HIGH PRESSURE RESISTIVITY RESULTS ON MIXED VALENT SYSTEMS IN WHICH MAGNETIC ORDER IS IMPORTANT*

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Summary

We discuss high pressure resistivity results on mixed valent cerium and europium systems in which magnetic order plays an important role. In the CeMn$_2$Si$_2$-based systems the magnetic order is due to the manganese sublattice, and the cerium mixed valent/heavy fermion effects persist at least in the antiferromagnetically ordered phase of these systems. In the EuO system, the europium ferromagnetic order is dramatically enhanced precursive to a high pressure hybridization-gap–mixed-valent phase.

1. Introduction

The phenomenon of valence mixing in rare earths involves the quenching of the 4f local magnetic moment via interactions with the itinerant band states [1]. Naturally the disappearance of the magnetic moments in mixed valent (MV) materials typically leads to the collapse of magnetic order which the moments support. We are concerned here with two very disparate MV systems, which have in common the attribute that magnetic order remains important in their physics. The cerium-based systems discussed here involve the very broad 4f level width limit of the MV field and strong magnetic effects not arising from the cerium sites. On the other hand, the europium-based system (discussed in the latter part of this paper) involves the more typical narrow 4f width MV behavior and gleams its magnetic effects from the europium sites.

The current understanding of mixed valent/heavy fermion (MV/HF) behavior in cerium systems is based on Anderson model treatments in which the cerium 4f hybridization width dominates the physics [1 - 5]. In this parameter regime, spin fluctuations induce a demagnetization of the
Ce³⁺ 4f¹ orbital on an energy scale $T_{SF}$ (the spin fluctuation temperature). The plethora of effects and diversity of behaviors of cerium systems is, within this picture, related to the tremendous variation in $T_{SF}$, from below 1 K to above 1000 K [1-5]. Recent theoretical work has emphasized that up to a 30% admixture of the Ce⁴⁺ 4f⁰ state can occur in this Anderson model parameter regime, and that indeed increases in $T_{SF}$ are naturally accompanied by increases in the average cerium valence state [3, 5]. Hence, it is reasonable to include cerium systems under the general heading of mixed valence although their disparity from the small hybridization width valence mixing of other rare earths must be recognized.

We will be discussing below systems based upon CeMn₂Si₂ in which cerium MV/HF effects occur in the presence of strong internal magnetism of the manganese sublattice [5]. The novelty of such materials is in exploring the interplay of MV/HF non-magnetic effects with internal magnetism effects with a much higher energy scale. First, however, we will briefly describe the high pressure resistivity technique we employ and illustrate its application to a more conventional non-magnetic cerium MV/HF system.

2. High pressure resistivity measurements

The high pressure resistivity measurements discussed here were performed by a modified two-probe method in a diamond anvil press [6, 7]. The press is capable of generating quasi-hydrostatic pressures in the 40-250 kbar range employing (layers) of poly(vinylidene chloride) as a pressure-transmitting medium. Since the sample geometrical parameters in the cell cannot be measured, sample resistance variations are measured. Ruby fluorescence methods have been used to determine the pressure and pressure gradient in this type of cell. We have employed a fixed point (the bismuth I-II, bismuth III-IV and GaP metallization transitions) [6] calibration of pressure vs. load relation.

High pressure is one of the longest-established methods of increasing the Ce⁴⁺ 4f⁰ admixture and the spin fluctuation temperature of cerium systems [8-12]. High pressure resistivity measurements on a large number of cerium systems all follow a characteristic pattern illustrated here by our laboratories' results on CeCu₂Si₂ (see Fig. 1). It should be noted that our results on CeCu₂Si₂ compare quite favorably with the results obtained by other methods [10, 13].

CeCu₂Si₂ is of course one of the most famous Kondo regime cerium systems with $T_{SF} \approx 10$ K and an $L_3$ valence of about 3.08 [14, 15]. At ambient pressure the resistivity of CeCu₂Si₂ (broken curve in Fig. 1) exhibits a crystalline electric field (CEF) type Kondo behavior [16] along with a sharp drop in resistivity below 10 K as coherence is established between the Kondo sites [14]. The characteristic temperature for coherence between Kondo sites in a perfect lattice is in general somewhat less than $T_{SF}$ [17]. The rounded maximum due to the depopulation of excited CEF level and
3. CeMn$_2$Si$_2$

CeMn$_2$Si$_2$ exhibits most of the earmarks of a traditional MV cerium system [5, 19]: the L$_3$ valence state is 3.12 (at 300 K) and 3.16 (at 11 K); the linear coefficient of specific heat, $\gamma$, has the enhanced value of 47 mJ mol$^{-1}$ K$^{-1}$; the low temperature resistivity exhibits an $AT^2$ variation with the ratio $A/\gamma^2 = 6.6 \times 10^{-5}$ $\mu\Omega$ cm mol$^2$ K$^2$ mJ$^{-2}$; the resistivity above 100 K exhibits an incoherent Kondo type scattering of magnitude about 100 $\mu\Omega$ cm$^{-1}$; and finally stoichiometric disorder rapidly induces a cross-over to a single impurity Kondo type resistivity [5]. The resistance vs. pressure results for this system (Fig. 2, top) show a steady decrease with increasing pressure. This behavior is typical of an MV cerium system and
is analogous to the results on CeCu$_2$Si$_2$ for $P > 150$ kbar. The temperature dependence of the resistance (Fig. 2, bottom) changes dramatically under pressure in a way that is consistent with an MV cerium material. Namely, the incoherent-coherent scattering maximum moves rapidly from near 70 K at $P = 0$ to nearly 270 K at $P = 50$ kbar. This would be consistent with a several-fold increase in the spin fluctuation temperature [1].

Thus, ambient and high pressure measurements all indicate that CeMn$_2$Si$_2$ is an MV material. The novelty of this compound is the fact that the manganese sublattice orders in an antiferromagnetic (AF) arrangement at $T_N = 376$ K [5]. The cerium lattice sites are located symmetrically between antialigned planes of manganese moments [20] and hence are presumably at nodes in the internal field. This has been suggested as a possible cause of the indifference of the cerium MV effects to the magnetic order [5].

4. CeMn$_2$(Si,Ge)$_2$

CeMn$_2$Ge$_2$ has a higher lattice volume than its silicon isomorph and a cerium $L_3$ valence very close to pure Ce$^{3+}$ [15, 21]. It should therefore have an extremely low spin fluctuation temperature (1 K or below). The manganese lattice exhibits ferromagnetic (FM) order in this material with an ordering temperature ($T_\text{c}$) above 300 K. Thus, this (Si,Ge) alloy system offers the opportunity of studying the response of the cerium MV/HF effects where the cerium $T_{\text{SF}}$ becomes disproportionately small (with respect to the manganese-ordering temperature) and where a manganese AF to FM cross-over occurs.
Fig. 3. Temperature vs. concentration phase diagram of the CeMn$_2$(Si$_{1-x}$Ge$_x$)$_2$ system as determined by magnetic, cerium L$_3$-XAS and transport measurements [21]. The high pressure extension of the phase diagram for CeMn$_2$Si$_2$ and CeMn$_2$Ge$_2$ incorporates information from high pressure resistivity measurements. The straight lines connecting the $T$-$x$ ($P = 0$) and $T$-$P$ ($x = 1$) planes serve as schematic estimates of potential pressure scales of interest. The AF, FM and PM label manganese sublattice phases. The shaded region represents the manganese AF–FM cross-over region. The labels MV (mixed valent) and K (Kondo) indicate regimes (not distinct phases) of cerium behavior.

We have carried out extensive magnetic, transport and cerium L$_3$ valence state studies of the CeMn$_2$(Si$_{1-x}$Ge$_x$)$_2$ system [21]. Some of these results are summarized in the $T$-$x$ portion of the phase diagram of Fig. 3 along with the schematic high pressure extension of this phase diagram (to be discussed below). The FM and paramagnetic (PM) phases for the manganese sublattice are indicated as well as the AF to FM cross-over region (Siek et al. [20] have also established a similar manganese magnetic phase diagram).

The regions of the cerium behavior labeled MV and K (Kondo) correspond roughly to cerium $T_{SF}$ values above and below 100 K respectively. (Compare for example, the $x = 0.0$ and $x = 0.2$ curves in Fig. 4.) It should be noted that $T_{SF}$ values as low as 10 K appear to occur in the K range and that well-resolved CEF anomalies also appear in the resistivity in this $0.1 < x < 0.5$ range (such a CEF effect is apparent in the $x = 0.2$ curve in Fig. 4). Finally, we note that the manganese FM phase of these alloys does not appear to support any appreciable cerium valence mixing or Kondo type scattering in the resistivity (see the $x = 1.0$ curve in Fig. 4) [4, 21].
5. High pressure results on CeMn$_2$Ge$_2$

The resistance vs. pressure for CeMn$_2$Ge$_2$ for Fig. 5 is reminiscent of that for CeCu$_2$Si$_2$. The broad maximum characteristic of a cross-over from a lower pressure Kondo regime to a high pressure MV regime occurs somewhat below 100 kbar. The resistivity vs. temperature curves at various pressures (Fig. 5) confirm this interpretation. The 115 and 150 kbar results are typical of a high $T_{SF}$ MV cerium system. The 40 and 65 kbar results on the other hand exhibit Kondo type resistivities at low temperatures. The absence of a low temperature coherency related decrease in the resistance at these pressures is presumably related to strain fields in the sample owing to the quasi-static nature of the pressure.

We wish to note in particular the resistivity minima in the 40 and 65 kbar results. In our exhaustive studies of CeMn$_2$Si$_2$-based systems [5, 21, 22] we have always found that minima of this type coincide closely with the entrance into the manganese AF phase. (Such a minimum at $T_N$ is illustrated by the $x = 0.4$ sample in Fig. 4.) That is the presence of a Kondo type negative temperature coefficient of resistivity (TCR) arises only after the manganese moments have ordered antiferromagnetically. The loci of these minima therefore provide estimates of the manganese FM to AF transition under pressure and are represented as diamond-shaped points on the FM/AF phase boundary in Fig. 3. The 115 kbar resistance curve shows a negative TCR near room temperature, indicating that the entrance into the AF phase at this pressure is above room temperature. This last
observation is represented in Fig. 3 by an arrow pointing to higher temperatures at this pressure.

These high pressure resistivity results allow the construction of the schematic high pressure phase diagram in Fig. 3. The reader should note that the manganese FM phase (in which we see little or no evidence for cerium MV/HF behavior) can be driven into the manganese AF phase (in which cerium MV/HF effects flourish) by the application of moderate pressures. This opens the study of the magnetism and MV/HF cross-over in these systems to study by a wide range of thermal, magnetic and transport measurements using more hydrostatic pressure methods.

On a more general note, our work indicates that the manganese AF phase of the CeMn$_2$(Si,Ge)$_2$ system can support cerium MV/HF behavior typical of non-magnetic hosts. Indeed, cerium MV/HF effects would appear to persist with quite low (10 K or less) energy scales despite the much higher manganese AF ordering energy scale (more than 300 K). In the manganese FM or PM phases of these materials, on the other hand, the cerium MV/HF effects would appear to be substantially quenched. Interestingly, high magnetic field measurements in these systems might also allow the study of the separate magnetism and lattice volume influences on the cerium MV/HF behavior in these systems.

6. High pressure results on EuO

Valence mixing for europium compounds entails a quantum tunneling of a europium atom between the 4f$^7$,Eu$^{2+}$ magnetic ($J = 7/2$) state and the
$4f^6\text{Eu}^{2+}$ non-magnetic ($J=0$) state [1]. In contrast to cerium one has a very narrow 4f width for europium and a much narrower class of materials which clearly show an MV state with the $4f^7$ level at the Fermi energy ($\varepsilon_F$). At ambient pressure, EuO is a ferromagnetic semiconductor in which the $4f^7$ level lies at $E_g = 1.14$ eV below the bottom of the empty 5d band [23]. Pressure (volume reduction) reduces $E_g$ at the rate of 5 meV kbar$^{-1}$ [23] via the increase in the 5d band $t_{2g}-e_g$ crystal field splitting. Extrapolation of this rate would suggest that pressures of the order of 200 kbar could reduce $E_g$ to zero, perhaps inducing a semiconductor–MV transition reminiscent of SmS [24]. Early pressure–volume work by Jayaraman [25], using an ungasketed diamond cell technique, did provide evidence for such an isostructural volume collapse and optical property change near 300 kbar. Recently, Zimmer et al. [26] have reported the onset of a continuous volume collapse coupled with a large free carrier increase near 130 kbar. The gasketed diamond anvil technique for Zimmer et al. [26] presumably guaranteed superior pressure hydrostaticity. Theoretical calculations by Nolting [27] propose a pressure-induced hybridization-gap–MV state in EuO. Such a state would be analogous to SmB$_6$ [28] or the gold phase of SmS [29] (below 20 kbar) where $\varepsilon_F$ lies in the hybridization gap.

Our high pressure, low temperature resistance measurements address both the important 4f–5d band gap variation and the role of the europium ferromagnetic order in EuO [30, 31]. The samples used were chips of very nearly stoichiometric (less than 0.03 mol.% O vacancies) single crystals [30, 31]. In Fig. 6, we show the resistance ($R$) vs. pressure (at room temperature) for EuO. If we assume an activated behavior for this resistance and that the pressure dependence of the resistance is dominated by the pressure dependence of the gap, then $E_g(P) = 2k_B T \ln\{R(P)/R_0\}$. Here the normalization constant $R_0$, which depends on geometrical and effective mass factors, has been assumed to remain constant [30, 31]. Also assuming

![Fig. 6. Resistance $R$ as a function of pressure at room temperature. The broken line is from the optical measurements of Zimmer et al. and the dash-dotted line is from Nolting's calculations. The right-hand scale is the effective 4f–5d energy gap.](image-url)
that \( E_g(0) = 1.14 \) eV one can assign an \( E_g(P) \) scale to Fig. 6 (right-hand scale).

Within these assumptions, we note that the results in Fig. 6 are consistent: at low pressures with the pressure-induced reduction of \( E_g \) at the rate of 5 meV kbar\(^{-1} \) [30, 31] and with the results of Zimmer et al. [26]; and at high pressures with the hybridization gap prediction of Nolting [27]. Between these two regions we note a non-linear decrease in \( E_g \) near 140 kbar. This resistive non-linearity is in the same pressure range that Zimmer et al. [26] reported a transition based on optical and volumetric data.

The thermal dependence of the resistivity of EuO (at \( P = 1 \) atm) has a complicated structure which involves an activated high temperature behavior, a large peak at a temperature (\( T_p \)) above the ferromagnetic \( T_c \), and a subtle inflection point at \( T_1 \) [30, 31]. A number of mechanisms have been proposed for the resistivity peak at \( T_p \); however, for our purposes, it suffices to point out that this strong feature is believed to be related to the short-range magnetic order above \( T_c \) [30, 31]. Hence \( T_p \) should track (on the high \( T \) side) the pressure variation of \( T_c \). Referring to Fig. 7, we note that \( T_p \) moves rapidly up in temperature for increasing pressures below 120 kbar but thereafter stabilizes near 230 K. The more subtle inflection temperatures, \( T_1 \), (which should mark \( T_c \)) were also obtained using numerical derivatives of the data and are also indicated in Fig. 7 [30, 31]. Thus, the temperature-dependent resistance data indicate the threefold enhancement of the ferromagnetic \( T_c \) between 0 and 130 kbar followed by the stabilization of \( T_c \) near 200 K at pressures above 130 kbar. High pressure Mössbauer effect measurements reported by Taylor and Farrell [32] support such an enhancement of \( T_c \).

We summarize our resistivity results for EuO in Fig. 8 along with the ferromagnetic \( T_c \) results of McWhan et al. [33]. The locus of the room temperature non-linearity in \( R(P) \) and optical non-linearity of Zimmer et al. [26] is also included as a hashed region in the figure. Combination of

![Fig. 7](image-url)

Fig. 7. Resistance \( R \) as a function of temperature for various pressures. \( T_p \) is the peak temperature and \( T_1 \) is the inflection point temperature.
our results with previous work supports the following picture for EuO. At pressures below 130 kbar the pressure-induced reduction in $E_g$ (via the standard 5d $t_{2g}$-$e_g$ splitting increase) dominates the behavior. In this region, the ferromagnetic $T_c$ is rapidly enhanced as $E_g$ decreases. Both the $T_p$ and $T_1$ variations reflect the $T_c$ increase under pressure and their correlation with the lower pressure results of McWhan et al. [33] is good. In the 120 - 140 kbar range, a non-linear closing of the gap occurs. At pressures above 150 kbar, one is in a phase where a small, pressure-insensitive hybridization gap has been stabilized. When $E_g$ saturates in this high pressure phase the ferromagnetic $T_c$ also stabilizes.

Implicit in the interpretation of the high pressure hybridization gap phase is the idea that some level of europium valence mixing is involved (as in the SmS gold phase [29] and SmB$_6$ [28] analogies). The high pressure volumetric data of Zimmer et al. [26] and the Mössbauer effect data of Farrell and Taylor [32] also support the high pressure increase of the europium valence state in EuO. Thus, the co-existence of magnetic order with a europium MV state appears to occur in EuO. This same effect also appears to occur in metallic europium compounds where the europium valence varies in the 2.0 - 2.3 range [34 - 39]. Specifically, the Eu(Pd, Au)$_2$Si$_2$ [34 - 36] system at ambient (and elevated) pressures, and elemental europium [37 - 39] all evidence such a co-existence. Indeed, as underscored by the low pressure EuO results, pressure- or alloy-induced increases in the europium valence initially appear to enhance strongly the magnetic ordering temperature in europium systems [30, 31, 34]. This initial enhancement of magnetic order as the 4f$^7$ level moves toward $\epsilon_F$ is followed eventually by the collapse of magnetic order when the magnetic 4f$^7$ level depopulates (i.e. moves above $\epsilon_F$). High pressure studies of the details of this magnetism enhancement followed by collapse are clearly of great interest.

Fig. 8. The loci in the T-P plane of the $T_1$ and $T_p$ points. The lower pressure $T_c$ values are from the work of McWhan et al. The room temperature non-linearity in resistivity and carrier concentration is also indicated.
Unfortunately, in EuO still higher pressures appear to be necessary to induce the metallic strongly mixed valent europium state where magnetism has given up the ghost.

References

38 J. N. Farrell and R. D. Taylor, to be published.