000	1^x-400^x	0.01-700	1-300^x	77^x-750^x	1-1200
Relative accuracy	10^{-2}	$<10^{-4}$	10^{-2} (10^{-1})	10^{-2}	10^{-1}-10^{-2}	10^{-1}
Problems	a) calibration of a_{n+1}, a_n b) valence linear in $(a_{n+1}-a_n)$?		calibration of δ_2, δ_3	final state effects?	a) bulk valence? b) final state effects	only useful at $T>>T_f$ for valence measurement.

Table I: Experimental methods to measure the intermediate valence.

All numbers given for the valence in the literature are afflicated by much larger absolute (systematic) errors. Quite througout, the limits of absolute uncertainity are ±10% roughly, not much better than 10 years ago. Therefore it is very difficult to distinguish e.g. between integral valent Ce and Yb compounds and the corresponding intermediate valence compounds in the high temperature limit (3.07 for Ce, 2.89 for Yb; see Table II) on the basis of direct valence measurements alone. The systematic errors in the case of ME measurements are due to uncertainity about the isomershifts of the fictious integral valent ($4f^{n+1}$ and $4f^{n}$) compounds. In the case of x-ray absorption (or XPS, UPS) the shape of the edge (or of the XPS-UPS spectrum) may be modified by the host (or the surface) and by shakeup and shakedown (final state) effects. In XPS/UPS the valence is measured on the surface, where it can be different from the bulk.

The sources of absolute error of the valence measurement through x-ray diffraction and capacitive thermal expansion are the same. The first is uncertainty about the lattice constant of the fictitious integral valent $4f^{n+1}$ and $4f^{n}$ compounds. The error is small for the 3^+ partner (the 3^+ lattice constant can be safely interpolated between 3^+ compounds with directly adjacent atomic number) but serious for the di- or tetravalent partner. The latter numbers usually come from an educated guess, guided by lattice constants in related series of compounds with actually existing divalent species or, lacking that type of information, from an extrapolation of the dependence of the trivalent lattice constants as function of ionic radius and the difference of the $4f^{n+1}$ and $4f^{n}$ ionic radii. For tetravalent Ce and Pr there is another problem (see Section 6). But even if one has reliable numbers for both fictious integral valent compounds, one faces another serious systematic error: the assumption that valence and lattice constant are linearly related. There are good reasons and mounting evidence for the conclusion that this assumption is wrong and that the nonlinearity is severe. The evidence is systematic deviations of the valence from lattice constant compared with the valence from other measurements, with growing tendency for valencies from all other measurements to cluster about some value and the lattice constant showing a more than 10% larger value (e.g. for TmSe L_{III} x-ray absorption (10), UPS (11), susceptibility (12) and neutron diffraction (13) give values around 2.58 while the lattice constant says 2.75 (12); for Yb compounds see (8); for SmB_6 see Table II.) The reason for this problem is discussed in (39).

3. THERMODYNAMICS OF FLUCTUATING VALENCE SYSTEMS

The symbol of this conference

(1) $$4f^{n+1} \leftrightarrow 4f^{n} + e$$

can be thought to describe a chemical reaction in a gas or liquid. Neglecting interactions, the free energy of a system with $N = N_{n+1} + N_n$ rare earth (RE) intermediate valence (IV) ions is

(2) $$F = -k_BT \ln Z = -k_BT\{N_{n+1} \ln (\zeta_{n+1}/N_{n+1}) +$$
$$+ N_n \ln(\zeta_n/N_n) + N_e\beta\varepsilon_F +$$
$$+ \sum_r \ln (1+\exp (\varepsilon_F-\varepsilon_r)\beta)\} .$$

Here ζ_i are the partition functions of the ionic configurations, $\varepsilon_F(N_e)$ is the Fermi energy, ε_r are the energy eigenstates of the conduction electrons and N_{n+1}, N_n and N_e the numbers of ions in the $4f^{n+1}$ and $4f^{n}$ configurations and of the conduction electrons. The condition for chemical equilibrium is

(3) $$\sum_j b_j \, \partial F/\partial N_j = 0$$

With $b_{n+1} = -b_n = -b_e = 1$ and for $\varepsilon_F\beta \ll 1$ this becomes

(4) $$\ln (\zeta_{n+1}/N_{n+1}) - \ln (\zeta_n/N_n) - \varepsilon_F\beta = 0$$

We name the lowest energy states of the configurational intraionic multiplett and crystal field spectra $E_{n+1,0}$ and $E_{n,0}$ (Fig. 1) and rewrite (4):

(5) $$[E_{n+1,0} - (E_{n,0} + \varepsilon_F)] - k_BT\,(\ln(\zeta'_{n+1}/\zeta'_n) -$$
$$- \ln(N_{n+1}/N_n)) = 0$$

Here ζ'_j are the configurational partition functions with energies ε_{ji} counted from $E_{j,0}$. We define the excitation energy by

(6) $$E_x \equiv E_{n+1,0} - (E_{n,0} + \varepsilon_F)$$

and the probability ν for the ion to be in the $4f^{n}$ configuration in the thermal average by

(7) $$\nu \equiv (1+N_{n+1}/N_n)^{-1} .$$

From (5)-(7) and with the charge of the lower valence, Z_{n+1}, we obtain the valence

(8) $$v(T) = Z_{n+1} + \nu = Z_{n+1} + [1+(\zeta'_{n+1}/\zeta'_n)\cdot$$
$$\cdot \exp(-E_x\beta)]^{-1}$$

Other thermal averages of ionic properties follow in the usual fashion from

(9) $$\langle A\rangle_T = \sum_{j=n+1,n} \exp(-E_{j,0}\beta)\sum_i (A_{ji}g_{ji}\cdot$$
$$\exp(-\varepsilon_{ji}\beta))/(\zeta_{n+1}+\zeta_n)$$

The only input parameters in equ. (8) are E_x, which is determined by chemical binding energies and depends on pressure and temperature and intraionic multiplet as well as ionic crystal field spectra. The value of the valence calculated from this equation cannot be affected much by the valence fluctuation as long as the associated shifts and broadenings of the configurational and conduction electron energies are small compared to k_BT. Thus equ. (8) gives a good approximation of the valence in the high temperature limit, without any need to consider complicated many body effects between ions and conduction electrons.

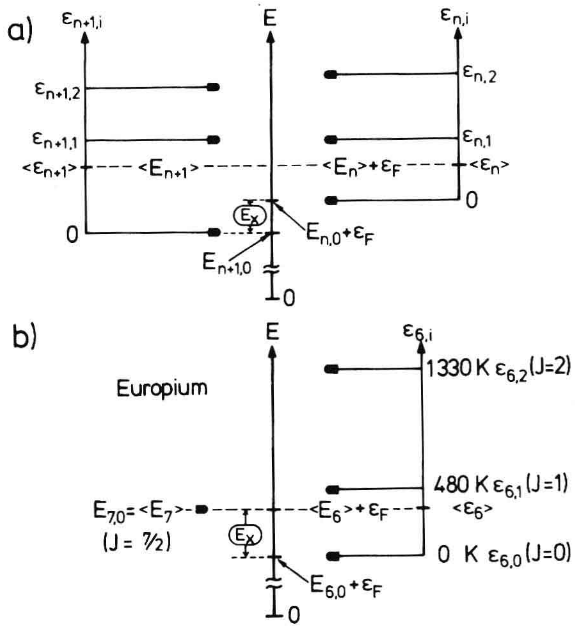

Fig. 1: a) The two configurational multiplet and CEF spectra, schematically.For chemical equilibrium

$$<E_{n+1}> = E_{n+1,0}(V)+<\varepsilon_{n+1}> = E_{n,0}(V)+ + \varepsilon_F + <\varepsilon_n>$$

Note: $E_x \equiv E_{n+1,0}-(E_{n,0}+\varepsilon_F) \neq 0$ for $T \neq 0$

b) Same as a) but for specific example of intermediate valent Europium.

There is every indication that the valence fluctuation does not effect the intraionic functions $\zeta_J^{\prime}$ very much even at lower temperatures. For a large class of IV compounds (those which do not order magnetically) the main effect of valence fluctuations seems to be a lifetime broadening of all configurational levels. This lifetime broadening is synonymous with finite occupation of excited intraionic levels at T=0. (Of course, intraionic energy levels should then no longer be confused with energy eigenstates of the entire systems.) Finite occupation at T=0 can formally be achieved by introduction of an effective temperature defined by

$$(10) \quad T^* \equiv (T^2 + T_f^2\,(T))^{1/2}$$

which replaces the actual temperature T in all preceding equations. $T_f(T)$ approaches a constant, finite value as $T \to 0$ and is closely related to the magnetic relaxation rates (quasielastic linewidths) measured directly by neutron spectroscopy ($k_B T_f(T) \approx \Gamma(T)/2$).

The definition of the effective temperature by the square root of the sum of squares is a significant improvement over an older expression (2) in this type of phenomenological thermodynamics ($T^* \equiv T_f(T) + T$) because Nernst's law is no longer violated and because the new form of T^* mimics nicely all kinds of Fermiliquid effects in the limit $T \ll T_f$ (e.g. the specific heat goes to zero there linearly with T, the valence changes proportional to T^2 etc.).

E_x and T_f depend on volume: the volume of the IV ion is about 20 - 30% larger in the $4f^{n+1}$ than in the $4f^n$ configuration. This is due to the different amount of screening of the nuclear charge experienced by the outer valence electrons when the 4f occupation number changes by one unit. This purely ionic effect is communicated to the solid and produces two volumes of the primitive cell of a compound, V_{n+1} and V_n, with difference $\Delta V \equiv V_{n+1}-V_n$. ΔV is usually larger than the difference of ionic volumes and very large compared to the slight volume changes associated with intra configurational transition from one crystal field or multiplet state to another. Therefore the volume dependence of the intraconfigurational partition functions $\zeta_J^{\prime}$ can be neglected and the volume dependence of the valence is entirely due to $E_x(V)$ and $T_f(V)$.

The effect on E_x of pressure applied from the outside can be obtained from the work done by transferring ions from the configuration $4f^{n+1}$ to $4f^n$, with volume difference ΔV (3)

$$(11) \quad \frac{dE_x}{dp} = V_{n+1}(p,T) - V_n(p,T) = \Delta V(p,T)$$

Another way of changing $E_x(V)$ is the ordinary thermal expansion of the matrix. The associated change of volume of the ionic cell produces a change of pressure on the ion, which can be obtained via

$$(12) \quad \left.\frac{dE_x}{dT}\right|_\alpha = \Delta V \frac{dp_\alpha}{dT} = \Delta V \frac{\alpha(T)}{\kappa(T)}$$

Here $\alpha(T)$ is the volume coefficient of thermal expansion and $\kappa(T)$ an effective compressibility.

Finally, upon heating, the ion changes its mean volume because of the temperature driven valence change. Equ. (5) contains the difference of the configurational entropies

$$(13) \quad \Delta S(T) = k_B T \ln (\zeta_{n+1}^{\prime}/\zeta_n^{\prime})$$

which is a function of temperature and produces a volume change through the valence change according to $dV_\nu/dT = -\Delta V d\nu/dT$ and a change of the excitation energy via a pressure p_ν analogous to equ. (12)

$$(14) \quad \left.\frac{dE_x}{dT}\right|_\nu = -\Delta V \frac{dp_\nu}{dT}$$

Altogether, the temperature dependence of E_x is complicated but should be traceable. Note that $E_x(T)$ must be found selfconsistently, since $\nu(T)$ is a function of $E_x(T)$ but also determines it through equ.(14).

4. THE HIGH TEMPERATURE LIMIT OF THE VALENCE

The intraionic multiplet structure with its Hund's rule ground states seems to survive the valence fluctuation, just as in integral valence it survives thermal motion and crystal field motion (van Vleck anomalies of susceptibility). The reason is obvious: The fluctuation temperatures range from a few Kelvin to a few 100 K, i.e. they are orders of magnitude smaller than the overall multiplet splittings. Given intermediate valence near T=0, there is every reason to also expect intermediate valence at higher temperatures: First, for intermediate valence at T=0, E_x must be of order T_f, since otherwise $\nu\to 1$ or $\nu\to 0$. Then for $T>T_f$ there seems no reason to expect E_x to shift with T by more than the available thermal energy k_BT, or $kT \gtrsim E_x$ always for $T>>T_f$. In other words: no system with intermediate valence at T=0 can possibly go into an integral, stable valence state by simple heating (e.g. Ce; the γ phase is in an intermediate valence state!). One can then predict the valence for E_x, $kT_f<<kT$ from equ. (8) with Hund's rules, most easily for Pr, Tm and Yb, which have no thermally accessible multiplet states. For $E_x/kT<<1$, we have simply (with the total angular momentum of the Hund's rule ground state J_j)

$$(15)\quad v(T)\to Z_{n+1}+\left[1+\zeta'_{n+1}/\zeta'_{n}\right]^{-1}\to v_{\infty}=Z_{n+1}+\left[1+g_{n+1}/g_{n}\right]^{-1}=Z_{n+1}+\left[1+(2J_{n+1}+1)/(2J_{n}+1)\right]^{-1}$$

Table II shows v_∞, the high temperature limit of the valence predicted from the entropy limit due to Hund's rules. For Pr there is no measurement of the valence yet (4). For Tm and Yb the valence from L_{III} x-ray absorption at 300 K is at the expected value within the (considerable) experimental uncertainty. For Ce we have to be careful when analysing high T data: the multiplet splitting between the J=5/2 and J=7/2 states is only 3000 K and might be reduced in the mixed valence state, because the Ce (and Pr) 4f wave functions are capable of considerable delocalization (5,6), which will bring down the spin orbit coupling and can therefore increase the thermally accessible degeneracy of the $4f^1$ configuration from 6 to 14. This tends to decrease v_∞ from 3.14 to 3.067, as indicated in the second row for Ce. Note that the valence from lattice constant analysis listed in Table II for Ce is shifted from the literature values by 50% towards 3^+ (e.g. from 3.45 (7) to 3.23 for $CePd_3$). For the reason see (8) and later in this paper. Note also that while at 300 K in the examples given for Tm and Yb, k_BT is large compared to kT_f (and presumably to E_x) this is not true for most Ce examples, i.e. the numbers for Ce are not really taken in the high temperature limit (except for $CePd_3$ at 1200 K and may be

SE	n+1 n	Z_{n+1} Z_n	J_{n+1} J_n	g_{n+1} g_n	High temper. limit of valence	Example	T[K]	T_f [K]	measured valence	Method	Ref.
Pr	2 1	3^+ 4^+	4 2.5	9 6	3.40						
Tm	13	2^+	3.5	8	2.62	TmSe	300	70	2.58±.07 2.75	L_{III} a	10 12
	12	3^+	6	13		$Y_{.95}Tm_{.05}Se$	300		2.55±.1	L_{III}	14
Yb	14	2^+	0	1	2.89	YbCuAl	300	~50	2.95	L_{III}	8
	13	3^+	3.5	8		$YbCu_2Si_2$	300	~80	2.9	L_{III}	8
Ce	1	3^+	2.5	6	3.14	γCe	300	~100	3.05	a	9
	0	4^+	0	1		αCe	300	~400	3.3	a	9
						$CeSn_3$	300	260	3.1	a	16
									3.3	a	17
						$CePd_3$	1200	220	3.14	χ	18
	1	3^+	5/2,7/2	6,8			300	220	3.23	a, L_{III}	7,8
					3.067		23	220	3.29	a, L_{III}	7,8
	0	4^+	0	1		$Th_{1-x}Ce_x$	300		3.13	a	19
Sm	6	2^+	0	1	2.67	SmS	300 (10kbar)	~50	2.77	a	see e.g. 20
	5	3^+	(5/2), Γ_6	2		SmB_6	0-600	~50	2.77	a	
	6	2^+	0,1	1,3	2.67				2.65	L_{III}	
	5	3^+	5/2	6					2.65	ME	

Table II: Comparison of expected high temperature valence with available data.

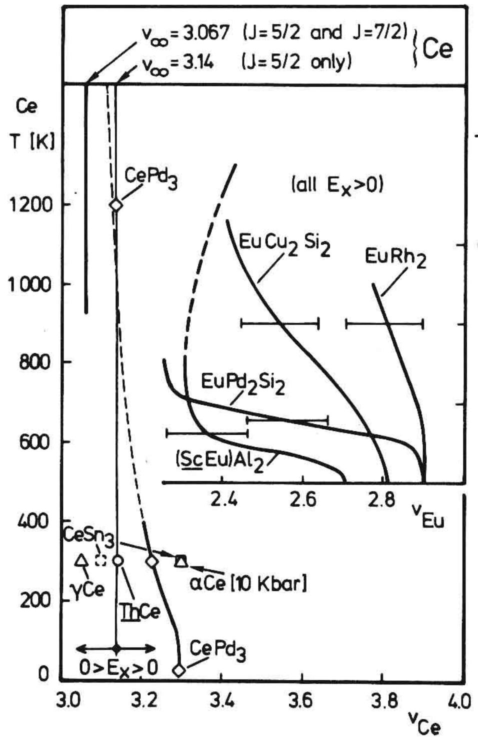

Fig. 2: The valence of some Ce and Eu compounds and dilute alloys (all numbers have absolute uncertainty ±0.1 but much better relative accuracy). For Ce the limit of the valence is at 3.067 for very high temperatures and at 3.14 at high temperatures. For Eu the high temperature variation of the valence is caused by the multiplet structure of $4f^6$.

for ThCe). The observed small deviations from the high temperature limit provide insight into the trend of valence change towards lower temperatures. While γCe (and many compounds like $CeAl_2$, $CeAl_3$) tend towards 3^+ with decreasing temperature, αCe (and many compounds, e.g. $CePd_3$, $CeBe_{13}$, $CeSn_3$) go towards 4^+. This is expected if $E_x \equiv E^{3+}-(E^{4+}+\varepsilon_F)$ is smaller than zero for the γCe class and larger for the αCe class. The trend is symbolically indicated in Fig. 2. At the pressure driven γ→α phase transition of Ce, E_x seems to make a sudden jump from negative to positive, while this motion occurs gradually at pressures larger than 25 kbar with decreasing temperature. The two values for $CeSn_3$ indicate the spread between earlier (16) and later (17) evaluations of the valence.

Eu^{3+}, Sm^{2+} and Sm^{3+} are RE ions with thermally accessible excited intraionic multiplet levels. In $4f^6$ (Eu^{3+}, Sm^{2+}) the first excited state is at E(J=1)-E(J=0)=480 K(Fig. 1b) and in $4f^5$ (Sm^{3+}) at E(J=7/2)-E(J=5/2) 800 K. This multiplet structure gives rise to very specific behaviour of the high temperature valence, which is best illustrated for intermediate valent Eu ions. First note (Fig. 1b) that the mean thermal energy of Eu^{2+} is always at $\langle E_7 \rangle = E_{7,0}$, because the next multiplet state is thermally inaccessible. For Eu^{3+}, on the other hand, the mean energy $\langle E_6 \rangle$ is larger than $E_{6,0}$ as soon as $T^*>0$. If we have intermediate valence at T=0, T_f must be larger than 0, say $T_f \approx 200$ K. Therefore we expect $E_x>0$ from purely thermal arguments (see eqs. (4) and (13) and Fig. 1b). The valence should then be near 3^+. Increasing temperature will shift the valence towards 2^+ for a while, because of the initially larger degeneracy of the 2^+ configuration (Fig. 1b). Both features are indeed observed through the temperature dependent Moessbauer isomershift in all known IV cases with Eu ($EuCu_2Si_2$ (22), $EuRh_2$ (22), $EuPd_2Si_2$(23) and dilute Eu in $ScAl_2$ (24)), Fig. 2. However, at sufficently large temperature, the valence must shift towards 3^+ again (dashed line for Eu in $ScAl_2$ in Fig. 2) because while the entropy of Eu^{2+} saturates at $k_B \ln 8$, that of Eu^{3+}, initially near zero, keeps increasing by thermal population of the excited multiplet states and is e.g. near $k_B \ln 14$ at 2600 K.

A discussion of IV Sm at high temperature is very complicated, because both configurations have thermally excitable multiplet structure. In Table II Sm is only included to demonstrate this. One may for instance argue that with $T_f \approx 50$ K all excited multiplet levels may be ignorable. If one also assumes a large CEF splitting of the J=5/2 state of Sm^{3+} with a doublet ground state, one can explain the valence of SmS at 10 kbar and of SmB_6 at 300 K ($v(300) \approx 2.7$; see Table I). Or alternatively (and better), with T=300 K and T_f= 50 K one may ignore all excited states in $4f^5$ but keep the J=1 level in $4f^6$ to find $\langle E^{2+} \rangle \approx E_x$ and v=2.67 once more.

5. INTERMEDIATE VALENCE ON DILUTE IONS

If it is hard to obtain good numbers for the valence of IV compounds, it is nearly impossible to find them for dilute alloys. This is a severe handicap for progress in the fluctuating valence field. There are many indications from concentration series or pressure experiments that the phenomenology of the IV ions does not change very much when changing concentration, or when applying pressure to a dilute alloy (e.g. in $Yb_{1-x}Y_xCuAl$ (25) or $Yb_{1-x}Y_xCu_2Si_2$ (26) the characteristic temperature remains essentially independent of concentration, and the critical pressure of Ce and Pr in La (27,4) as seen via the depression of superconductivity of La, is very near the pressure for the valence transition of Ce (9) and Pr (4). But somehow, in spite of nearly identical phenomenology, a valence fluctuation temperature in a compound usually ends up to be called a Kondo temperature in a dilute alloy.

As long as there is no microscopic proof positive for intermediate valence on a sufficiently large number of such dilute alloys with macroscopic anomalies very similar to IV compounds, it will probably be impossible to effectively dispel the historical notion that these alloys are Kondo alloys (with the implication of nearly integral valence carried by this term).

In Table II and Fig. 2 I have included the only three cases of sufficiently dilute alloys, where the valence could be determined, to my knowledge. In $ThCe_x$ the $x=0$ Ce valence is obtained by extrapolation of the lattice constant as function of x (19). All three clearly show intermediate valence; Ce in Th and Tm in YSe at the respective high temperature limits, and Eu in $ScAl_2$ with qualitatively the same temperature dependence as in $EuCu_2Si_2$, $EuRh_2$ and $EuPd_2Si_2$ (including a valence change by nearly 40% between 4 and 300 K) All three cases indicate remarkably low fluctuation temperatures. One may conclude from this very limited ensemble of three successful microscopic valence measurements on dilute alloys with macroscopic anomalies that the score is 3:0 for intermediate valence and against the Kondo effect on essentially integral valent dilute ions.

A word seems in place here concerning intermediate valence in concentrated alloys. Such alloys are often used to obtain information on the effects of pressure on intermediate valence by varying the concentration of some component between similar compounds with different lattice constants. Unfortunately in such alloys translational symmetry is lost. This results in practice in a number of distinctly inequivalent sites for the fluctuating valence ions. Clearly the parameters E_x and T_f and the crystal field will then depend on the site. Yet almost all measurements (e.g. transport, susceptibility, specific heat, lattice constant, neutron inelastic spectroscopy etc.) will see an average IV anomaly. Anybody interested in a case where the components of such an average could be resolved microscopically should look at the Moessbauer spectra of the system $La_{1-x}Eu_xRh_2$ and $La_{1-x}Eu_xPt_2$ (22). For a given concentration there are several sites with valence ranging all the way from 2^+ to 3^+. Changing concentration (or temperature) changes the distribution over sites and in some cases the valence of a given site. This feature of several sites with distincly different physical properties is also well known from concentrated transition metal alloys (28). There is no proof (and, in my opinion, little hope) that concentrated alloys with other RE IV ions than Eu are microscopically more homogeneous. For this reason concentrated IV alloys can only serve to study some qualitative, average trends. Single site systems are definitely required for quantitative analysis of the fluctuating valence phenomenon. Such systems can only be certain well prepared stochiometric compounds or sufficiently dilute alloys. On the long run there seems to be no way around hydrostatic pressure experiments (in spite of their difficulty) if one wants to gain control over the pressure dependence of the IV phenomenon quantitatively (4).

6. THE VALENCE OF CERIUM

As mentioned in section 2, L_{III} x-ray absorption seems a generally applicable tool to measure the valence of compounds with good relative accuracy over a wide range of temperature (and hopefully soon pressure). This technique has been known from SmB_6 for a long time (29), but it was again applied in a systematic fashion to the IV problem only since 1978 (10, 14, 30, 31). We have had the data presented elsewhere at this conference (8) since more than two years now, but did not know how to interpret the Cerium spectra. The interpretation presented in (8) took a long time to grow together. Briefly the story is this: L_{III} edges of all integral valent compounds of potentially unstable RE ions (Ce^{3+} , Pr^{3+}, Sm^{2+}, Eu^{2+}, Eu^{3+}, Tm^{2+}, Tm^{3+}, Yb^{2+}, Yb^{3+}) show a strong, single and simply shaped peak except Ce^{4+} (Pr^{4+} and IV Pr has not yet been measured). The peak position scatters by about ±1 eV from one metallic compound to the next due to chemical shift, but within experimental resolution (the peak is several eV wide, the experimental resolution is ±2 eV and is also subject to change) there is no hint of any double peaked structure yet. Thus one may safely say that in none of the above integral valent cases bandstructure or final state effects have so far been detected in several hundred such measurements. On this background the "Ce^{4+}" spectrum is utterly abnormal: all compounds which are traditionally classified as tetravalent (from lattice constant and magnetic data) show a double peaked edge, with the stronger leading peak at the position of the peak in trivalent Ce compounds, and the trailing peak shifted by nearly 10 eV to higher energy. Bona fide Ce IV compounds (e.g. $CePd_3$) show similar spectra and the traditional valence can be extracted by superposition of a normal spectrum from a trivalent case and one of the abnormal double edged "tetravalent" spectra. If one, however, naively interprets a "tetravelant" spectrum as one due to intermediate valence itself, as one can do successfully in all double peaked IV classes of Sm (29), Eu (30), Tm (10) and Yb (8), one is forced to conclude that the valence of the socalled tetravalent Ce compounds is actually near 3.3 . This was very hard to accept and we tried explanations via bandstructure and final state effects for a long time. But finally we realized that the "tetravalent" lattice constants of Ce and Pr are also abnormal: the ionic volume change from the Ce^{3+} to "Ce^{4+}" is less than half of the value extrapolated from those of Eu, Sm, Tm and Yb (8). Therefore the L_{III} anomaly seems actually to be mainly due to an initial state anomaly. Final state effects (shakeup and shakedown) cannot definitely be excluded altogether at this time in the analysis of the "Ce^{4+}" anomaly. However, if they exist, their effect will be secondary as far as extraction of the valence of "tetravalent" Ce from L_{III} spectra is concerned. Primarily Cerium seems to have two intermediate valence states, one like in αCe, the other like in α'Ce, and nobody has so far identified a truely tetravalent Ce compound