

Chapter 11

KONDO EFFECT: ALLOYS AND COMPOUNDS*

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Symbols

C = specific heat
 ΔC = specific heat jump at the superconducting transition
 E_{exc} = excitation energy between lanthanide electron configurations $4f^n$ and $4f^{n-1}$
 E_F = Fermi energy
 E_c = energy separating centroid of localized state and Fermi level

E_n = energy of lanthanide electron shell configuration $4f^n$
 g = Landé's g -factor
 h = Planck's constant
 H = magnetic field
 H_c = critical magnetic field
 \mathcal{H} = exchange hamiltonian
 \mathcal{H}_R = exchange hamiltonian for lanthanides
 \mathcal{J} = exchange interaction parameter
 \mathbf{J} = total angular momentum operator
 k_B = Boltzmann's constant
 \mathbf{L} = orbital angular momentum operator
 n = impurity concentration
 $N(E_F)$ = conduction electron density of states at the Fermi level
 \mathbf{S} = spin angular momentum operator
 s = conduction electron spin density
 T = temperature
 T_c = superconducting transition temperature
 T_K = Kondo temperature
 T_F = Fermi temperature
 T_0 = magnetic moment fluctuation temperature
 T_{sf} = magnetic moment fluctuation temperature
 T_{RKKY} = characteristic temperature of RKKY interaction
 \mathcal{U} = intra-atomic Coulomb repulsion parameter
 V_{kl} = conduction electron-localized electron state admixture matrix element
 γ = electronic specific heat coefficient

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Δ = half width in energy of localized state	ν_0 = valence fluctuation frequency
δ = crystal field splitting	ρ = electrical resistivity
$\epsilon(n)$ = fraction of time $4f$ shell has configuration $4f^n$	θ = Curie-Weiss temperature
χ = magnetic susceptibility	τ_{M} = magnetic moment lifetime
μ_{B} = Bohr magneton	τ_0 = valence or interconfiguration fluctuation lifetime
μ_{eff} = effective magnetic moment	

1. Introduction

The interaction between impurity ions with partially filled d or f electron shells and the conduction electrons of a metallic host can lead to variations in certain physical properties with temperature and magnetic field which have come to be associated with the "Kondo effect". In zero magnetic field, these temperature-dependent anomalies in the physical properties scale with a characteristic temperature T_K , the so-called Kondo temperature, above which the matrix-impurity system behaves *magnetically* and below which the matrix-impurity system behaves *nonmagnetically*. The physical properties which exhibit anomalies attributable to the Kondo effect include the electrical resistivity, magnetic susceptibility, thermoelectric power, specific heat; and, in systems where appropriate, superconducting properties such as the critical temperature T_c and the jump in specific heat which occurs at T_c .

With respect to the electrical resistivity, the Kondo temperature roughly separates a high temperature region ($T \gg T_K$) where the resistivity varies linearly with the logarithm of the temperature, and a low temperature region ($T \ll T_K$) where the resistivity saturates to the so-called "unitary limit" as $T \rightarrow 0$. For temperatures well above T_K , the magnetic susceptibility resembles a Curie-Weiss law with a Curie-Weiss temperature which is of the order of several times T_K , whereas for temperatures well below T_K , the susceptibility exhibits at most a weak temperature dependence and approaches a finite value as $T \rightarrow 0$. The specific heat and thermoelectric power exhibit broad maxima as a function of temperature which peak in the vicinity of T_K .

In matrix-impurity systems in which the matrix is a superconductor and T_K is sufficiently low compared to T_{c0} , the critical temperature of the pure host, the temperature dependent scattering of conduction electrons by impurity spins may even lead to the striking phenomenon of *re-entrant superconductivity* (where alloys within a certain impurity concentration range exhibit a transition to the superconducting state at a critical temperature T_{c1} which is followed by a return to the normal state at a second lower critical temperature T_{c2}) as well as pronounced deviations of the specific heat jump from the BCS law of corresponding states.

Historically, the types of normal state "Kondo anomalies" described above were first studied in *dilute* alloys of 3d (Fe-group) transition metals dissolved in "simple" metal hosts such as the noble metals Cu, Ag and Au. However, in 1965,

Sugawara observed the first resistance minimum phenomenon due to a lanthanide solute in the dilute alloy system YCe. Following this discovery of the Kondo effect in the YCe system, numerous dilute and concentrated lanthanide metallic systems have been investigated over the past decade. Of the thirteen lanthanide ions with partially-filled 4f shells, Kondo-like behavior has been observed for Ce, Pr, Sm, Eu, Tm and Yb.

The Kondo-like anomalies in the normal state physical properties of concentrated lanthanide systems closely resemble those of dilute lanthanide systems. This is true for two reasons. First, the spatial extent of the 4f wave functions of the lanthanide ions is only of the order of one-tenth of an interatomic spacing (substantially smaller than the spatial extent of the 3d wave functions of transition metal ions) so that direct exchange coupling via overlap of the neighboring 4f wavefunctions is virtually negligible. Second, the magnitude of the exchange interaction between the 4f and conduction electrons is only of the order of 0.1 eV so that indirect RKKY exchange (Ruderman and Kittel, 1954; Kasuya, 1956; Yosida, 1957) is relatively weak. In view of the similarity in their physical properties, we consider in this review concentrated as well as dilute assemblages of lanthanide ions with partially-filled 4f electron shells immersed in a sea of conduction electrons. In these systems, the magnetic character of the lanthanide ions can span the entire range between magnetism and nonmagnetism, and with a particular system there can be associated a characteristic temperature above which the lanthanide ions behave magnetically and below which they behave nonmagnetically.

It should be noted that when the characteristic temperature is low, it is invariably referred to as the Kondo temperature T_K , whereas when it is high, it is often identified with a magnetic moment fluctuation temperature which is usually denoted by T_{sf} or T_0 [recent experimental evidence from studies on concentrated lanthanide metallic systems suggests that these magnetic moment fluctuations may be due to temporal fluctuations of the lanthanide ions between two ionic configurations whose occupation number differs by one electron (see section 2)]. These correspondences are, however, based on two distinct microscopic models. One of the models appears to be valid in the magnetic (low T_K) limit; the other seems to be valid in the weakly magnetic or nonmagnetic (high T_{sf} or T_0) limit. To date, no successful unified theory has been developed to connect these two limits in a continuous fashion. This is in spite of the substantial body of experimental data which documents in detail the continuous demagnetization of a lanthanide ion with a partially-filled 4f shell in a metallic environment. Therefore, *we emphasize that there is generally a continuum of types of magnetic behavior between the extreme magnetic and nonmagnetic limits.* (Of course, a dense array of lanthanide ions in a metallic system may undergo a discontinuous cooperative phase transition between two distinct magnetic states upon alloying with another element or the application of an external pressure.) Moreover the physical properties in each magnetic state of this continuum are similar when the temperature is scaled with the appropriate characteristic temperature – hence *it seems highly probable that there is a single physical mechanism that is respon-*

sible for the entire spectrum of magnetic behavior exhibited by numerous metallic lanthanide systems which incorporates the Kondo and spin fluctuation models as limiting cases.

Because of the wide range of magnetic character displayed by the lanthanide metallic systems reviewed herein, they provide a rich testing ground for the concepts and theories which have been advanced to account for Kondo-like anomalies in the physical properties of these systems. However, before reviewing the Kondo-like behavior of dilute and concentrated lanthanide metallic alloys and compounds in sections 3 and 4 of this article, respectively, we briefly discuss a number of models in the following section which have been proposed to describe the systems which exhibit Kondo-like behavior in their physical properties. The article is concluded in section 5.

2. Concepts and models for Kondo-like systems

In the traditional view, the interaction which is believed to be responsible for the Kondo effect proceeds via the conduction electron-impurity spin exchange interaction. The hamiltonian for this interaction (the so-called s-d or s-f hamiltonian) is

$$\mathcal{H} = -2\mathcal{J}\mathbf{S} \cdot \mathbf{s}, \quad (11.1)$$

where \mathcal{J} is a parameter that characterizes the sign and magnitude of the interaction, \mathbf{S} is the spin on the impurity ion, and \mathbf{s} is the conduction electron spin density at the impurity site. The strong spin-orbit coupling found in lanthanide ions suggests that a more appropriate interaction hamiltonian (deGennes, 1962a) is

$$\mathcal{H}_R = -2\mathcal{J}(g-1)\mathbf{J} \cdot \mathbf{s} \quad (11.2)$$

which is obtained by replacing \mathbf{S} by its projection onto the total angular momentum vector $\mathbf{J} = \mathbf{L} + \mathbf{S}$ of the Hund's rule multiplet, i.e.,

$$\mathbf{S} \rightarrow [(\mathbf{S} \cdot \mathbf{J})/J(J+1)]\mathbf{J} = (g-1)\mathbf{J}, \quad (11.3)$$

where g is the Landé g -factor for the appropriate Hund's rule ground state.

Calculations based on the conduction electron-impurity spin exchange hamiltonian [eq. (11.1)] yield the characteristic anomalies in the physical properties which are associated with the Kondo effect when \mathcal{J} is negative. This was first demonstrated by Kondo in 1964 when he explained the "resistance minimum phenomenon" first observed for 3d transition element impurities in noble metal hosts. Kondo's theory consisted of a perturbation calculation of the scattering of conduction electrons by the impurity spins to third order in the exchange coupling parameter \mathcal{J} . His calculation of the electrical resistivity yielded a logarithmic temperature dependence in agreement with experiment, but exhibited a divergence at a characteristic temperature, T_K , given by

$$T_K \sim T_F \exp[-1/N(E_F)|\mathcal{J}|] \quad (11.4)$$

which has since come to be known as the Kondo temperature. Here, T_F is the Fermi temperature and $N(E_F)$ is the host density of states at the Fermi level.

Since Kondo's original calculation, a great deal of effort has been put forth by theorists to calculate the various physical properties of matrix-impurity systems for temperatures both above and below T_K (see, for example, Suhl, 1973; Grüner and Zawadowski, 1964). This has led to a physical interpretation of the Kondo temperature as the characteristic temperature for the formation of a "quasi-bound" state in which the conduction electron spins tend to antiferromagnetically compensate the spins of the impurities with the degree of compensation increasing gradually as the temperature is lowered through T_K . At temperatures well below T_K the many-body electron-impurity spin system behaves non-magnetically (i.e., the magnetic susceptibility approaches a constant value as $T \rightarrow 0$) whereas at temperatures well above T_K , it behaves magnetically, giving rise to a Curie-Weiss temperature dependence of the magnetic susceptibility and the temperature-dependent anomalies in the electrical resistivity, specific heat and thermoelectric power noted in the introduction.

The reader is cautioned to observe, however, that existing theories for the various physical properties of Kondo systems do not provide a self-consistent definition for the characteristic temperature as defined by the temperatures of the typically broad anomalies in the thermoelectric power, electrical resistivity, heat capacity and magnetic susceptibility. Thus the values of the characteristic temperature inferred from different measurements may differ by as much as an order of magnitude.

Many of the earlier theories gave satisfactory results for temperatures above and around T_K , but were inadequate at temperatures below T_K . Recently, new theoretical techniques, pioneered by Wilson (see, for example, Wilson, 1975; Nozieres, 1975), have been successfully applied to the Kondo problem and allow one to pass continuously through T_K from the weak coupling ($T \gg T_K$) to the strong coupling ($T \ll T_K$) limit. The interested reader is referred to a brief critical discussion of these theoretical developments in a recent article in *Physics Today* (July, 1976, p. 17).

The antiferromagnetic conduction electron-impurity spin exchange interaction ($\mathcal{J} < 0$) which is responsible for the temperature-dependent Kondo anomalies originates from hybridization (mixing) between the conduction electron states and the localized impurity states (Anderson and Clogston, 1961; Kondo, 1962; deGennes, 1962b). Schrieffer and Wolf (1966) showed that when hybridization is included, the exchange hamiltonian can be written with an effective *negative* conduction electron-impurity spin exchange interaction parameter of the following form

$$\mathcal{J} \sim \frac{\langle V_{ki}^2 \rangle \mathcal{U}}{E_c(E_c + \mathcal{U})}, \quad (\Delta \ll \mathcal{U}) \quad (11.5)$$

if the hybridization between conduction electron and localized electron states is *not too strong*. Here, V_{ki} is the matrix element of the interaction which admixes conduction electron and localized electron states, \mathcal{U} is the intra-atomic Coulomb

repulsion parameter which scales the splitting of spin-up and spin-down states in the Friedel-Anderson model (Friedel, 1958; Anderson, 1961). E_c is the energy separating the centroid of the localized impurity state and the Fermi level E_F , and Δ is the half-width in energy of the localized state. The "Schrieffer-Wolf transformation" [eq. (11.5)] has been generalized to include orbital contributions for the lanthanides and applied to Ce and its "4f-hole" counterpart Yb by Coqblin and Schrieffer (1969). This negative contribution competes with the positive Heisenberg contribution to the exchange interaction, and if the hybridization is strong enough, the net conduction electron-impurity spin exchange interaction can be negative. Here it is assumed that the amount of hybridization is strong enough to generate a negative exchange interaction, but not so strong as to threaten the long-lived status of the impurity moment and hence to make the exchange interaction hamiltonian inappropriate as a model describing the interaction between the conduction electrons and the impurity ions.

The term "long-lived" signifies that the lifetime τ_{sf} of the impurity moment is large compared to thermal fluctuation lifetimes in the temperature or magnetic field range of interest. In other, so-called "localized spin fluctuation" models (consult Mills et al., 1975; and references cited therein), the local moment on the impurity site is alleged to fluctuate with a frequency τ_{sf}^{-1} . The magnetic moment lifetime decreases as the amount of hybridization between conduction electron and impurity electron states increases. This implies an increase in V_{kl} or a decrease in $|E_c|$ [cf. eq. (11.5)]. Thus it is apparent that only a moderate admixture of conduction electron and impurity electron states is admissible for the exchange hamiltonian to remain a reasonable starting point for a theoretical description of Kondo systems. That is to say, the very same increase in hybridization (increase in V_{kl} or decrease in $|E_c|$) which leads to an increase in the Kondo temperature T_K , results in a decrease of the localized spin fluctuation lifetime, which, in turn, ultimately jeopardizes the validity of the exchange hamiltonian as a description of systems with arbitrarily large characteristic temperatures.

In the event that the amount of hybridization is too strong for the exchange hamiltonian to be an adequate starting point for a theoretical description of the Kondo-like anomalies in the physical properties, the characteristic temperature is often identified with a spin fluctuation temperature T_{sf} which has the obvious definition $T_{sf} \equiv h/k_B\tau_{sf}$. In this view, T_{sf} , rather than T_K , is a boundary which separates high temperature (compared to T_{sf}) magnetic behavior from low temperature nonmagnetic behavior.

At temperatures much higher than T_{sf} , the temporal fluctuations of the magnetic moment are slow compared to thermal fluctuations, and the susceptibility is expected to be strongly temperature dependent, behaving like a Curie-Weiss law with a Curie-Weiss temperature of the order of T_{sf} . At temperatures much lower than T_{sf} , the intrinsic magnetic moment fluctuations are rapid compared to thermal fluctuations, and the resultant dynamical magnetic moment averages to zero over the timescale of interest so that the susceptibility approaches a constant value in the limit $T \rightarrow 0$. In this model, anomalies in other

physical properties are expected such as a peak in the thermoelectric power near T_{sf} . Low temperature resistivity minima are anticipated with solute contributions which vary as $1 - (T/T_{sf})^2$ for $T \ll T_{sf}$ as well as large enhancements of the electronic specific heat coefficient γ .

Although the basic mechanism involved in spin fluctuation models is quite different from models based on the exchange interaction, the general behavior of the physical properties as a function of temperature and magnetic field are quite similar; and, in practice, it is difficult to distinguish a matrix-impurity system with a high Kondo temperature from one which exhibits localized spin fluctuations. For this reason we consider systems which have been associated with both models in this article, realizing that the Kondo effect, when approached from the point of view of the exchange model, is simply one regime in a continuous spectrum corresponding to differing degrees of hybridization of conduction electron and localized electron states.

It is also appropriate to mention recent experimental work on *concentrated* metallic lanthanide alloys and compounds which exhibit Kondo-like anomalies in their physical properties. This work indicates that lanthanide ions which behave "nonmagnetically" below a characteristic temperature T_0 (as evidenced by a magnetic susceptibility which, below T_0 , approaches a finite value as $T \rightarrow 0$) can be quite generally pictured to have a time-averaged 4f shell occupation which is nonintegral. The nonintegral 4f shell occupation (or nonintegral valence) can actually be observed by means of measurements of the lattice constant, Mössbauer isomer shift, soft X-ray absorption and X-ray photoemission spectroscopy (XPS).

A physical interpretation for the correlated existence of the "nonmagnetic" susceptibility at low temperatures ($T \ll T_0$) and the intermediate 4f shell occupation number has recently been advanced by Maple and Wohleben (1971, 1974) using a model proposed by Hirst (1970). They propose that the 4f shell of a lanthanide ion in these intermediate valence systems undergoes temporal valence or interconfigurational fluctuations (ICF) between the configurations $4f^n$ and $4f^{n-1}$ accompanied by the emission and absorption of a conduction electron. The lifetime τ_0 associated with the fluctuations between the states $4f^n$ and $4f^{n-1}$ is believed to be of the order of 10^2 K for several compounds which is roughly the temperature below which the magnetic susceptibility saturates to a constant value as $T \rightarrow 0$. This idea is consistent with "slow" Mössbauer measurements as well as "fast" XPS measurements. Mössbauer measurements cannot resolve the isomer shift for the two configurations $4f^n$ and $4f^{n-1}$, but rather yield an isomer shift which is intermediate between that expected for the two configurations. The characteristic measuring time appropriate for this experiment is of the order of 10^{-9} – 10^{-7} sec which gives a lower limit $\sim 10^7$ – 10^9 cps for the ICF frequency τ_0^{-1} . On the other hand, the "fast" XPS measurements are able to resolve f-hole excitation spectra which correspond to the simultaneous presence of both configurations $4f^n$ and $4f^{n-1}$. The characteristic time for XPS is of the order of 10^{-17} sec which provides an upper limit $\sim 10^{17}$ cps for τ_0^{-1} .

These interconfiguration fluctuations are believed to occur when the energies

E_n and E_{n-1} of the configurations $4f^n$ and $4f^{n-1}5d^1$ are approximately degenerate in energy within the width $\Delta \approx \pi \langle V_{ki}^2 \rangle N(E_F)$. The energy broadening Δ of the $4f$ states again is supposed to arise from hybridization of the localized $4f$ states and the extended states of the conduction band. Thus at temperatures well below T_0 , the physical properties of lanthanide ICF systems are expected to, and indeed do, resemble those of a metal with a narrow band of width Δ which overlaps the Fermi level. In such cases one expects to observe large linear specific heat coefficients γ which can be as high as $\sim 10^2$ states/eV atom (compared to a few states/eV-atom for normal nonmagnetic metals) and the characteristic saturation (absence of a divergence in susceptibility or magnetic order) of the magnetic susceptibility in the limit $T \rightarrow 0$ (reminiscent of exchange enhanced paramagnets such as Pd). Although no microscopic theory for ICF systems has been developed, it is significant to note that Kondo-like anomalies are often observed such as a pronounced peak in the specific heat and thermoelectric power near the characteristic temperature T_0 and an electrical resistivity minimum followed by an increase in resistivity with decreasing temperature.

In contrast, in systems where the excitation energy between the two configurations, $E_{exc} = E_n - E_{n-1}$ is much larger than Δ , interconfiguration fluctuations are "blocked" by energy considerations, and the simple ionic limit ($\tau_0 \rightarrow \infty$), which typifies the behavior of most lanthanide ions in a metallic environment, is recovered. Here, the lanthanide ions carry well-defined magnetic moments which are consistent with Hund's rules, giving rise to Curie-Weiss behavior of the magnetic susceptibility as a function of temperature with crystal-field and Van Vleck modifications, magnetic order, and so on.

Finally, it is interesting to note that the criterion for the formation of a local moment in the ICF model is roughly given by the relation

$$\Delta/E_{exc} \ll 1 \quad (11.6)$$

which can be compared to the Hartree-Fock criterion which is given by

$$\Delta/\mathcal{U} \ll 1 \quad (11.7)$$

where \mathcal{U} is the previously mentioned intra-atomic Coulomb repulsion which splits spin-up and spin-down states in the Friedel-Anderson model. Thus in the ICF model, one can retain the strong correlations between electrons within the $4f$ shell, which have a characteristic energy $\mathcal{U} \sim 5-10$ eV, and still describe nonmagnetic situations even though Δ is only of the order of 10^{-2} eV, as long as $E_{exc} < \Delta$. Physically, the nonmagnetic behavior can be visualized as arising from the "randomizing" influence of the interconfiguration fluctuations on the orientation of the magnetic moment for either of the correlated Hund's rule $4f^n$ and $4f^{n-1}$ configurations in an applied magnetic field. In magnetic fields which are small compared to T_0 , the magnetic moment cannot survive an appreciable fraction of the period of its Zeeman precession in the magnetic field before the $4f$ shell spontaneously emits or absorbs an electron during the passage to any of the Zeeman levels of the complementary configuration. Phenomenologically, this leads to the following form for the magnetic susceptibility (Maple and

Wohlleben, 1974; Sales and Wohlleben, 1975)

$$\chi(T) = \frac{\epsilon(n)[\mu_{\text{eff}}(n)]^2 + [1 - \epsilon(n)][\mu_{\text{eff}}(n-1)]^2}{3k_B(T + T_0)} \quad (11.8)$$

where $\epsilon(n)$ is the fraction of the time that the 4f shell has the configuration $4f^n$ and T_0 represents the randomizing influence of the interconfiguration fluctuations.

For more detailed reviews of various theoretical aspects concerning mixed-valence rare earth alloys and compounds, the reader is referred to articles by Hirst (1975), Mott (1974), Varma (1976), Goncalves da Silva and Falicov (1975), Rosengren and Johansson (1976), Khomskii and Kocharjan (1976), Anderson and Chui (1974), Stevens (1976), Wohlleben and Coles (1973), and references cited therein, (also see ch. 20, section 6).

3. Kondo-like behavior in dilute lanthanide impurity systems

3.1. Introduction

Dilute magnetic impurity systems are interesting with respect to the problem of the physical behavior of a localized magnetic moment in a metallic environment because they approximate the simplest possible system: one in which the conduction electrons of the host interact with a single *isolated* impurity. The various theoretical models treating this interaction are generally restricted to the dilute impurity limit to avoid the additional complications introduced when the magnetic impurities are allowed to interact with each other via the indirect RKKY exchange interaction.

Early work on dilute lanthanide systems was motivated by the vast experimental and theoretical effort that had been expended on understanding dilute magnetic 3d impurities in noble metal hosts. In 1965, Sugawara discovered a resistance minimum in the YCe system, providing the first evidence of Kondo behavior for a lanthanide solute. This led to the discovery of numerous lanthanide Kondo systems which exhibited anomalies in their physical properties qualitatively identical to those found in 3d Kondo systems.

Working with lanthanide systems offers two major advantages over their 3d counterparts. First, with lanthanide systems, one can deal with relatively concentrated alloys and yet preserve the isolated impurity limit to a good approximation. As we noted in the Introduction (section 1), this is due to the small spatial extent of the 4f wavefunctions (of the order of one-tenth of an interatomic spacing) which implies little direct interaction between neighboring lanthanide ions, and the relatively small magnitude of the exchange interaction parameter ($|J| \sim 0.1$ eV). The concentrated systems are discussed in the next section; however, it should be emphasized that the anomalies observed in the physical properties of both concentrated and dilute lanthanide systems are qualitatively identical. Hence, one frequently can perform measurements on a

concentrated system, where the measurement is simpler due to the larger impurity-host signal ratio, and then extrapolate to the dilute impurity limit. This is a very powerful technique since the variety of experiments possible is greatly increased.

Second, it was noticed by Matthias and coworkers (Matthias et al., 1958) that the superconducting transition temperature of La was strongly depressed by the addition of magnetic lanthanide impurities (particularly Ce). This led to considerable experimental and theoretical research on the effects of magnetic impurities on the superconducting properties of the host. The subsequent agreement between experiment and theory is quite striking as evidenced, for example, by the early success of the Abrikosov-Gor'kov (AG) theory (Abrikosov and Gor'kov, 1961) and the prediction by Müller-Hartmann and Zittartz (1971) of re-entrant superconductivity which was subsequently observed in several matrix-Ce impurity systems. Because of the close correspondence between experiment and theory for matrix-impurity systems, it has been possible to use magnetic impurities to investigate the superconductivity of a host, or the effects of impurities on the superconductivity of a host to probe the magnetic state of the solute ions (see, for example, several reviews by Maple, 1972, 1973, 1976).

In this section, we discuss examples of dilute lanthanide systems which exhibit Kondo-like anomalies in both their normal and superconducting state physical properties.

3.2. Cerium impurity systems

The system LaCe is one of the first and the most extensively studied of the dilute lanthanide systems in which the Kondo effect has been observed. Measurements of the low temperature electrical resistivity by Sugawara and Eguchi (1966) revealed a resistivity minimum near 6 K in LaCe similar to that first observed in the noble metal based $-3d$ (Fe group) impurity systems (Heeger, 1969 and references therein). Measurements on this system to lower temperatures have revealed that the Ce incremental resistivity varies as $(-\log T)$ between 0.4 and 6 K for sufficiently dilute Ce concentrations (Sugawara and Eguchi, 1969) and that there is a concentration dependent maximum which extrapolates to $T_m = 0.17$ K as $n \rightarrow 0$ where n is the Ce impurity concentration (Wollan and Finnemore, 1970). These features suggest that T_K is low, probably of the order of 0.2 K, since the resistivity is expected to saturate to the unitarity limit for $T \ll T_K$. This value is close to other estimates of the Kondo temperature for LaCe which range from ~ 0.1 to ~ 0.6 K (Sugawara and Eguchi, 1969; Kim and Maple, 1970; Gey and Umlauf, 1971; Flouquet, 1971). The absence of a peak in the thermoelectric power above 7 K is consistent with a low Kondo temperature for this system (Sugawara and Eguchi, 1969).

Sugawara and Eguchi (1966) also reported on the behavior of the magnetic susceptibility of LaCe alloys which they interpreted in terms of a splitting of the

Ce $J = \frac{5}{2}$ multiplet into a Γ_7 doublet and a Γ_8 quartet in the cubic crystal field of the fcc La matrix. They also reported on the superconducting properties (Sugawara and Eguchi, 1966, 1967) such as the anomalously large depression of the superconducting transition temperature T_c of La by Ce additions (compared to other R additions) first reported by Matthias et al. (1958) and on the behavior of T_c as a function of Ce concentration as well as the temperature dependence of the critical magnetic field H_c . From this work, they inferred that the Kondo temperature T_K was ~ 0.1 K.

Following the pioneering work of Sugawara and Eguchi, measurements of the magnetic susceptibility of LaCe alloys were reported in two publications by Edelstein (1968) and Edelstein et al. (1971). From these measurements, they inferred values of T_K of the order of 20 K. However, these analyses did not take into account crystal field effects. Recent calculations of the magnetic susceptibility of matrix-impurity systems which simultaneously exhibit crystal-field effects and the Kondo effect have been carried out by DeGennaro and Borchia (1973, 1974). Their analysis of Edelstein's magnetic susceptibility data for the LaCe system gave reasonable values for the Γ_7 ground state- Γ_8 excited state splitting of 110-130 K and low values ~ 0.4 - 0.8 K for T_K . Nuclear orientation measurements on the LaCe system reported by Flouquet (1971) yield a value of ~ 0.1 K for T_K . Specific heat measurements on the LaCe system by Culbert and Edelstein (1974) show a broad Kondo anomaly with a peak near 1.2 K which is not inconsistent with a low Kondo temperature. We note that Hall effect measurements on the LaCe system have been reported by Fert and Jaoul (1972).

A number of measurements on the LaCe system have been made under pressure. Smith (1966) reported that the depression of T_c of La by Ce impurities increases markedly with pressure in the range 0-10 kbar, whereas the depression of the T_c of La by other R impurities shows only a small decrease with pressure in this range. A subsequent study by Maple et al. (1969) to pressures as high as 140 kbar revealed that the depression of T_c actually exhibits a pronounced maximum near 15 kbar which is followed by a decrease to a relatively small depression which is nearly constant above ~ 100 kbar. These results were interpreted as due to a pressure-induced continuous demagnetization of the Ce impurities due to the increased mixing of the Ce localized 4f states with conduction electron states as the pressure was increased. Kim and Maple (1970) studied the change in the logarithmic slope of the Ce incremental resistivity, $d(\Delta\rho)/d(\log T)$, associated with the Kondo effect in the LaCe system under pressure to ~ 20 kbar. They found that $|d(\Delta\rho)/d(\log T)|$ also exhibited a maximum near 15 kbar as a function of pressure. Similar results for the behavior of the depression of T_c and $|d(\Delta\rho)/d(\log T)|$ for LaCe as a function of pressure were obtained by Gey and Umlauf (1971), although their interpretation of the data differed somewhat from that of Maple et al. (1969) and Kim and Maple (1970). The reader is referred to several review articles for a detailed description of these pressure experiments on LaCe and their interpretation (Maple, 1972, 1973, 1976). Nuclear orientation measurements under pressure to ~ 10 kbar were recently reported by Benoit et al. (1974a), who inferred that T_K increases initially with

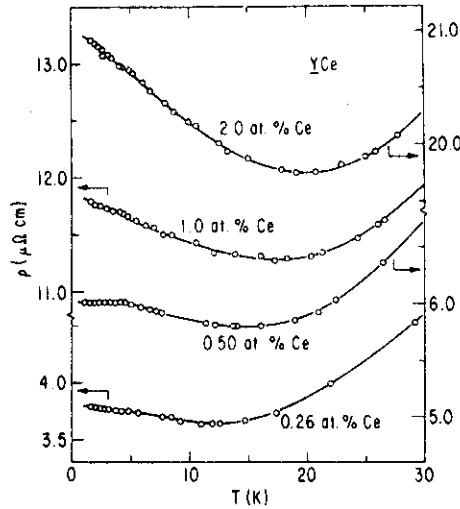


Fig. 11.1. Electrical resistivity of $\underline{\text{Y}}\text{Ce}$ alloys vs temperature. The break in slope near 4.3 K is due to superconductivity of Ta impurities in the Y starting material [after Sugawara (1965)].

pressure, which is consistent with an increased amount of itinerant-local electron mixing with increasing pressure.

Prior to the studies on the $\underline{\text{La}}\text{Ce}$ system, Sugawara (1965) had found that Ce impurities dissolved in an Y host give rise to the resistance minimum phenomenon. Sugawara's original data are shown in fig. 11.1. From these and additional low temperature data, Sugawara and Yoshida (1968) extracted the temperature dependence of the incremental resistivity $\Delta\rho$ contributed by the Ce impurity ions; i.e., $\Delta\rho(T) = \rho_{\text{YCe}}(T) - \rho_{\text{Y}}(T)$. These data are shown in fig. 11.2. The incremental resistivity was found to have the following characteristic form below 5 K –

$$\Delta\rho = \rho_0[1 - (T/\Theta)^2] \quad (11.9)$$

where $\Theta = 42$ K. For this type of variation of $\Delta\rho$ with temperature which is appropriate for the temperature range $T \ll T_K$, T_K is expected to be of the order of Θ , or 40 K. This is consistent with a previous estimate of T_K for the $\underline{\text{Y}}\text{Ce}$ system of 20–40 K by Nagasawa et al. (1968), which was based on magnetic susceptibility and thermoelectric power measurements. The magnetic susceptibility conformed to a Curie-Weiss temperature dependence between ~ 20 and 200 K with an effective moment of $\sim 2.3 \mu_B$ and a Curie-Weiss temperature of ~ -40 K, while the thermoelectric power exhibited a peak near 20 K. Again, splitting of the Ce^{3+} $J = \frac{1}{2}$ multiplet into three doublets in the hexagonal crystal-line electric field of the Y matrix was not taken into account in this work. Crystal field effects were considered, however, in a later investigation of single crystal $\underline{\text{Y}}\text{Ce}$ samples in which magnetic susceptibility, electrical resistivity and specific heat measurements were made (Sugawara and Yoshida, 1971). Borch and

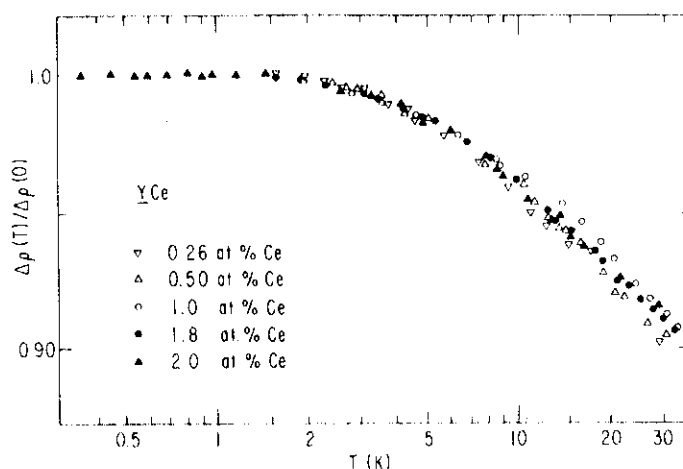


Fig. 11.2. Cerium solute contribution to the electrical resistivity of YCe alloys, normalized to its value at 0 K, vs temperature. The Ce contribution at 0 K is equal to $12.0 \pm 1.5 \mu\Omega \text{ cm/at.\% Ce}$ [after Sugawara and Yoshida (1968)].

DeGennaro (1974) calculated the magnetic susceptibility for single crystal YCe alloys, including crystal field and Kondo effects simultaneously, as they did for LaCe , and obtained good agreement with experiment for the case where the external magnetic field was parallel to the c -axis of the crystal. The technique of nuclear magnetic resonance has also been applied to YCe alloys (polycrystalline) by Silhouette (1970).

Like the LaCe system, the YCe system has been studied under pressure. The electrical resistivity has been measured as a function of pressure to ~ 140 kbar by Maple and Wittig (1971) and to 40 kbar by Dietrich et al. (1972). The results are consistent with a pressure-induced demagnetization of the Ce impurity ions, and an initial increase of T_K with pressure.

Several other binary matrix-Ce impurity systems have been studied in connection with the Kondo effect. Delfs et al. (1975) measured the depression of T_c as a function of Ce concentration and the normal state electrical resistivity anomaly associated with the Kondo effect in quench-condensed films of PbCe and InCe . Their analysis of the results indicated that $T_K \sim 1$ K for PbCe and $T_K \leq 0.1$ K for InCe . Nuclear orientation measurements have been made on AuCe alloys by Flouquet and Marsh (1970) and on AgCe alloys by Flouquet (1971). The results of both studies indicate that the Ce magnetic moments are long-lived in Au and Ag hosts, but there is probably no Kondo effect (i.e., $\mathcal{J} > 0$). This is in contrast to the thermoelectric power measurements of Gainon et al. (1967) which indicated unusually large room temperature values for AuCe and AgCe . Hedgcock and Petrie (1970) performed magnetic susceptibility and electrical resistivity measurements on MgCe alloys. From these results they inferred that Ce was magnetic, but that there was no Kondo effect. Burr and Pirich (1975)

interpreted their magnetic susceptibility measurements on monocrystalline MgCe alloys in terms of a crystal field splitting of the $\text{Ce}^{3+} J = \frac{5}{2}$ multiplet.

A continuous demagnetization of Ce impurities which proceeds with increasing Th composition in the $(\text{La}, \text{Th})\text{Ce}$ system appears to be an analog of the pressure-induced demagnetization of Ce impurities in the LaCe system. This was first inferred from a recent study of superconductivity in the $(\text{La}, \text{Th})\text{Ce}$ system which showed that the initial depression of T_c with Ce concentration, $(-dT_c/dn)_{n=0}$, exhibits a pronounced maximum as a function of Th composition similar to that which occurs as a function of pressure in the LaCe system (Ortega et al., 1974). Following this initial work, detailed measurements were made of T_c/T_{c0} vs Ce impurity concentration (Huber et al., 1974) and $\Delta C/\Delta C_0$ vs T_c/T_{c0} for various La, Th host compositions (Luengo et al., 1974; Luengo et al., 1975). The resultant T_c/T_{c0} vs n curves displayed in the three dimensional plot in fig. 11.3, show the various types of behavior which are found across the continuum from LaCe to ThCe ; the pronounced maximum in the initial depression of T_c vs n , the smooth sweep from negative to positive curvature, and the appearance of re-entrant superconductivity, similar to that

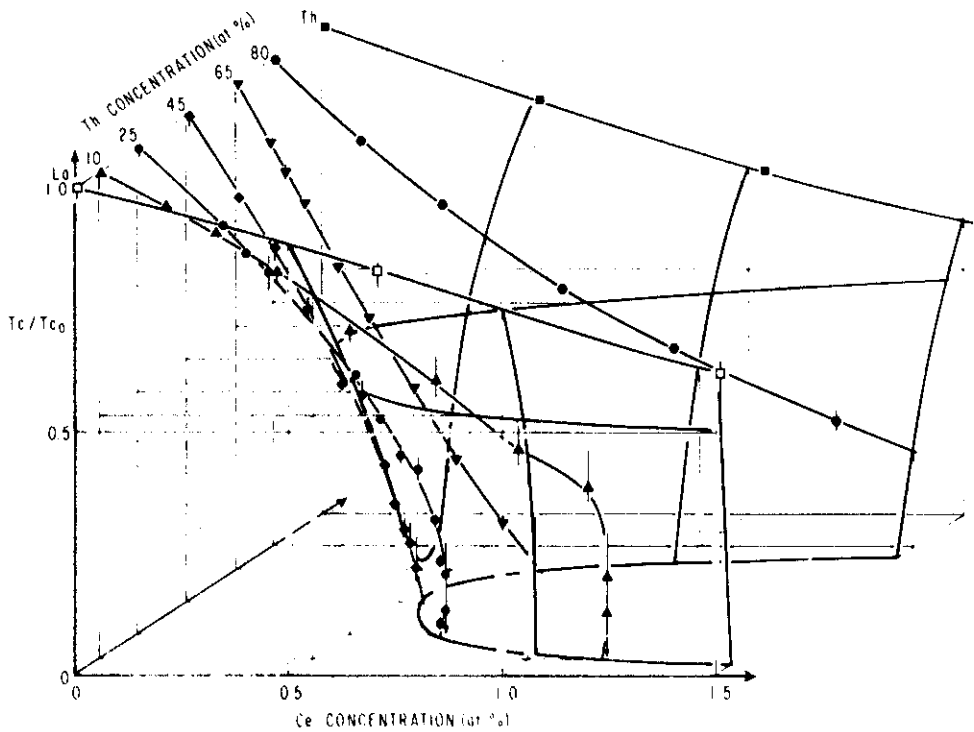


Fig. 11.3. Normalized transition temperature T_c/T_{c0} vs. Ce concentration and Th concentration for $(\text{La}, \text{Th})\text{Ce}$. The curves of T_c/T_{c0} vs Ce concentration for the $(\text{La}_{0.90}\text{Th}_{0.10})\text{Ce}$ and the $(\text{La}_{0.75}\text{Th}_{0.25})\text{Ce}$ systems are re-entrant [after Huber et al. (1974)].

observed first in the (LaCe)Al₃ system (Riblet and Winzer, 1971; Maple et al., 1972) to be discussed below. Like the initial depression of T_c with n which exhibits a maximum at a La, Th host composition of ~ 45 at.% Th, the initial depression of $\Delta C/\Delta C_0$ with T_c/T_{c_0} sweeps through a maximum at a La, Th composition of ~ 15 at.% Th. These characteristic resonant variations of the initial depression of T_c/T_{c_0} with n and $\Delta C/\Delta C_0$ with T_c/T_{c_0} in the (La, Th)Ce system have been interpreted as due to the continuous passage of the Ce impurity magnetic moments from long-lived in La-rich La, Th matrices to short-lived in Th-rich La, Th matrices.

Indeed, an earlier investigation of the ThCe system revealed that the depression of T_c/T_{c_0} with n followed a modified exponential relation of the form $T_c/T_{c_0} = \exp[-An/(1-Dn)]$, while the depression of $\Delta C/\Delta C_0$ with T_c/T_{c_0} conformed to the linear BCS law of corresponding states (Huber and Maple, 1970). The modified exponential relation for T_c/T_{c_0} vs n was derived theoretically by Kaiser (1970) for matrix-impurity systems in which the impurities contribute localized d or f states which are nonmagnetic in the sense of the Friedel-Anderson model (i.e., $\pi\Delta/U > 1$); A and D can be related to the Friedel-Anderson parameters $N_f(E_f)$ and U which characterize the localized d or f state. On the basis of thermoelectric power measurements, Cooper and Rizzuto (1973) have suggested that the characteristic spin fluctuation temperature of the ThCe system is of the order of 10^3 K. Measurements of the lattice constant as a function of relative Th-Ce composition indicate that the valence of Ce is ~ 3.25 in the ThCe system up to ~ 20 at.% Ce (Harris and Raynor, 1964).

The data for the initial depression of T_c/T_{c_0} with n and $\Delta C/\Delta C_0$ with T_c/T_{c_0} for the (La, Th)Ce system have been analyzed in terms of the theory of Müller-Hartmann and Zittartz (1970; 1972) for superconducting-Kondo systems and found to be consistent with an increase of T_K with increasing Th content over an appreciable range of La, Th host compositions. However, it was found that the theory failed to describe the specific heat data for Th-rich (La, Th)Ce alloys. This discrepancy between theory and experiment was attributed to the inappropriateness of the conduction electron-impurity spin exchange hamiltonian for situations in which the solute moments are short-lived. The studies of the superconducting properties of the (La, Th)Ce system also include measurements of the upper critical field for a series of $\text{La}_{0.80}\text{Th}_{0.20}\text{Ce}$ alloys which exhibit re-entrant superconductivity (Fertig, 1976). In addition to the aforementioned superconducting properties, the normal state electrical resistivity (Peña and Meunier, 1974) and magnetic susceptibility (Huber et al., 1975) of the (La, Th)Ce system have been measured as a function of La, Th composition. The slope of the Ce solute resistivity which is linear in $\log T$ exhibits an initial increase and then falls off smoothly to zero at ~ 50 at.% Th as the Th concentration is increased. The magnetic susceptibility measurements are especially interesting since they document the Ce impurity demagnetization directly. The diminution of the Ce magnetic moment with increasing Th concentration is evident in the inverse susceptibility vs temperature plots for various (La, Th)Ce alloys which are reproduced in fig. 11.4.

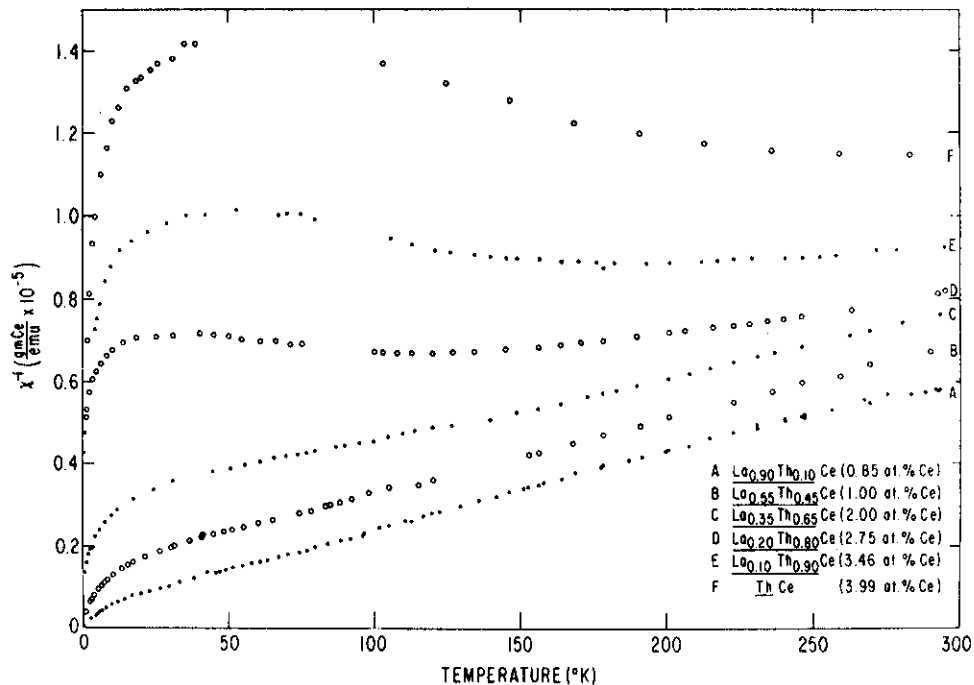


Fig. 11.4. Inverse magnetic susceptibility vs temperature for $(\text{La}, \text{Th})\text{Ce}$ alloys with La, Th matrix compositions of 10, 45, 65, 80, 90 and 100 at.% Th [after Huber et al. (1975)].

There have been a number of other experiments in which the composition of a binary alloy solvent has been varied to induce changes in the magnetic character of Ce solutes which yield results similar to those discussed above for the $(\text{La}, \text{Th})\text{Ce}$ system. The $(\text{Y}, \text{Th})\text{Ce}$ and $(\text{Sc}, \text{Th})\text{Ce}$ systems have been studied through measurements of T_c/T_{c_0} vs n by Huber and Maple (1972) and $\Delta C/\Delta C_0$ vs T_c/T_{c_0} by Sereni et al. (1975). The results show that Ce impurities become more magnetic as Y is alloyed with Th and less magnetic when Sc is alloyed with Th with respect to their magnetic behavior in the pure Th host. Masuda and coworkers (Aio et al., 1974; Takeuchi et al., 1975) have studied the $(\text{La}, \text{Y})\text{Ce}$ system through measurements of the depressions of T_c/T_{c_0} with n and $\Delta C/\Delta C_0$ with T_c/T_{c_0} and of the variation of the upper critical field with temperature. Here, the effect of adding Y to La is similar to that of adding Th to La in that it results in an increase of T_K . Peterson et al. (1976) have studied the Ce solute resistivity in the $(\text{La}, \text{Y})\text{Ce}$ and $(\text{Lu}, \text{Y})\text{Ce}$ systems for a fixed Ce concentration of 2 at.%. They find that the slope $|d(\Delta\rho)/d(\log T)|$ varies markedly with the average atomic volume of the alloy host and shows a sharp maximum for the host composition $\text{La}_{0.95}\text{Y}_{0.05}$. These authors discuss the analogy of their experiments with the pressure experiments on LaCe and YCe described previously.

The Kondo effect in a matrix-lanthanide impurity system in which the metallic matrix is a compound, rather than an element, was first discovered for the

system $(\text{LaCe})\text{Al}_2$ by Maple and Fisk (1968; Maple, 1969). Since then, many other matrix-impurity systems in which the matrix is a compound that exhibits Kondo-like anomalies have been discovered and studied. These include $(\text{LaCe})\text{B}_6$ (Winzer and Samwer, 1975), $(\text{YCe})\text{B}_6$ (Maple and Fisk, 1968), $(\text{LaCe})_3\text{Al}$ (Aoi and Masuda, 1974), $(\text{LaCe})_3\text{In}$ (Maple and Kim, 1969; Jones et al., 1972), $(\text{LaCe})\text{In}_3$ (van Maaren and van Haeringen, 1975), $(\text{LaCe})\text{Pd}_3$ (Rao et al., 1971) and $(\text{YCe})\text{Al}_2$ (Purwins et al., 1972). Of all these, the system $(\text{LaCe})\text{Al}_2$ has been by far the most extensively investigated, and we therefore discuss the properties of this exemplary matrix-impurity Kondo system in some detail. Moreover, the $(\text{LaCe})\text{Al}_2$ system offers the desirable features that single-phase alloys may be readily prepared and that Ce interimpurity interactions are relatively weak in contrast to the case of LaCe alloys.

The first indication of the existence of a Kondo effect in the $(\text{LaCe})\text{Al}_2$ system was provided by measurements of the initial depression of T_c , $(-dT_c/dn)_{n=0}$, of LaAl_2 by R impurities (Maple and Fisk, 1968; Maple, 1969). The results of these measurements, which are shown in fig. 11.5, revealed that $(-dT_c/dn)_{n=0}$ is anomalously large for Ce impurities. This is similar to the behavior previously observed in the LaCe system (Matthias et al., 1958), also displayed in fig. 11.5, and suggests by analogy that the conduction electron-impurity spin exchange coupling in the $(\text{LaCe})\text{Al}_2$ system is large and antiferromagnetic. These measurements were followed by measurements (Maple and Fisk, 1968; Maple, 1969) of the low temperature electrical resistivity and the magnetic suscep-

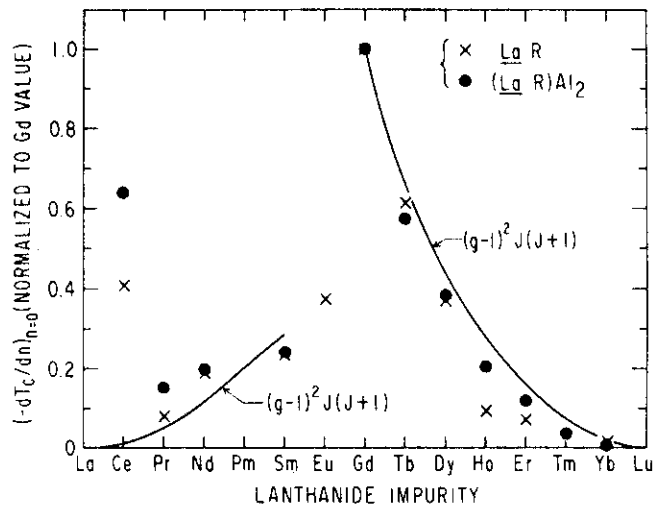


Fig. 11.5. Initial rate of depression of the superconducting transition temperature of LaR alloys (Matthias et al., 1958) and $(\text{LaR})\text{Al}_2$ alloys (Maple, 1970) vs R impurity (normalized to the Gd value). The solid line is the deGennes factor $(g-1)^2 J(J+1)$, normalized to the Gd value. The values of $-(dT_c/dn)_{n=0}$ for Gd impurities are 5.3 and 3.79 K/at.% Gd substitution in La for LaR and $(\text{LaR})\text{Al}_2$, respectively [after Maple (1973)].

tibility. The electrical resistivity revealed a resistivity minimum and a Ce impurity contribution which varied logarithmically with temperature, thus corroborating the existence of a Kondo effect in the $(\text{LaCe})\text{Al}_2$ system. The magnetic susceptibility measurements indicated that the Ce^{3+} $J = \frac{5}{2}$ Hund's rule multiplet is split by the cubic crystalline field of the LaAl_2 matrix into a ground state doublet and an excited state quartet with a splitting $\delta \sim 10^2$ K. However, the behavior of the susceptibility could not be described in terms of crystal field effects alone as illustrated in fig. 11.6(a). Here χT vs T data for several

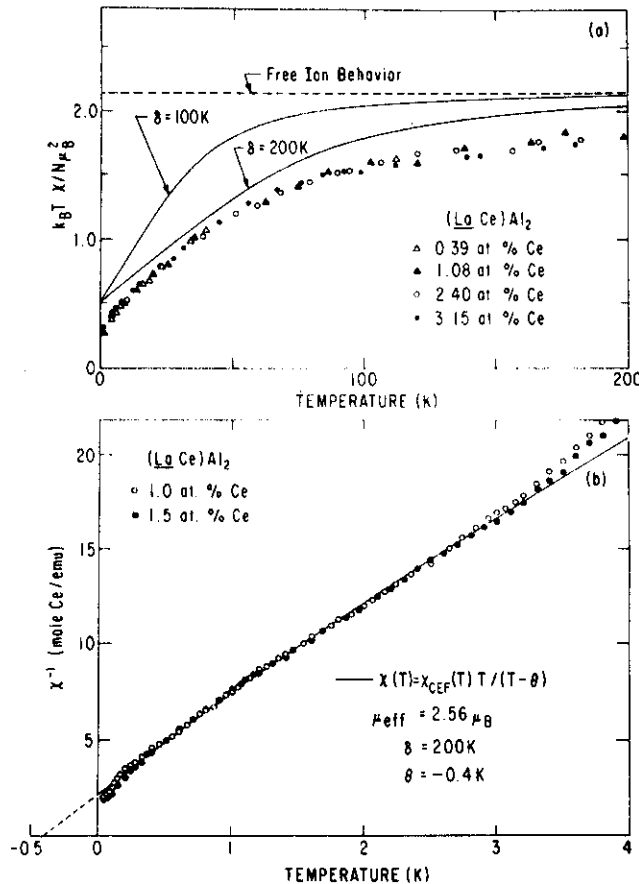


Fig. 11.6. (a) χT vs T plot of the magnetic susceptibility (corrected for the susceptibility of LaAl_2) of $(\text{LaCe})\text{Al}_2$ alloys. The dashed line gives the value for free Ce^{3+} ions for which $k_B T \chi / N \mu_B^2 = g^2 J(J+1)/3 = 2.14$. The solid curves represent the susceptibility appropriate to a cubic crystal field which splits the Ce^{3+} $J = \frac{5}{2}$ multiplet into a Γ_8 quartet and a ground state Γ_7 doublet [after Maple (1969); Maple and Fisk (1968)]. (b) Inverse magnetic susceptibility (corrected for the susceptibility of LaAl_2) vs temperature for two $(\text{LaCe})\text{Al}_2$ alloys below 4 K. The solid line represents a modified Curie-Weiss law with a temperature-dependent Curie constant $C(T) = \chi_{\text{CEF}}(T)T$ where $\chi_{\text{CEF}}(T)$ is the susceptibility for a $\Gamma_7-\Gamma_8$ splitting δ of 200 K in the cubic crystalline electric field [after Felsch et al. (1975)].

(LaCe)Al₂ alloys are compared with the expected ionic behavior for a Ce³⁺ Γ_7 ground state doublet and a Γ_8 excited state quartet with either a splitting of 100 or 200 K.

Borchi and DeGennaro (1975) calculated the magnetic susceptibility for the (LaCe)Al₂ system, again taking into account the simultaneous existence of a Kondo effect and crystal field splitting of the Ce³⁺ $J = \frac{5}{2}$ multiplet. They find that the temperature dependence of the magnetic susceptibility can be well described by theory for a Γ_7 - Γ_8 splitting $\delta = 200$ K and $N(E_F)(g-1)\rho = 0.035$. Magnetic susceptibility measurements on the (LaCe)Al₂ system to lower temperatures, which are shown in fig. 11.6(b), have recently been carried out by Felsch et al. (1975). The magnetic susceptibility, which is dominated by the Γ_7 doublet ground state at these lower temperatures, resembles a Curie-Weiss law with a Curie-Weiss temperature θ of -0.4 K. This suggests that T_K is of the order of 0.1 K, in analogy with other matrix-impurity Kondo systems for which $|\theta|$ is generally 3 to 4 times larger than T_K .

Heat capacity measurements on the (LaCe)Al₂ system in zero and high magnetic fields were carried out by Bader et al. (1975). Typical results for a (LaCe)Al₂ alloy with 0.64 at.% Ce are shown in fig. 11.7. There is a pronounced Kondo heat capacity anomaly in zero field with a peak near 0.140 K which is well described by the Bloomfield-Hamann theory (Bloomfield and Hamann, 1967) for $S = \frac{1}{2}$ and $T_K \cong 0.42$ K. In the Bloomfield-Hamann theory, $T_K \sim 3 T_{\max}$

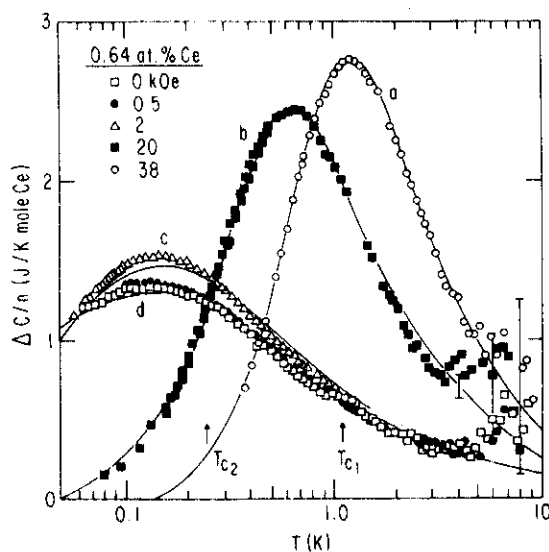


Fig. 11.7. Heat capacity per mole Ce of a (LaCe)Al₂ alloy of composition 0.64 at.% Ce vs temperature in various magnetic fields up to 38 kOe. Curves a-c, which have been drawn to fit more accurate data (not shown) for a (LaCe)Al₂ alloy with 0.906 at.% Ce, correspond to an entropy of $k_B \ln 2$ per Ce ion, showing that the Ce³⁺ ground state is a doublet. Curve d is based upon calculations of Bloomfield and Hamann (1967) for $S = \frac{1}{2}$ and $T_K = 0.42$ K. The zero field superconducting transition temperatures are indicated [after Bader et al. (1975)].

where T_{\max} is the temperature at which the magnetic heat capacity attains its maximum value. In high fields (up to 38 kOe), the anomaly becomes more pronounced and the peak moves to higher temperatures. This allows an assessment of the magnetic entropy associated with the anomaly which is found to be equal to $k_B \ln 2$ per Ce impurity ion, confirming that the Ce^{3+} ground state is indeed a Γ_7 doublet. The thermoelectric power of a series of $(LaCe)Al_2$ alloys has recently been measured (Mooser et al., 1974) and the results are shown in fig. 11.8. There is a characteristic peak in the thermoelectric power near 1 K which is in accord with a low value for T_K . Nuclear orientation measurements on the $(LaCe)Al_2$ system yield a value for T_K of 0.1 K (Benoit et al., 1973). A large negative magnetoresistivity for the $(LaCe)Al_2$ system has been reported by Felsch and Winzer (1973). Large Kondo anomalies in the thermal conductivity and Lorentz ratio of $(LaCe)Al_2$ have been observed by Mooser and Steglich (1975).

Perhaps the most striking manifestations of the Kondo effect are those which occur in the superconducting state for the case when the matrix is a superconductor and $T_K \ll T_{c_0}$ (T_{c_0} is the superconducting transition temperature of the matrix). The literature concerning the Kondo effect in superconducting matrix-impurity systems is extensive, and the interested reader is referred to several review articles (Maple, 1972, 1973, 1976) for detailed discussions of the subject and citations of the original literature. In this article, we will only refer to a few of the more unusual superconductive properties that are manifestations of the anomalous conduction electron-impurity spin exchange scattering associated with the Kondo effect which are exemplified by the $(LaCe)Al_2$ system.

The condition $T_K \ll T_{c_0}$ is satisfied in the $(LaCe)Al_2$ system ($T_{c_0} = 3.3$ K), and it exhibits a most unusual phenomenon referred to as re-entrant superconductivity wherein alloys with Ce impurity concentrations within a certain range exhibit two critical temperatures. As an alloy within this Ce concentration range is

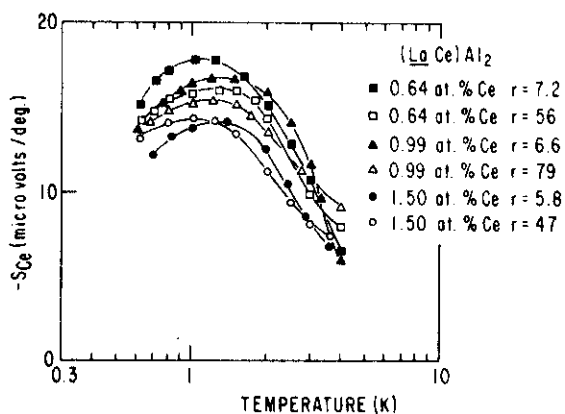


Fig. 11.8. Negative thermoelectric power contributed by Ce impurities in various $(LaCe)Al_2$ alloys as determined from the Gorter-Nordheim relation. The symbol r denotes the resistance ratio $R(300\text{ K})/R(12\text{ K})$ of each sample [after Mooser et al. (1974)].

cooled to low temperatures, it first enters the superconductivity state at a critical temperature T_{c1} and then remains superconducting to a lower critical temperature T_{c2} at which it then returns to the normal state for all temperatures $T < T_{c2}$. Re-entrant superconductive behavior was first predicted on theoretical grounds by Müller-Hartmann and Zittartz (1971) and by Ludwig and Zuckermann (1971) and observed by Riblet and Winzer (1971). According to these theories, there should actually be a third transition temperature T_{c3} , in addition

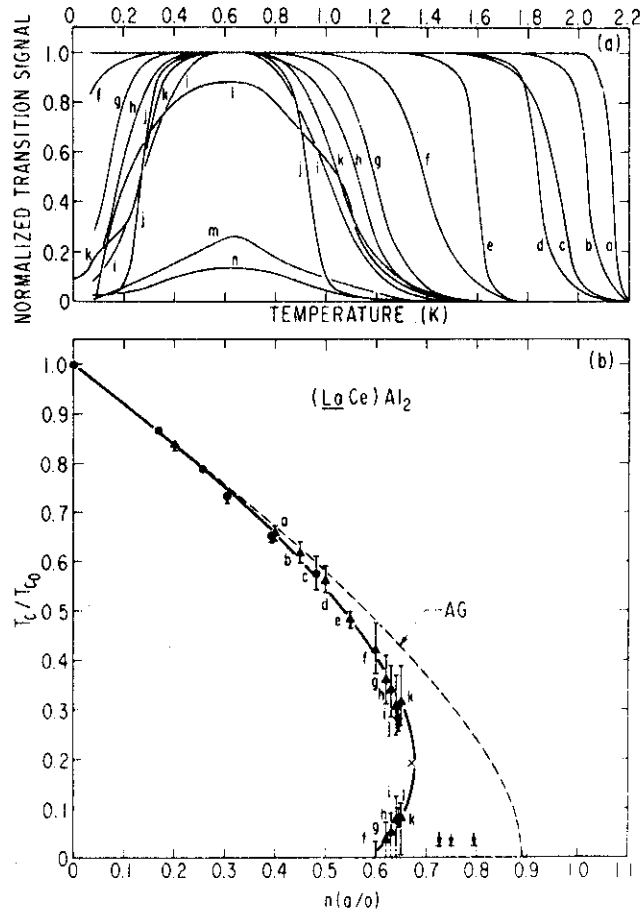


Fig. 11.9. (a) Normalized transition signal vs temperature for several $(\text{LaCe})\text{Al}_2$ alloys. The superconducting state corresponds to a transition signal of unity. The sequence of letters a-n identifies the transition curves in the order of increasing Ce impurity concentration. (b) Reduced transition temperature T_c/T_{c0} vs impurity concentration n for the $(\text{LaCe})\text{Al}_2$ system. Transition temperatures corresponding to the transition curves in (a) are identified. The symbol (\times) denotes the estimated turning point of the T_c/T_{c0} vs n curve, while the solid circles and triangles distinguish two separately prepared sets of alloys. The Abrikosov-Gor'kov (1961) curve (dashed) is shown for comparison [after Maple et al. (1972)].

to and below T_{c_2} , at which an alloy with the appropriate magnetic impurity concentration again becomes superconducting for all temperatures $T < T_{c_1}$. No evidence for the existence of the third transition temperature T_{c_3} has been found experimentally, and several refinements of the theory have recently appeared which cast doubt on the existence of T_{c_3} (Schlottmann, 1975a, 1975b; Matsuura and Nagaoka, 1976; Müller-Hartmann et al., 1976).

Examples of transition curves (ac susceptibility) which undergo a return to the normal state at a lower critical temperature and the corresponding re-entrant reduced transition temperature vs Ce concentration curve for the $(\text{LaCe})\text{Al}_2$ system are shown in figs. 11.9(a) and (b) (Maple et al., 1972). The data are also compared with the predictions of the Abrikosov-Gor'kov (AG) theory (Abrikosov and Gor'kov, 1961) (dashed line) which hold for superconducting matrix-impurity systems for which there is no Kondo effect ($\mathcal{J} > 0$) and for which the degeneracy of the Hund's rule impurity ion multiplet is not lifted by a crystalline electric field.

In addition to the remarkable re-entrant behavior of the T_c/T_{c_0} vs n curve, the depression of the specific heat jump ΔC at T_c as a function of T_c (Armbrüster et al., 1974; Luengo et al., 1972; Bader et al., 1975) also displays some interesting features which are shown in fig. 11.10. Here, it can be seen that the curve of reduced specific heat jump $\Delta C/\Delta C_0$ vs reduced transition temperature T_c/T_{c_0} shows a pronounced downward deviation from both the BCS law of corresponding states and, as well, the AG theory. It is worth noting that recent specific heat measurements (Bader et al., 1975) on a re-entrant $(\text{LaCe})\text{Al}_2$ specimen (0.64 at.% Ce) to temperatures lower than T_{c_2} indicate that the tran-

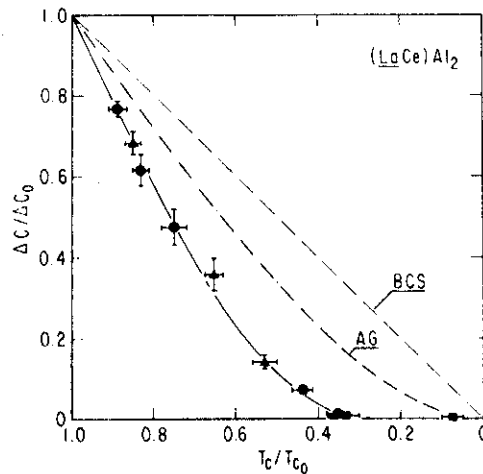


Fig. 11.10. Reduced specific heat jump $\Delta C/\Delta C_0$ vs. reduced transition temperature T_c/T_{c_0} for the $(\text{LaCe})\text{Al}_2$ system. The solid triangles, circles and squares represent data from Luengo et al. (1972), Armbrüster et al. (1974), and Bader et al. (1975), respectively. The dashed line represents the BCS law of corresponding states, the dot-dashed line indicates the AG result, and the solid line is a smooth curve drawn through the data [after Maple (1976)].

sition at T_c is second order as it is at T_{c1} . The two reduced specific heat jumps for this specimen are indicated in fig. 11.10 by the solid squares.

Figures 11.9 and 11.10 exemplify the behavior of T_c/T_{c0} vs n and $\Delta C/\Delta C_0$ vs T_c/T_{c0} for matrix-impurity systems which exhibit a Kondo effect ($\mathcal{J} < 0$) with $T_K \ll T_{c0}$.

3.3. Praseodymium impurity systems

The first observation of anomalous behavior in a dilute alloy containing Pr impurities was made by Fisk and Matthias (1969) in the system $(\text{ZrPr})\text{B}_{12}$. They observed an extremely large initial depression of the superconducting transition temperature of ZrB_{12} with the addition of Pr impurities. This value of $(-dT_c/dn)_{n=0} \approx 13 \text{ K/at.}\%$ Pr was approximately an order of magnitude larger than the initial depressions of T_c due to the addition of any other lanthanide to ZrB_{12} .

These authors also performed resistivity measurements on several $(\text{ZrPr})\text{B}_{12}$ compositions and found a resistance minimum at about 35 K in each of the samples studied (Pr concentrations smaller than 3 at.%). Their measurements of magnetic susceptibility revealed a simple Curie law for $(\text{ZrPr})\text{B}_{12}$ with an effective magnetic moment of approximately $3.6 \mu_B$ for the Pr^{3+} impurities.

Fisk and Matthias explained their experimental results by assuming that the effective lattice pressure exerted on the Pr impurities by the ZrB_{12} host environment was about 200 kbar, thus giving rise to a virtual bound 4f level close to the Fermi level.

Hillenbrand and Wilhelm (1972) observed a large initial depression of the superconducting transition temperature in the $(\text{LaPr})\text{Ru}_2$ system. This value of $(-dT_c/dn)_{n=0} = 1.1 \text{ K/at.}\%$ Pr was much larger than their value of $(-dT_c/dn)_{n=0} = 0.45 \text{ K/at.}\%$ Gd in the analogous $(\text{LaGd})\text{Ru}_2$ system. Their susceptibility measurements revealed an effective magnetic moment of $3.84 \mu_B$ in contrast to the Hund's rule value of $3.58 \mu_B$ for Pr^{3+} . They suggested that this discrepancy might be evidence for a magnetic polarization cloud associated with conduction electrons in the vicinity of the Pr local moments.

Recalling the above-mentioned work of Fisk and Matthias on $(\text{ZrPr})\text{B}_{12}$, they pointed out that while there should be almost no lattice pressure effect in $(\text{LaPr})\text{Ru}_2$, Ce impurities were known (Hillenbrand and Wilhelm, 1970) to be nonmagnetic in $(\text{LaCe})\text{Ru}_2$, and thus the possibility of a virtual bound 4f state in $(\text{LaPr})\text{Ru}_2$ could not be ruled out.

Recent experiments on $(\text{LaPr})\text{Sn}_3$ alloys have rekindled interest in the possibility of a Kondo effect in a Pr impurity system. The early observation by Bucher et al. (1968) of a large depression of the superconducting transition temperature T_c of LaSn_3 by Pr impurities (relative to other R impurities) is shown in fig. 11.11. This initial observation stimulated McCallum et al. (1975a) to perform more detailed measurements of the depression of T_c with Pr concentration, the superconducting and normal state heat capacity, and the normal state magnetic susceptibility of $(\text{LaPr})\text{Sn}_3$ alloys. Calculated values of the ther-

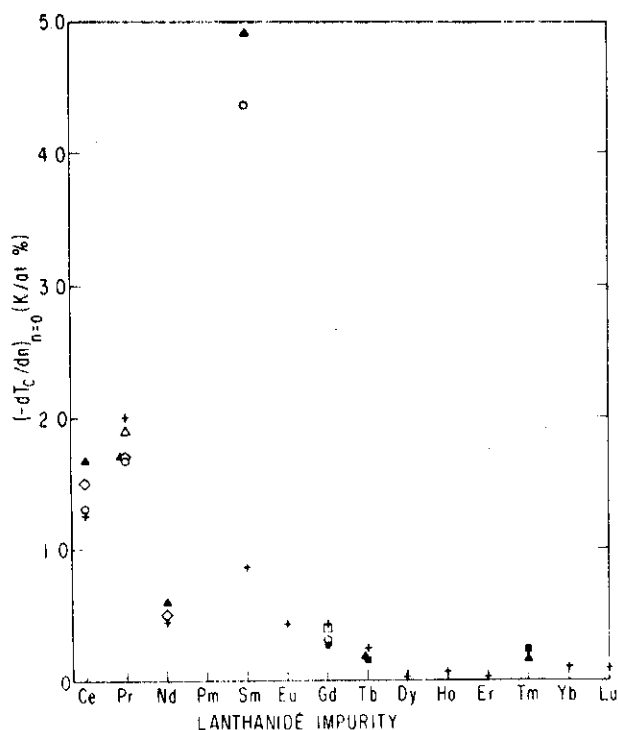


Fig. 11.11. Initial rate of depression of the superconducting transition temperature of $(\text{LaR})\text{Sn}_3$ alloys vs R impurity. The data are taken from: Schmid and Umlauf (1976) – crosses; McCallum et al. (1975a) and DeLong et al. (1975, 1976) – open circles; Abou Aly et al. (1976) – solid triangles; van Maaren and van Haeringen (1975) – open diamonds; Lethuillier (1975) – open triangles; Toxen et al. (1968) – open squares; Guertin et al. (1973) and Bucher et al. (1968) – solid circles; Hoening et al. (1975) – solid squares.

modynamic critical fields of $(\text{LaPr})\text{Sn}_3$ alloys have also been reported by McCallum et al. (1975b) using the specific heat results of McCallum et al. (1975a).

The strong positive curvature of the T_c vs Pr concentration data for $(\text{LaPr})\text{Sn}_3$ is good evidence for the nonmagnetic nature of the crystal field ground state of Pr^{3+} in LaSn_3 . A pronounced Schottky anomaly in the normal state heat capacity and the Van Vleck contribution to the magnetic susceptibility are consistent with a unique energy level scheme for the Pr^{3+} ion in the LaSn_3 crystalline electric field (CEF) in which the ground state is a Γ_1 singlet.

However, the most remarkable results of the measurements of McCallum et al. (1975a) were the large, positive deviations of the reduced specific heat jump $\Delta C/\Delta C_0$ from the predictions of the BCS theory as shown in fig. 11.12. This was the first time such a positive deviation has been observed for any superconductor. It is most important to point out that *all* of the above phenomena in $(\text{LaPr})\text{Sn}_3$ can be adequately described by the theories of Fulde and coworkers

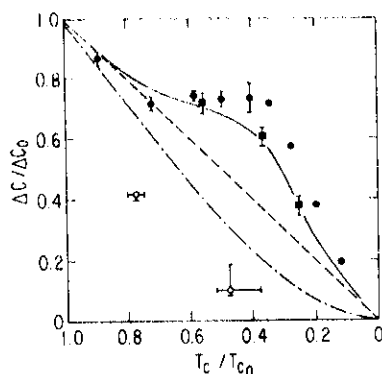


Fig. 11.12. Reduced specific heat jump $\Delta C/\Delta C_0$ vs reduced transition temperature T_c/T_{c0} for $(\text{LaPr})\text{Sn}_3$ alloys (solid circles and solid squares; McCallum et al., 1975a) and $(\text{LaSm})\text{Sn}_3$ alloys (open circles; DeLong et al., 1976). The solid line is derived from numerical calculations based on the theory of Keller and Fulde (1973) for crystal field-split lanthanide impurities in a superconductor. The BCS law of corresponding states behavior (dashed curve) and the AG behavior (dot-dashed curve) are shown for comparison. The negative deviations of the $\Delta C/\Delta C_0$ vs T_c/T_{c0} data from the AG curve are consistent with Kondo behavior (see fig. 11.10) for $(\text{LaSm})\text{Sn}_3$ alloys.

(Keller and Fulde, 1973; Fulde and Peschel, 1972) for magnetic impurities with CEF-split ground states in superconductors without the introduction of Kondo mechanisms (McCallum et al., 1975a).

However, subsequent measurements of the electrical resistivity (Haen and Lethuillier, 1975; Abou Aly et al., 1975; Lethuillier and Haen, 1975) and the pressure dependence of T_c (DeLong et al., 1975) were performed which may prove difficult to reconcile with a simple ionic behavior for Pr impurities in LaSn_3 . The electrical resistivity measurements show weak minima in the vicinity of 10–20 K at a Pr concentration of greater than, or the order of, 10 at.%. The resistivities also exhibit a local maximum around 7.5 K for Pr concentrations less than 80 at.%, which is the lowest Pr concentration where the resistivity maximum and the Néel temperature (as determined by static susceptibility measurements) coincide. For Pr concentrations well below 80 at.%, the resistivity maximum and the rapid decrease in the resistivity below 7.5 K have been associated with a thermal depopulation of the CEF excited states of Pr.

Attempts (Haen and Lethuillier, 1975; Abou Aly et al., 1975; Lethuillier and Haen, 1975) to apply the theory of Rao and Wallace (1970) for the resistivity introduced by magnetic scattering from a CEF-split ionic configuration have only been marginally successful in that the minimum in the $(\text{LaPr})\text{Sn}_3$ resistivity cannot be accounted for if one includes all of the known Pr CEF levels in the calculation.

DeLong et al. (1975) have measured the pressure dependence of T_c in the $(\text{LaPr})\text{Sn}_3$ system and found an anomalously large decrease in T_c with pressure when compared to their results for $(\text{LaGd})\text{Sn}_3$, a system which is free from CEF effects. An examination of the Pr^{3+} energy level scheme of McCallum et al.

(1975a) and the predictions of a simple point charge model forced them to conclude that either the overall splittings of the Pr^{3+} energy level scheme were decreasing under pressure, contrary to the point charge model, or the magnitude of the conduction electron-impurity exchange interaction parameter \mathcal{J} was increasing more rapidly than would be predicted from the $(\text{LaGd})\text{Sn}_3$ data. They pointed out that such large pressure dependences of \mathcal{J} are frequently found in Kondo systems.

In spite of the large amount of data in existence for the $(\text{LaPr})\text{Sn}_3$ system, the evidence for a Kondo effect in these alloys is still ambiguous. In particular, the expected negative deviations (Maple, 1976, and references therein) from the BCS law of corresponding states for $\Delta C/\Delta C_0$ vs T_c/T_{c_0} accompanying the Kondo effect have not been observed in the $(\text{LaPr})\text{Sn}_3$ system (compare the $(\text{LaPr})\text{Sn}_3$ data to those for $(\text{LaCe})\text{Al}_2$ in fig. 11.10 and $(\text{LaSm})\text{Sn}_3$ in fig. 11.12). In addition, there has been a lack of any serious theoretical discussion of the results of the resistivity and pressure experiments which might include more general treatments of this problem (including the effects of anisotropic exchange scattering, for example); nor have a sufficient number of experiments been performed on other $(\text{LaR})\text{Sn}_3$ systems to ascertain the details of the impurity-conduction electron interactions in these host-impurity systems.

3.4. Samarium impurity systems

Although several concentrated alloys and compounds of Sm (notably the Sm monochalcogenides and SmB_6) have been studied in connection with valence fluctuation phenomena, there is only one dilute alloy system reported to date containing Sm impurities which exhibits Kondo-like behavior.

The existence of an unusually large depression of the superconducting transition temperature of LaSn_3 by Sm impurities has been reported by Schmid and Umlauf (1976) and Abou Aly et al. (1976). The data of fig. 11.11 show that the value of $(-dT_c/dn)_{n=0}$ for Sm impurities in LaSn_3 is much greater than the initial depressions for all other lanthanides dissolved in LaSn_3 .

Recently, DeLong et al. (1976) reported measurements of the depression of T_c , the magnetic susceptibility, specific heat and pressure dependence of T_c for $(\text{LaSm})\text{Sn}_3$ alloys. The extremely large value of the initial depression of T_c was confirmed by ac susceptibility and specific heat measurements in the superconducting state.

Measurements of the normal state specific heat of $(\text{LaSm})\text{Sn}_3$ alloys revealed an enhancement of the LaSn_3 host density of states by Sm impurities which is the largest (207 states/eV-atom-spin direction) observed to date for a dilute alloy system. The superconducting state specific heat data for $\Delta C/\Delta C_0$ are plotted vs T_c/T_{c_0} in fig. 11.12, and show strong negative deviations from both the BCS law of corresponding states and the predictions of the AG theory. These data are similar to the corresponding specific heat jump measurements for the Kondo systems $(\text{LaCe})\text{Al}_2$ (fig. 11.10) and $(\text{La, Th})\text{Ce}$ mentioned in section 3.2, and strongly support the existence of a Kondo effect in the $(\text{LaSm})\text{Sn}_3$ system.

Measurements of the temperature dependence of the magnetic susceptibility of a 1.1 at.% (LaSm)Sn₃ sample yielded a temperature independent Sm impurity contribution of about 1.3×10^{-3} cm³/mole Sm from 300 K down to around 50 K. Below 50 K a small "tail" appeared in the impurity susceptibility, but no divergence in the susceptibility was observed to a lowest temperature of 1.4 K, indicating a nonmagnetic impurity state for the Sm ions at low temperatures. Although Sm is known to be trivalent in SmSn₃ (Malik, 1970 and references therein), the combined effects of the CEF and *J*-mixing can lead to very unusual behavior for the magnetic susceptibility in Sm systems, making a unique theoretical description of experimental data difficult (de Wijn et al., 1975). The low temperature susceptibility data, therefore, do not necessarily imply either purely divalent (nonmagnetic, *J* = 0) Sm or a nonmagnetic ICF state for Sm in LaSn₃.

The recent measurements of the temperature dependence of the electrical resistivity of (LaSm)Sn₃ alloys by Bakanowski et al. (1977) indicate the presence of resistivity minima in the samples studied (all of which were for Sm concentrations of less than 20 at.%). These observations would favor a more nearly trivalent state for Sm in LaSn₃ and clearly support the presence of a Kondo effect in (LaSm)Sn₃ alloys. However, the situation is incomplete at the time of this writing; further data may reveal an entirely new class of behavior represented by this interesting system.

3.5. Europium impurity systems

Gainon et al. (1967) observed a "giant" thermoelectric power in AgEu and AuEu alloys. Their magnetic susceptibility measurements for temperatures greater than 40 K indicated paramagnetic behavior in these alloys with Curie-Weiss temperatures of 11 ± 3 K for AuEu and 15 ± 3 K for AgEu. The effective moments were $7.6 \pm 0.2 \mu_B$ and $7.7 \pm 0.2 \mu_B$, respectively, for AuEu and AgAu suggesting a divalent state for Eu in both alloys. Annealing of the samples caused expected variable behavior for the thermoelectric power since the concentrations of Eu employed were close to the believed solubility limit for Eu in noble metals. Thus these measurements should be treated with caution; however, they do suggest that further work on these alloys might prove rewarding.

3.6. Ytterbium impurity systems

The evidence for the Kondo effect in dilute alloys containing Yb lacks the numerous cases of model behavior as have been found for dilute alloys containing Ce impurities, and (Ag, Au)Yb remains to date the only extensively-documented example of anomalous behavior for Yb impurities in a dilute alloy. Unfortunately, this system is also a classic example of the severe limitations that metallurgical effects can place on the clarity of the interpretation of even the most carefully performed experiments. The crux of the problem lies in the rather poorly understood levels of solubility of the lanthanides in Ag and Au.

Early studies of the solubilities of various lanthanides in Au (Rider et al., 1965) and Ag (Bijvoet et al., 1966) suggested that Yb was slightly less than trivalent in Au and divalent in Ag. The low temperature thermoelectric power and magnetic susceptibility of Yb in both Ag and Au were reported by Gainon et al. (1967), Hirst et al. (1968) and Williams and Hirst (1969). The magnetic susceptibility of AuYb showed that for temperatures of about 100 K or higher the susceptibility was well described by a Curie-Weiss law with an effective moment of $4.3 \mu_B$ (close to the trivalent Hund's rule value of $4.54 \mu_B$). Large deviations of the susceptibility from free ion behavior below 50 K were ascribed to crystal field effects resulting in a Γ_7 ground state with a Γ_8 first excited state at 79 K and a Γ_6 second excited state at 83 K. A weakly temperature dependent susceptibility was found for AgYb confirming the presence of divalent Yb.

Hirst and coworkers also performed EPR measurements (Hirst et al., 1968; Williams and Hirst, 1969) on AuYb and AgYb. No resonance was found in AgYb, but the resonance discovered in AuYb corresponded to a g value of 3.30 ± 0.10 , consistent with a Γ_7 ground state for Yb in Au, and a value of $|\mathcal{J}| = 0.22$ eV. Tao et al. (1971) confirmed the results of Hirst et al. by performing their own EPR measurements on AuYb. They determined a value* of $\mathcal{J} = -0.43$ eV which they asserted was indicative of a large (negative) covalent mixing contribution to \mathcal{J} due to the proximity of the $4f^{13}$ and $4f^{14}$ levels of Yb to the Fermi level of Au.

Indeed, the resistivity studies of AuYb by Murani (1970, 1973) demonstrated that resistance minima did exist in AuYb alloys. Using the theory of Kondo (1964), Murani found a value of $\mathcal{J} = (-0.14 \pm 0.01)$ eV, which he discussed in terms of Hirst's ideas (1970) concerning ICF phenomena.

Mössbauer experiments have also been performed on AuYb and extensively analyzed by Stöhr and coworkers (Stöhr, 1975; Shenoy et al., 1974), and Gonzalez-Jimenez and coworkers (Gonzalez-Jimenez and Imbert, 1972, 1973; Gonzalez-Jimenez et al., 1974a, 1974b, 1974c, 1975; Hartmann-Boutron, 1974). Some of these experimental results (Gonzalez-Jimenez and Imbert, 1972, 1973; Gonzalez-Jimenez et al., 1974a, 1974b, 1974c, 1975; Hartmann-Boutron, 1974) indicate $T \ln T$ behavior in the temperature dependence of the Mössbauer relaxation rate for $T < 10$ K. A recent theoretical analysis by Bhattacharjee and Coqblin (1976) found that the AuYb Mössbauer data are consistent with a very low Kondo temperature and an effective value of $\mathcal{J} \approx -0.38$ eV.

Benoit et al. (1974b; Flouquet and Brewer, 1975) have made nuclear orientation measurements on AuYb alloys and determined that $T_K \ll 10$ mK. Unfortunately, the detailed analysis of these experiments is greatly complicated by interaction effects (at very low temperatures), lattice defects and the possible presence of Yb intermetallic compounds.

Some of the more recent results on AuYb have more accurately determined limits for the magnitude of T_K . Cornut and Coqblin (1975) measured the

*This value has been corrected for a difference of a factor of 2 in the hamiltonian of these authors and that used by most other authors cited in this review.

magnetization of very dilute unannealed alloys (Yb concentrations less than 0.3 at.%) of AuYb as a function of magnetic field up to 90 kOe and in the temperature range 0.07 K to 50 K and performed electrical resistivity measurements between 1.1 K and 300 K. They determined that AuYb was well described by single impurity ionic behavior (reflecting a very low T_K) when the combined effects of Kondo scattering and the Au CEF were considered. This interpretation was supported by the elegant measurements of the electronuclear susceptibility of unannealed AuYb alloys by Frossati et al. (1975, 1976) using SQUID magnetometry to a lowest temperature of 7 mK. They were able to show that the T_K of AuYb is much less than 1 mK.

There have also been more refined attempts to uncover magnetic behavior in AgYb alloys. The resistivity measurements of Murani (1974a) on AgYb alloys revealed weak resistance minima around 5 K. Murani explained his results on the basis of an ICF state for Yb in Ag which is also consistent with the small temperature dependence of the susceptibility of AgYb (Gainon et al., 1967).

Murani's interpretation of his work on AgYb has been challenged by Bekker and van Duren (1974), whose measurements of the thermoelectric power in AgYb revealed a strong dependence of their experimental results on annealing procedure. They asserted that this constituted evidence for the presence of an additional scattering mechanism in their alloys which they analyzed theoretically in terms of the presence of Fe impurities. However, these authors did not attempt to analyze their data in terms of the clustering of Yb impurities or the possible formation of regions containing Ag-Yb intermetallic compounds within their samples.

The experimental results just discussed for AgYb and AuYb strongly suggest that it should be possible to study the gradual valence change of Yb from a divalent state to a trivalent state as the host composition is varied from pure Ag to pure Au in *perfectly random* alloys of the type (Ag, Au)Yb. The (Ag, Au)Yb system might then be thought of as a nearly exact analog of the (La, Th)Ce system discussed earlier in this article with AuYb constituting the f-hole analog of LaCe.

The first study of (Ag, Au)Yb alloys was done by Boes et al. (1968), who observed that for Yb concentrations of less than 0.15 at.% in a Ag, Au host a Kondo minimum in the temperature dependence of the electrical resistivity was found in annealed alloys for Au concentrations between 10 and 40 at.%. However, the resistive behavior was also found to depend markedly on the details of the alloy heat treatment.

Allali and coworkers (1969, 1970) performed susceptibility and thermoelectric power measurements on (Ag, Au)Yb alloys. They found that for Au concentrations ≥ 5 at.% a Curie-Weiss fit to the magnetic susceptibility yielded an effective moment of around $4.3 \mu_B$, as shown in fig. 11.13. For Au concentrations < 5 at.% the effective moment μ_{eff} rapidly goes to zero. For Au concentrations ≥ 30 at.% the Curie-Weiss temperature θ is approximately constant and equal to -10 K due to CEF effects. A small composition-dependent anomaly in the Curie-Weiss temperature occurs for Au concentrations between 5 and 30 at.%

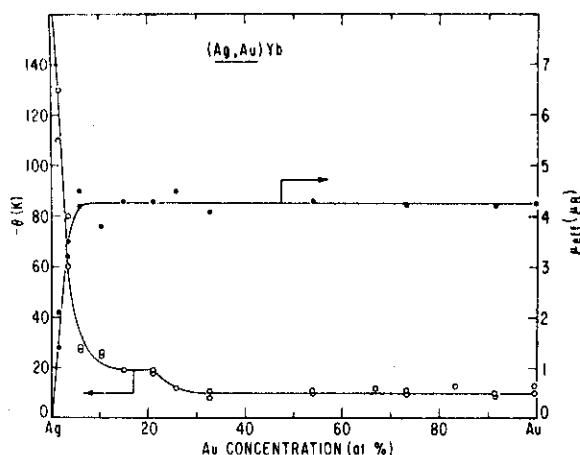


Fig. 11.13. Curie-Weiss temperature θ and effective magnetic moment μ_{eff} for $(\text{Ag}, \text{Au})\text{Yb}$ alloys vs. Au composition of the Ag, Au matrix from magnetic data of Allali et al. (1970).

which these authors attributed to the presence of a Kondo effect. The Curie-Weiss temperature rapidly increases in magnitude as the Au concentration goes to zero (for Au concentration < 5 at.%). All of these observations reflect the absence of a divergent susceptibility as T goes to zero for Au concentrations ≤ 10 at.%. In addition, magnetization curves taken at 1.5 K exhibited marked saturation for Au concentration > 10 at.%, and no such effect for Au concentrations < 10 at.%. Measurements of the thermoelectric power contribution due to Yb impurities showed a sharp "edge" at a Au concentration of 7.5 at.% and a negative "peak" for Au concentrations between 10 and 30 at.%.

The more recent EPR measurements of Nagel et al. (1973) on $(\text{Ag}, \text{Au})\text{Yb}$ alloys were analyzed for the temperature dependence of the resonance linewidth where a resonance was observed. No resonance signal was detected for Au concentrations < 70 at.%, but in varying the Au concentration from 100 to 70 at.%, $|\mathcal{A}|$ can be inferred to double while the g factor changes continuously from 3.34 to 3.22.

All of the work on $(\text{Ag}, \text{Au})\text{Yb}$ mentioned above has been discussed (Boes et al., 1968; Allali et al., 1969, 1970; Nagel et al., 1973) in terms of Kondo phenomena for Au concentrations between 10 and 30 at.%. However, the previously mentioned evidence for Kondo behavior in both AuYb and AgYb are consistent with a smooth dependence of T_K on Au concentration as occurs in the $(\text{La}, \text{Th})\text{Ce}$ system discussed earlier in this article, thus making a restricted concentration "regime" for the presence of Kondo behavior in $(\text{Ag}, \text{Au})\text{Yb}$ unlikely. Particularly interesting is that only a 1 at.% addition of Au to a pure Ag host results in an approximately five-fold increase in the magnitude of the resistivity contribution of Yb in Ag (Murani, 1974a). However, solubility problems for Yb in Ag make these data difficult to interpret. Measurements of the thermoelectric power (Bekker and van Duren, 1975) of a $\text{Ag}_{0.8}\text{Au}_{0.2}\text{Yb}$ alloy place $T_K \approx 1$ K, a value which is certainly reasonable compared to inferred values of T_K for AuYb or AgYb .

Murani (1974b) has subsequently performed measurements of electrical resistivity on (Ag, Pd)Yb and found that the maximum Kondo slope in the resistivity of (Ag, Pd)Yb alloys was one-third the maximum slope in (Ag, Au)Yb, but this could be due to the severe Yb solubility problems encountered in this system.

The recent work of Talmor and Sierro (1975) on the electrical resistivity of (Ag, Au)Yb alloys is directly addressed to the problem of sample characterization. They found that the values of \mathcal{F} obtained from their data varied by as much as a factor of three depending on the sample heat treatment. Talmor and Sierro also showed (fig. 11.14) that there is a sharp peaking of the depth of the Kondo resistance minimum $\Delta\rho_{\min}$ and of the logarithmic slope of the resistivity $|d(\Delta\rho)/d(\log T)|$ at Au concentrations ≈ 25 at.%. This suggests a region favorable to the formation of additional metallurgical phases. X-ray results for a $\text{Ag}_{0.70}\text{Au}_{0.30}\text{Yb}$ sample indicated the presence of Au_3Yb and a microprobe analysis detected a precipitated phase in the alloy.

Attempts to prepare single phase AuYb and Au_3Yb compounds for resistivity studies resulted only in mixed phase $\text{Au}_3\text{Yb}-\text{Au}_4\text{Yb}$ and $\text{AuYb}-\text{Au}_2\text{Yb}$ samples. However, Talmor and Sierro found relatively enormous resistance minima in both types of composite samples followed by steep drop-offs at lower temperatures due to magnetic ordering.

Thus the present state of understanding of the Kondo effect in (Ag, Au)Yb alloys is complicated by solubility problems and the presence of additional phases of Yb intermetallic compounds which are known to produce resistance minima.

Fisk et al. (1969) have measured the resistivity of a sample of approximate composition $(\text{Sc}_{0.95}\text{Yb}_{0.05})\text{B}_{12}$ and found a very pronounced minimum near 45 K. No additional measurements have been performed, but this system is of interest

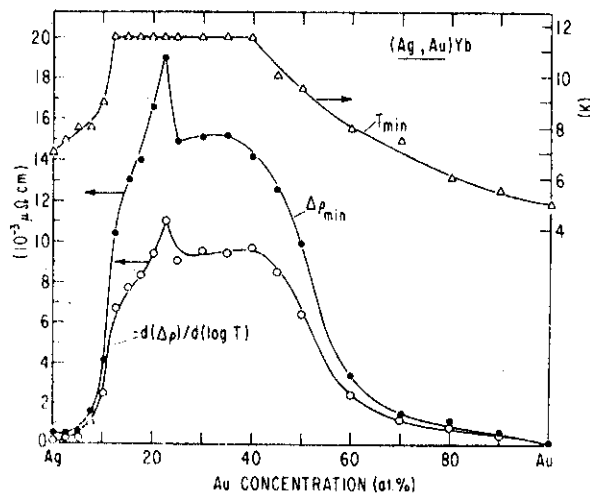


Fig. 11.14. Temperature of the Kondo resistance minimum T_{\min} , depth of the resistance minimum $\Delta\rho_{\min}$, and logarithmic slope of the solute incremental resistivity $-d(\Delta\rho)/d(\log T)$ for (Ag, Au)Yb alloys vs Au composition of the Ag, Au matrix from resistivity data of Talmor and Sierro (1975).

since it is the only other dilute alloy containing Yb impurities [other than (Ag, Au)Yb] which exhibits a resistance minimum.

4. Kondo-like behavior in concentrated lanthanide alloys and compounds

4.1 Introduction

The greatest advantage of studying single impurity effects in metallic lanthanide systems is that one can work with concentrated alloys and even compounds. The extreme local nature of the 4f wavefunction (typically about 0.1 lattice spacing) means that there is virtually no direct overlap of nearest neighbor 4f wavefunctions. This is in contrast to the 3d metals where one must work with ppm concentrations of 3d impurities in a nonmagnetic metallic host to insure no direct 3d interactions, and must then try to extract the impurity signal from a relatively large host background. One can perform a much wider variety of measurements on concentrated lanthanide systems since the 4f contribution to a physical property is a much larger fraction of the total measured quantity. This provides not only a broader variety of possible experiments but allows one to better characterize the sample.

However, concentrated lanthanide systems have two major disadvantages. First, in concentrated *alloys* one can have several different local environments for the rare earth ions. The local environment of an A atom in an AB alloy can vary depending on how many nearest neighbor B atoms it has. The lanthanide ions may therefore exhibit a characteristic temperature T_0 for *each* local environment, which makes the interpretation of the experimental data more difficult. Second, in concentrated alloys and compounds there are interaction effects between the lanthanide ions. The interaction is indirect and is mediated through the conduction electrons (RKKY interaction). In some concentrated systems this interaction can be neglected ($T_{\text{RKKY}} \ll T_0$), while in others, particularly compounds, it is dominant ($T_{\text{RKKY}} \gg T_0$) and magnetic ordering results.

As mentioned in the Introduction (section 1), the electrical resistivity, specific heat, magnetic susceptibility and thermoelectric power anomalies of concentrated lanthanide Kondo systems are qualitatively similar to those found in the dilute lanthanide systems discussed previously. *However the importance of the concentrated systems is that they provide a totally new view of Kondo-like phenomena.* Lattice constant, X-ray photoemission (XPS) and Mössbauer isomer shift measurements indicate a strong correlation between systems that exhibit Kondo-like anomalies and systems in which the lanthanide ion has a mixed or intermediate valence. By mixed valence we mean that there are two 4f electron configurations accessible to *each* rare earth ion (e.g., Ce^{3+} - Ce^{4+} , Eu^{2+} - Eu^{3+} , Yb^{2+} - Yb^{3+}). Phenomenologically the traditional Kondo anomalies are qualitatively consistent with the mixed valence picture, although at present there is no "first principles" theory based on the mixed

valence concept. These ideas will be discussed in more detail in this section with respect to specific systems.

4.2. Cerium systems

As is the case in dilute lanthanide systems, Kondo anomalies in concentrated alloys and compounds are most frequently found in Ce systems. Kondo anomalies in a concentrated system were first observed in the electrical resistivity of CeAl_2 by Buschow and van Daal (1969). Although CeAl_2 orders antiferromagnetically at 3.4 K (Barbara et al., 1975; Hill and Machado da Silva, 1969; Swift and Wallace, 1968; Maple, 1969), above this temperature a minimum in the resistivity was observed suggesting a Kondo effect. This conclusion was supported by the high temperature heat capacity work of Deenadas et al. (1971). In CeAl_2 the Ce^{3+} $J = 5/2$ multiplet is split into a doublet groundstate and quartet excited state (splitting about 100 K) by the cubic crystalline electric field. The high temperature heat capacity showed a Schottky type anomaly due to the splitting but the anomaly was much broader than expected from two sharp levels – a feature characteristic of a Kondo anomaly.

The compound CeAl_3 and its associated alloys is one of the most thoroughly studied concentrated lanthanide systems. Above 25 K the magnetic susceptibility of CeAl_3 follows a Curie-Weiss law with a Curie-Weiss temperature of -46 K and an effective moment of $2.63 \mu_B$ (Buschow and Fast, 1966; Mader and Swift, 1968). Below 25 K the curvature in χ^{-1} was attributed to the effects of a hexagonal crystal field. The ground state of the Ce^{3+} ion must at least be a doublet due to Kramer's theorem; however, the susceptibility exhibits neither magnetic order nor diverges as $T \rightarrow 0$. The lack of magnetic order above 2 K has also been verified by neutron diffraction measurements (Mahoney et al., 1973; Edelstein et al., 1976). The electrical resistivity of CeAl_3 (a metal) is unusual as it increases upon cooling below 300 K suggesting a minimum in the resistivity above room temperature (van Daal and Buschow, 1970; Buschow et al., 1971; Edelstein et al., 1974). At 40 K the resistivity reaches a maximum followed by a rapid decrease upon further cooling. We also note that Percheron et al. (1973) have studied the effects of pressure on the resistivity of CeAl_3 .

The "Kondo side-band" explanation of the electrical resistivity of CeAl_3 (and other transport properties) was first given by Maranzana (1970; Maranzana and Bianchessi, 1971) using the s - f exchange hamiltonian. He showed that in the presence of crystal fields, the conduction electron scattering rate diverges not at the Fermi energy, as calculated by Kondo without consideration of crystal fields, but at energies displaced from the Fermi energy by the crystal field splitting δ . This leads to a maximum in the resistivity at $T = \delta/3k_B$ and to a resistivity curve qualitatively similar to the resistivity of CeAl_3 . A more detailed calculation of the side-band model based on an Anderson-like hamiltonian including orbital quantization has been given by Cornut and Coqblin (1972).

The thermoelectric power of the (La, Ce) Al_3 system has been investigated by van Aken et al. (1974). The thermoelectric power of CeAl_3 has a large peak of

40 $\mu\text{V/K}$ at about 60 K (roughly the same temperature as the maximum in the resistivity). The low and high temperature heat capacity of CeAl_3 exhibits several Schottky type anomalies at 25 K, 6 K and 4 K; however, these anomalies as well as the total measured entropy are not explainable in terms of crystal field effects alone (van Maaren et al., 1971; Mahoney et al., 1973). Recent measurements by Andres et al. (1975) showed that at very low temperatures ($T = 10\text{--}200\text{ mK}$) the specific heat of CeAl_3 follows a γT law with $\gamma = 1620\text{ mJ/mole}\cdot\text{K}^2$ and the electrical resistivity a T^2 law.

Another interpretation of the CeAl_3 data in terms of a fluctuating Ce valence was given by Sales (1974). The series of rare earth compounds CeAl_3 through GdAl_3 crystallize in the hexagonal Ni_3Sn structure. The lattice constants (van Vucht and Buschow, 1965) of CeAl_3 deviate from the trend established by the other RAl_3 compounds suggesting a valence of about 3.1 for Ce in CeAl_3 . In addition, the magnetic susceptibility and electrical resistivity of CeAl_3 are qualitatively identical to those of CeCu_2Si_2 (Sales and Viswanathan, 1976). For the CeCu_2Si_2 compound it has been shown that one can quantitatively interpret the data in terms of a phenomenological model based on the fluctuating valence idea. This interpretation has recently been supported by neutron diffraction measurements on CeAl_3 by Edelstein et al. (1976). They found a Ce valence between 3.0 and 3.1 and no evidence of a spin compensating conduction electron cloud at low temperatures.

Several Ce compounds of the form CeX_3 ($X = \text{Pb, In, Pd, Sn}$) exhibit one or more anomalies associated with the Kondo effect. All these compounds crystallize in the cubic Cu_3Au structure.

CeIn_3 is similar to CeAl_3 in that although it orders antiferromagnetically at 10.4 K (van Diepen et al., 1971), above this temperature there is a broad minimum in the electrical resistivity at about 170 K (van Daal and Buschow, 1970). The high

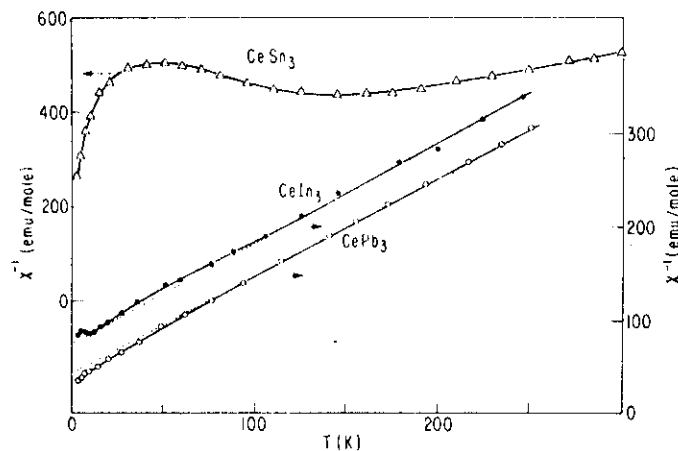


Fig. 11.15. Inverse magnetic susceptibility vs temperature for CeSn_3 (open triangles), CeIn_3 (solid circles) and CePb_3 (open circles). Measurements were made in a magnetic field of 19 kOe [after Tsuchida and Wallace (1965)].

temperature magnetic susceptibility (fig. 11.15) follows a Curie-Weiss law with $\theta = -62$ K and $\mu_{\text{eff}} = 2.7 \mu_B$ (Tsuchida and Wallace, 1965). The thermoelectric power of CeIn_3 (Gambino et al., 1973) has a maximum of $40 \mu\text{V/K}$ at 75 K.

For the three compounds CeSn_3 , CePb_3 (fig. 11.15) and CePd_3 there is no evidence of magnetic order (Tsuchida and Wallace, 1965; Shenoy et al., 1970; Malik and Vijayaraghavan, 1973; Cooper et al., 1971; Gardner et al., 1971, 1972; Hutchens et al., 1971; Harris et al., 1972), the electronic specific heat coefficients are very large (53,200 and 37 mJ/mole-K^2 respectively) (Malik and Vijayaraghavan, 1973; Cooper et al., 1971; Hutchens et al., 1972) and there are large peaks in the respective thermoelectric powers. CeSn_3 has a very broad thermoelectric power maximum of $33 \mu\text{V/K}$ from 100–300 K (Cooper et al., 1971) while CePd_3 (Gambino et al., 1973) and CePb_3 (Cooper et al., 1971) have sharper thermoelectric power maxima of $120 \mu\text{V/K}$ and $40 \mu\text{V/K}$ at 125 K and 40 K respectively.

Using lattice constant measurements Gardner et al. (1972) have determined that the Ce ion valence in CePd_3 is about 3.45 when the expansion of the Pd lattice is taken into account. The electrical resistivity of CePd_3 (Hutchens et al., 1971; Rao et al., 1971) is qualitatively similar to that of CeAl_3 and CeCu_2Si_2 discussed previously. Upon cooling the resistance increases from room temperature to 80 K exhibiting a local maximum at about 120 K. At 80 K there is a sharp drop in the resistivity with decreasing temperature. The magnitude of the resistance is large – more than a factor of 10 larger than the resistance of LaPd_3 .

Harris and Raynor (1965) found the lattice constant of CeSn_3 to be strongly temperature dependent suggesting a temperature dependent Ce valence. The electrical resistivity of CeSn_3 is relatively normal although the increase of resistance with temperature at room temperature is slower than T^1 (van Daal and Buschow, 1970). Misawa (1974) analyzed CeSn_3 in terms of the Fermi liquid approach and was able to account for the broad maximum in the magnetic susceptibility at about 150 K and the finite susceptibility at $T = 0$.

The compound CeBe_{13} crystallizes in the cubic NaZn_{13} structure and has a lattice constant which suggests an intermediate Ce valence (Shoemaker et al., 1952). The magnetic susceptibility of CeBe_{13} (Cooper et al., 1971; Bucher et al., 1975a; Borsa and Olcese, 1973) shows no evidence of magnetic order and is very similar to the susceptibility of CeSn_3 . The electronic specific heat coefficient (Cooper et al., 1971) is 115 mJ/mole-K and there is a large peak in the thermoelectric power of $60 \mu\text{V/K}$ at 120 K. The electrical resistivity of CeBe_{13} has no sharp anomalies but at room temperature the resistance rise is slower than T^1 . Borsa and Olcese (1973) measured the nuclear magnetic resonance and relaxation rate of the Be nucleus in CeBe_{13} . They interpreted their data in terms of a variable Ce valence with Ce^{3+} - Ce^{4+} resonance lifetime of order 10^{-13} sec.

Several other Ce compounds (such as CeAs , CeN , CeB_4 , CeP) (Tsuchida et al., 1970; Sales, 1974; Fisk et al., 1972; Weaver and Schirber, 1976) exhibit one or more Kondo-like anomalies; however, none of these compounds have been extensively studied.

Elliott et al. (1969) have studied the resistive and magnetic properties of

concentrated Ce-La and Ce-Y alloys. They observed resistance minima in all Ce-Y alloys with 2-75 at.% Ce and in Ce-La alloys with 14-18 at.% La.

Lawrence et al. (1975) have studied the electronic properties of the Ce, Th system in some detail. While there are definite "Kondo anomalies" in this system, the main thrust of this work is concerned with the thermodynamic behavior near valence instabilities, particularly near the critical point. A detailed discussion of the work is beyond the scope of this article and we refer the reader to the following references: Parks and Lawrence (1976) and Varma (1976 and references therein).

The element cerium is known to exhibit several anomalies in its physical properties which have been attributed to the Kondo effect; however, the body of literature on the various phases of cerium metal is vast, and we refer the reader to ch. 4 by Koskenmaki and Gschneidner which is devoted to this fascinating element, especially see section 4.3.2.

4.3. *Samarium systems*

It was remarked earlier that there is a strong correlation between systems which exhibit a mixed or fluctuating valence and systems which show Kondo-like anomalies. This connection was particularly clear in the Ce systems considered previously. A wide variety of experimental measurements has shown that in SmB_6 and "collapsed" SmS , the Sm ions have a mixed valence (Sm^{2+} - Sm^{3+}). We consider these systems not because they are classic Kondo systems (they are not), but because they provide considerable insight into the nature of the mixed valence state. These systems are also interesting with respect to the study of metal-insulator transitions, but this aspect will be discussed in ch. 20 by Jayaraman.

SmB_6 crystallizes in the cubic CsCl structure with only one type of site for the Sm ion. If the Sm ion is divalent ($4f^6$) the compound should be a semiconductor, while if the Sm ion is trivalent ($4f^5$) the compound should be a metal. The size of the Sm^{2+} ion is much larger than the Sm^{3+} ion. From lattice constant measurements as a function of temperature, Nickerson et al. (1971) showed that the Sm ion has a temperature independent valence of about 2.7. The electrical resistivity (Menth et al., 1969; Nickerson et al., 1971; Sturgeon et al., 1974) of SmB_6 is relatively constant from 300-70 K but increases two orders of magnitude from 70-8 K at which point it saturates. The Hall coefficient and Hall mobility (Nickerson et al., 1971) change sign twice between 1 and 300 K and exhibit sharp minima at 15 K. The thermoelectric power data of Paderno et al. (1969) is similar to the Hall mobility in shape and sign changes, and exhibits a large negative maximum of $350 \mu\text{V/K}$ at about 15 K.

At high temperatures the magnetic susceptibility (Menth et al., 1969; Nickerson et al., 1971) of SmB_6 (fig. 20.10) falls between the susceptibilities of the Sm^{2+} and Sm^{3+} configurations. At low temperatures the susceptibility saturates with no evidence of magnetic order down to 0.35 K. The electronic contribution to the SmB_6 heat capacity (Nickerson et al., 1971) is large

(determined by comparison to the isostructural compound LaB_6) but complicated, possibly due to interband transitions between closely adjacent valence and conduction bands. Soft X-ray absorption measurements by Vainshtein et al. (1965) and X-ray photoelectron spectroscopy results of Aono et al. (1975) indicate the presence of both valence configurations ($4f^6$ and $4f^5 5d^{0.8} 6s^{0.2}$) at room temperature. Mössbauer isomer shift measurements on the Sm nucleus by Cohen et al. (1970) showed *one* temperature independent absorption line centered between the positions characteristic of Sm^{2+} and Sm^{3+} ions.

The transport properties of SmB_6 were explained by Nickerson et al. (1971) using a semiconductor band model with two valence bands: a normal parabolic "s type" band and a very narrow "d or f like" band situated at a slightly higher energy. Using this model they found that the total change in carrier concentration (valence) accompanying the electrical resistivity change below 65 K is relatively small. This is consistent with the Mössbauer and lattice constant measurements which indicate no appreciable valence change as a function of temperature. Chui (1976) explained the resistance of SmB_6 in terms of the coulomb interaction between the d and f electrons producing excitonic effects. This leads to an increase in the resistance upon cooling without a change of valence.

The results for "collapsed" SmS are similar to those for SmB_6 . At zero pressure SmS is a narrow gap semiconductor and the Sm ion is divalent. Jayaraman et al. (1970a), however, showed that at 6 kbar there was a pressure-induced semiconductor-metal transition without a change of crystal structure.

The SmS semiconductor to metal transition was later verified by the direct observation of a discontinuous change in the optical reflectivity at 6 kbar (Kirk et al., 1972). This is consistent with a first order magnetic phase transition which was directly verified by magnetic susceptibility measurements under pressure by Maple and Wohleben (1971). In the collapsed phase the susceptibility of SmS showed no magnetic order down to 0.35 K and was almost identical to the susceptibility of SmB_6 (see fig. 20.10 of volume 2). Bader et al. (1973) measured the heat capacity (fig. 11.16) and electrical resistivity (fig. 11.17) of SmS under pressure. They found a large electronic contribution to the heat capacity ($\gamma = 145 \text{ mJ/mole-K}^2$) and a resistivity reminiscent of SmB_6 . Mössbauer isomer shift measurements of SmS under pressure by Coey et al. (1976) reveal the transition from a Sm^{2+} isomer shift at zero pressure to an intermediate value at pressures above 6 kbar (fig. 11.18). The isomer shift of SmS above 6 kbar was found to be about the same as the isomer shifts for "chemically collapsed" $\text{Sm}_{0.77}\text{Y}_{0.23}\text{S}$ and SmB_6 at zero pressure.

Jayaraman et al. (1973) demonstrated that one could chemically collapse the Sm ion in SmS by alloying with Gd [(Sm,Gd)S]. Chemically collapsing the Sm ions in SmS through alloying is extremely useful since one can then study the mixed valence state at atmospheric pressure by varying the alloy composition. Subsequent X-ray photoemission spectroscopy studies on this and similar alloys [(Sm, Th)S, (Sm, As)S] by Campagna et al. (1974a), Freeouf et al. (1974) and

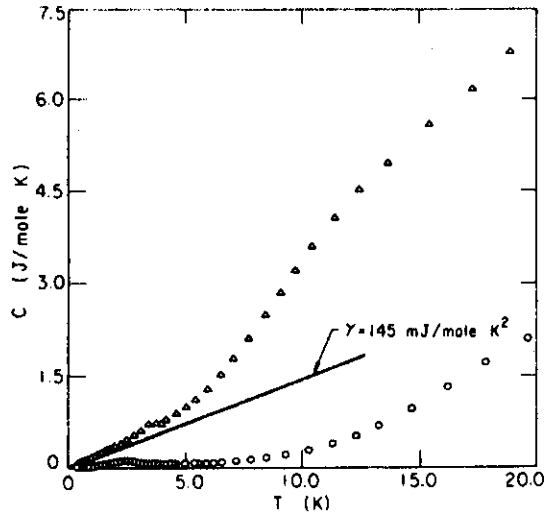


Fig. 11.16. Heat capacity C vs. temperature of SmS at approximately 15 kbar (triangles) and at zero pressure (circles). A plot of C/T vs. T^2 shows that the limiting coefficient γ of the linear term in the heat capacity of the collapsed metallic phase is $\gamma \approx 145 \text{ mJ/mole K}^2$ [after Bader et al. (1973)].

Pollak et al. (1974), showed the presence of both Sm^{2+} and Sm^{3+} configurations (see fig. 11.19)

We note that electrical resistivity, Hall coefficient, optical measurements and Raman scattering measurements have been reported on the (Sm, Y)S system (Penny and Holtzberg, 1975; Guntherodt and Holtzberg, 1976; Tsang, 1976).

The Mössbauer, magnetic susceptibility, X-ray absorption and X-ray photoemission results for SmB_6 and SmS can be qualitatively understood in terms of the fluctuating valence notion proposed by Maple and Wohleben (1971; see section 2). They envisioned the Sm ion as fluctuating in time between the two configurations, Sm^{2+} and Sm^{3+} , with a frequency $\nu_0 = \tau_0^{-1}$. This frequency is related to the strength of the interaction of the 4f shell with the conduction electrons and the energy separation between the two configurations. For SmS and SmB_6 they determined $T_0 = h\nu_0/k_B \approx 100 \text{ K}$, which is consistent with the narrow d or f like bandwidth of 100 K found by Nickerson et al. (1971) for SmB_6 .

If measurements are made on a time scale large compared to $\tau_0 = 10^{-12} \text{ sec}$, then one will "see" a time average of the two configurations. Magnetic susceptibility and Mössbauer isomer shift experiments are "slow" measurements (measuring times of order 10^{-10} sec and 10^{-8} sec , respectively) on such a time scale. At high temperatures ($T \gg T_0$) the susceptibility is the weighted average of the susceptibilities of the two configurations, but at low temperatures ($T \ll T_0$) saturates to a constant value. The Mössbauer isomer shift experiment should show only one absorption line at a position intermediate between that associated with either Sm^{2+} or Sm^{3+} . Soft X-ray absorption and X-ray photoemission, however, are relatively fast measurements ($\sim 10^{-17} \text{ sec}$) and hence will "see"

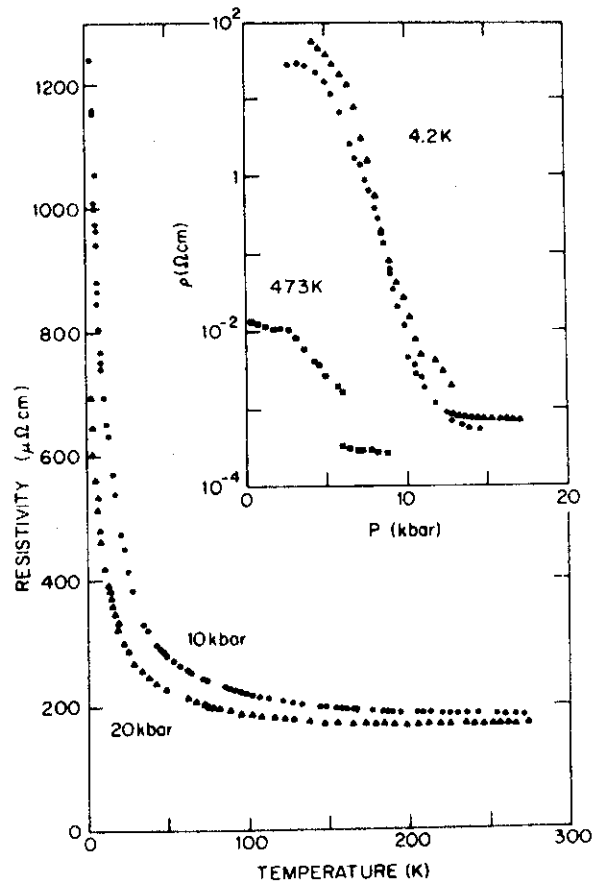


Fig. 11.17. Electrical resistivity ρ vs temperature of SmS at 10 and 20 kbar. The inset compares the insulator-metal transition as a function of pressure at 4.2 and 473 K. The pressure transmitting medium was AgCl (circles), frozen (triangles) or liquid (squares) n-pentane isoamyl alcohol [after Bader et al. (1973)].

either one configuration or the other over the period of a measurement. This results in effects due to the presence of both configurations appearing in the final spectra.

4.4. Europium systems

Two concentrated Eu systems have been found to exhibit "Kondo-like" anomalies: EuCu_2Si_2 and $(\text{Eu}, \text{La})\text{Rh}_2$. Mössbauer experiments on both systems have been performed by Bauminger et al. (1973). For the EuCu_2Si_2 system, which has only one site for the Eu ion, they found one temperature dependent absorption line situated between the two regions corresponding to either Eu^{2+} or Eu^{3+} . Previously no Eu compound had exhibited an isomer shift in this

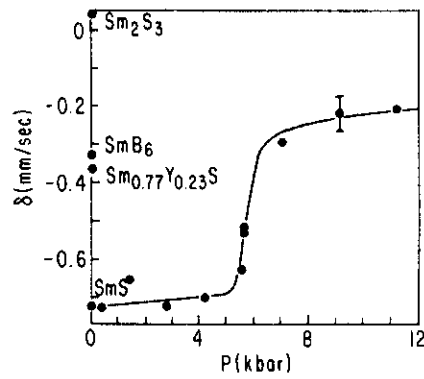


Fig. 11.18. Mössbauer isomer shift of ^{149}Sm in SmS vs pressure at room temperature. The isomer shifts are relative to a source of ^{149}Eu in EuF_3 . At zero pressure the isomer shifts of $\text{Sm}_2\text{S}_3(\text{Sm}^{3+})$, SmB_6 and $\text{Sm}_{0.77}\text{Y}_{0.23}\text{S}$ (mixed valence) are shown for comparison [after Coey et al. (1976)].

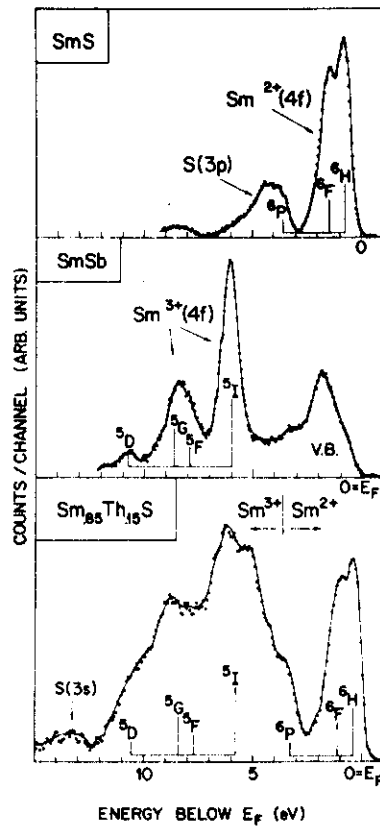


Fig. 11.19. Comparison of the X-ray photoemission spectra of 4f electrons in SmS (zero pressure, divalent Sm), SmSb (trivalent Sm) and the mixed valence ($\text{Sm}_{0.85}\text{Th}_{0.15}\text{S}$) alloy. The vertical bars indicate the calculated multiplet intensities using the method of fractional parentage [after Campagna et al. (1976)].

intermediate region. The data were interpreted in terms of a fluctuating valence ($4f^6-4f^7$) and a lower limit of 3×10^{10} cps was placed on the fluctuation frequency. Similar results were obtained for the (Eu, La)Rh₂ system (Bauminger et al., 1974), but in this alloy there are five different environments for the Eu atoms depending on the number of nearest neighbor La atoms. This results in a complicated absorption spectrum with each different Eu environment having a different characteristic fluctuation frequency.

Mössbauer measurements on Eu_{0.25}La_{0.75}Rh₂ under pressure have been made by Wortmann et al. (1976). They found a strong pressure induced shift of the resonance lines which they explained by an increase in the energy separation between the Eu²⁺ and Eu³⁺ valence states. We note that Bauminger et al. (1976) have recently reported Mössbauer measurements on the Eu(A, B)₂ (A = Rh, Ir, B = Pt, Al) systems.

The magnetic susceptibility, electrical resistivity, thermoelectric power and heat capacity of EuCu₂Si₂ have been measured by Sales and Viswanathan (1976). The susceptibility shows no evidence of magnetic order down to 0.4 K, and has a value intermediate between that of Eu²⁺ and Eu³⁺ over the temperature range 0.4–300 K. At room temperature the susceptibility is strongly pressure dependent with $d\chi/dP = -1.6 \times 10^{-4}$ emu/mole·kbar. The resistivity has no sharp features but follows a T^3 law at low temperatures and exhibits pronounced negative curvature near room temperature. The thermoelectric power shows a very broad maximum of 9 μ V/K from 20–200 K—similar in shape to that of CeSn₃ which also has a strongly temperature dependent valence (see section 4.2). The electronic contribution to the heat capacity is large with $\gamma = 67.5$ mJ/mole·K². Sales and Viswanathan (1976) interpreted their data in terms of a fluctuating Eu valence with a fluctuation frequency of 2×10^{12} cps (50 K).

4.5. Thulium systems

TmTe and TmSe have been investigated with respect to valence fluctuations. The lattice constants of the R-tellurides and R-selenides were reported by Iandelli (1961) and from these data it appears that TmTe is divalent and TmSe has an intermediate valence at room temperature. All of these compounds crystallize in the rock salt structure.

Jayaraman et al. (1970b) found a very strong pressure induced decrease in the lattice parameter and electrical resistivity of TmTe. Wohlleben et al. (1972) have investigated the magnetic susceptibility of TmTe over the temperature range from 0.4–300 K and at pressures from 0–50 kbar. They found no clear evidence of magnetic order, although the magnetization curves at low temperatures are highly nonlinear. Three different electronic regimes were found as a function of pressure and explained as different temporal mixtures of Tm²⁺ and Tm³⁺ configurations. X-ray photoemission measurements on TmTe by Campagna et al. (1974b) (at atmospheric pressure and room temperature) indicated the presence of both Tm²⁺ and Tm³⁺ configurations. They interpreted their results in terms of valence fluctuations. However, recent optical absorption and ultraviolet photo-

emission measurements by Suryanarayanan et al. (1975) on thin films of TmTe indicated that the Tm was essentially divalent. They found that a small ultraviolet photoemission spectroscopy (UPS) signal corresponding to Tm^{3+} was obtained but that this signal was strongly dependent on the surface condition. This conclusion is supported by the reflectivity measurements on TmTe by Batlogg et al. (1976) and Ward et al. (1975). It should be noted, however, that the lattice constants of the various TmTe samples studied differed appreciably and that there may be problems related to variations in stoichiometry and vacancies. (See Bucher et al., 1975a and Batlogg et al., 1976.)

The TmSe lattice constant, resistivity and magnetic susceptibility were investigated by Bucher et al. (1975b). From these data as well as XPS measurements by Campagna et al. (1974b), it was concluded that TmSe had a nonintegral valence and underwent temporal fluctuations between Tm^{2+} and Tm^{3+} configurations. However, low temperature specific heat and magnetization measurements by Bucher et al. (1970) revealed that TmSe ordered at 3 K although there was no evidence of long range magnetic order or crystal fields in neutron diffraction experiments performed at 1 K (Cox et al., unpublished). Ott et al. (1975) have investigated in detail the nature of the ordered state of TmSe by means of thermal expansion, magnetostriction and a.c. susceptibility measurements in different magnetic fields. They found that the ordering is antiferromagnetic in nature but that there appear to be at least three different phases below the Néel temperature. The reflectivity measurements of Batlogg et al. (1976) and Ward et al. (1975) are in disagreement with respect to the presence of valence fluctuations in TmSe. As is the case with the TmTe samples there may also be problems (related to stoichiometry and vacancies) with the TmSe samples. Further investigation of this interesting system is needed.

4.6. Ytterbium systems

With the exception of Ce systems, lanthanide compounds and alloys made with Yb most frequently exhibit Kondo anomalies. Two of the most thoroughly studied Yb systems are YbAl_2 and YbAl_3 . The phase diagram for the Yb-Al system has been reported by Palenzona (1972). YbAl_2 crystallizes in the cubic MgCu_2 Laves phase while YbAl_3 forms in the cubic Cu_3Au structure. Iandelli and Palenzona (1972) measured the lattice constants of both compounds from 80–800 K.

For YbAl_3 the Yb ion appears to have a temperature independent valence of about 2.9, while in YbAl_2 the Yb valence is about 2.5 at 800 K, but is almost completely divalent at 80 K (Iandelli and Palenzona, 1972). The magnetic susceptibility of YbAl_3 (van Vucht and Buschow, 1965; Iandelli and Palenzona, 1972; Sales and Wohlleben, 1975; Havinga et al., 1973) (fig. 11.20) follows a Curie-Weiss law at high temperatures with a Curie-Weiss temperature $\theta = -143$ K and an effective moment $\mu_{\text{eff}} = 3.89 \mu_B$. At about 120 K there is a broad maximum in the susceptibility and there is subsequently no evidence of magnetic order down to 0.4 K. At room temperature there was no effect of pressure

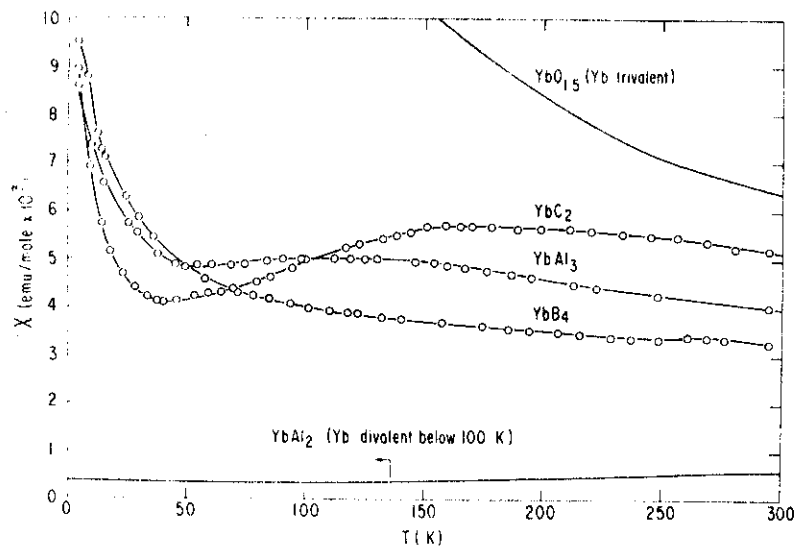


Fig. 11.20. Magnetic susceptibility vs temperature for several nonmagnetic Yb compounds with nonintegral valence. The rapid increase below 50 K is attributed to less than 1% of Yb_2O_3 impurity. For comparison, the magnetic susceptibility of Yb_2O_3 (Yb^{3+}) and YbAl_2 (Yb^{2+}) are also shown [after Sales (1974); Maple and Wohleben (1974)].

($P < 15$ kbar) on the YbAl_3 susceptibility ($d\chi/dP < 1.5 \times 10^{-6}$ emu/gm-kbar) Sales, 1974). The magnetic susceptibility of YbAl_2 is temperature independent at low temperatures (0.6×10^{-6} emu/mole), but increases with increasing temperatures reaching a maximum of 5.5×10^{-6} emu/gm at 850 K (Klasse et al., 1973). At room temperature the susceptibility of YbAl_2 is strongly pressure dependent with $d\chi/dP = 2 \times 10^{-5}$ emu/mole-kbar (Sales, 1974).

The electrical resistivities of both compounds YbAl_2 and YbAl_3 have no sharp anomalies. The electronic specific heat coefficients are $\gamma = 16.8$ mJ/mole \cdot K² and $\gamma = 45$ mJ/mole \cdot K² for YbAl_2 and YbAl_3 , respectively (Havinga et al., 1973) as compared to $\gamma = 5.7$ mJ/mole \cdot K² for LuAl_2 (Hungsberg and Gschneidner, 1972). The magnitude of the thermoelectric power of YbAl_3 (van Daal, 1974) has a maximum of -90 μ V/K at 250 K – a factor of 30 higher than the thermopower of LuAl_3 at the same temperature. Havinga et al. (1973) interpret the YbAl_3 and YbAl_2 data at low temperatures in terms of a virtual bound 4f state just below the Fermi level, while at high temperatures a two level model is employed with an Yb^{2+} ground state and an Yb^{3+} excited state.

YbCu_2Si_2 crystallizes in the tetragonal ThCr_2Si_2 structure (Rieger and Parthe, 1969). At room temperature the lattice constant suggests an Yb valence of about 2.8. The high temperature magnetic susceptibility (Sales and Viswanathan, 1976) follows a Curie-Weiss law with $\mu_{\text{eff}} = 4.19 \mu_B$ and $\theta = -160$ K for $H \parallel a$ and $\theta = -42$ K for $H \parallel c$. Below 75 K the susceptibility flattens out in both directions with no evidence of magnetic order down to 0.4 K. At room temperature there was no effect of pressure on the susceptibility ($d\chi/dP < 1.5 \times$

10^{-6} emu/mole·kbar). The electrical resistivity is a monotonic function of temperature but at room temperatures the increase is much slower than T^1 . The thermoelectric power has a maximum of $40 \mu\text{V/K}$ at 60 K, as compared to $5 \mu\text{V/K}$ for YCu_2Si_2 at the same temperature. The electronic specific heat coefficient is large with $\gamma = 135 \text{ mJ/mole}\cdot\text{K}^2$. Sales and Viswanathan (1976) interpreted their data in terms of a fluctuating Yb valence with an intrinsic lifetime of the Yb^{3+} configuration of 0.3×10^{-12} sec (75 K).

The compounds YbC_2 , YbB_4 , YbIn_3 , and YbCu_2 (Gschneidner, 1961; Klaasse et al., 1973; Fisk et al., 1972; Sales, 1974) exhibit one or more anomalies associated with the Kondo effect. However, with the exception of a minimum at 40 K in the electrical resistivity of YbC_2 (Sales, 1974), the three compounds discussed previously typify the anomalies found in Yb systems.

5. Concluding remarks

In this chapter, we have shown that both dilute and concentrated assemblages of lanthanide ions with partially-filled 4f electron shells in a metallic environment exhibit a continuum of magnetic behaviors which span the entire range between magnetism and nonmagnetism. We have emphasized that with each magnetic state of a lanthanide ion in this continuum there can be associated a phenomenological characteristic temperature above which the metallic lanthanide system behaves *magnetically* and below which the system behaves *nonmagnetically*. The characteristic temperature increases with the amount of hybridization or admixture of the localized 4f electron states of the lanthanide ions with the extended states of the conduction band. Thus within a given temperature range, increasing hybridization tends to drive the metallic lanthanide system towards nonmagnetic behavior. This 4f-conduction electron hybridization is also responsible for the striking temperature-dependent Kondo-like anomalies which occur in a growing number of dilute and concentrated metallic lanthanide systems. Among the thirteen lanthanide ions with partially-filled 4f electron shells, Ce, Pr, Sm, Eu, Tm and Yb have been observed to exhibit Kondo-like behavior in numerous metallic alloys and compounds.

An important point we have stressed in this chapter is that the magnetic state of lanthanide ions can often be profoundly varied through the application of external pressure or by alloying with another element. This has made it possible to follow the evolution of the physical properties throughout the entire range of magnetic character of the lanthanide ion in a number of dilute and concentrated lanthanide systems. In the (La, Th)Ce system, the superconducting and normal state physical properties have been documented in detail throughout the continuous demagnetization of the Ce solute ions which proceeds as the La, Th matrix composition is varied from pure La to pure Th. This, and similar studies, have made it possible to study the response of the superconducting electron gas to the presence of localized states of solutes whose magnetic character spans the entire range from magnetism to nonmagnetism. These studies have also revealed

that a strong correlation exists between the behavior of the superconducting properties and the magnetic state of a solute ion. This, in turn, has provided a means whereby the magnetic state of a solute dissolved in a superconducting metallic matrix may be determined by studying the modification of the superconducting properties of the matrix caused by the introduction of the impurity ion.

We have also emphasized that in metals interactions between lanthanide ions are relatively weak compared to interactions between their transition metal ion counterparts. This is perhaps the most significant advantage afforded by lanthanide ions in the study of Kondo-like behavior in both dilute and concentrated lanthanide systems. The weak Ce inter-impurity interactions in the $(\text{LaCe})\text{Al}_2$ system have permitted the classic single impurity Kondo anomalies in both the superconducting and normal state of this exemplary system to be documented in great detail as a function of temperature and magnetic field. The extensive data which have been accumulated for $(\text{LaCe})\text{Al}_2$ have provided strong tests of several theories which have been developed to account for the striking temperature dependent Kondo effects in both the superconducting and normal state.

The relatively weak interactions between lanthanide ions in concentrated lanthanide systems often allow Kondo-like anomalies (which are qualitatively identical to those which occur in dilute lanthanide systems) to be investigated without the additional complications which are introduced by the occurrence of magnetic order. The Kondo anomalies in the physical properties of concentrated lanthanide systems are large and generally dominate over the ordinary lattice and conduction electron contributions. This minimizes the ambiguities often encountered in the study of Kondo phenomena in dilute impurity systems (particularly those which involve 3d transition metal impurity ions) where the variation of the normal state properties with temperature and magnetic field can only be obtained after the large background of the matrix has been subtracted.

Studies on concentrated lanthanide metallic systems have also made it possible to establish a correlation between nonintegral valence (observable in *concentrated* lanthanide systems through lattice constant, Mössbauer isomer shift, soft X-ray absorption and X-ray photoemission spectroscopy measurements) and *nonmagnetic* behavior of a lanthanide ion below the characteristic temperature. This has led to the concept of valence fluctuations (or inter-configuration fluctuations) which has stimulated the current intense activity among theorists and experimentalists alike.

SmS , Ce metal and CeAl_3 are three of the most thoroughly studied concentrated systems which exhibit Kondo-like anomalies. In analogy with the dilute $(\text{La, Th})\text{Ce}$ system, the magnetic state of the lanthanide ions in these concentrated materials has also been varied by applying external pressure or by alloying with other elements.

From this review, it is apparent that lanthanide metallic systems exhibit many varied and striking types of superconducting and normal state behavior in their physical properties, and that they provide a rich testing ground for concepts and models describing Kondo-like anomalies. We have made an effort to point out

that the field is still in the developing stage. A unified "first principles" theoretical description for the formation of a localized magnetic moment in a metal and the attendant Kondo-like anomalies in the physical properties has yet to emerge, despite the considerable amount of experimental data which have been accumulated and the intense theoretical effort which has been expended over the past decade. Thus our understanding of lanthanide systems which exhibit Kondo-like behavior is far from complete, and there is a large amount of room for future contributions from both theorists and experimentalists. Undoubtedly, new effects and types of behavior await to be discovered, studied and explained as our knowledge of this fascinating class of materials advances.

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There have been a number of developments in this subject since this article was concluded during the summer of 1976. Most of these developments were reported in the following conference proceedings:

- (1) Proc. Int. Conf. on Valence Instabilities and Related Narrow Band Phenomena, Rochester, New York, 1976, R.D. Parks, ed., (Plenum, New York, 1977).
- (2) Proc. Int. Conf. on Magnetism, Amsterdam, The Netherlands, 1976 (North-Holland, Amsterdam, 1977).
- (3) Proc. Twenty-Third Annual Conf. on Magnetism and Magnetic Materials, Minneapolis, Minnesota, 1977.