CONF-791142--5

Presented at the International Conference on Crystalline Electric Field and Structural Effects in f-Electron Systems, Philadelphia, 1979.

MASTER**ENERGY PARAMETERS AND CRYSTAL FIELD EFFECTS IN THE MIXED VALENCE****PROBLEM: CHEMICALLY COLLAPSED CERIUM****R. D. Parks***

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Previous neutron scattering studies of the mixed valence state in rare earth systems [e.g., CePd_3 (Ref. 1) and $\text{Ce}_{0.74}\text{Th}_{0.26}$ (Ref. 2)] failed to reveal the presence of crystal electric field (CEF) effects. In the cases studied the characteristic charge fluctuation energies were comparable to the expected CEF energies. The motivation for the present study was to design and study a system in which it is possible to systematically vary the charge fluctuation energy E_c from the regime $E_c \sim \Delta$ to $E_c \ll \Delta$, where Δ is the characteristic CEF energy.

A system which, from the work of Ref. 3, appeared ideal for this study is $\text{Ce}_{0.9-x}\text{La}_x\text{Th}_{0.1}$, in which the valence transition temperature is rapidly depressed by the addition of La through the combined effects of the valence and atomic size of the La additive. The Th additive is present for the purpose of stabilizing the fcc phase. For the present study the phase diagram (Fig. 1) was extended to higher La concentrations than reported in Ref. 3. The

* Work supported in part by NSF and ONR.

**Work supported by Div. Basic Energy Sciences, DOE, under Contract No. EY-76-C-02-0016.

Fig. 1. Valence transition temperature T_0 versus La concentration in $\text{Ce}_{0.9-x}\text{La}_x\text{Th}_{0.1}$. Solid line: first order transitions; dashed line: continuous transitions.

phase diagram is characterized by a line of first order phase transitions which terminate in a critical point at $x = 0.094$. Beyond the critical point (up to $x = 0.2$), it is possible to define the midpoints of the continuous transitions, labelled T_0 , by measuring the inflection points in the magnetic susceptibility (see, e.g., Fig. 2). For the first order transitions, T_0 is defined as the midpoint of the hysteresis. In Fig. 2 the dashed curves represent the measured susceptibilities and the solid curves the corrected susceptibilities after an impurity contribution $\chi_{\text{imp}} = T^{-1}$ is subtracted. This impurity tail can be explained by assuming that some fraction of the Ce atoms (always less than 1% of the total), located, e.g., in grain boundaries or other strained regions, remain trivalent in the mixed valence phase ($T \ll T_0$).

A dramatic result of the present study is the strict correspondence between the Fermi liquid susceptibility $\chi(0)$ and T_0^{-1} , seen in Fig. 3, even up to $x = 0.20$ where T_0 ceases to depend linearly on x . In this figure are shown the results of the present study together with the result for pure fcc Cerium.⁵ Explicitly, the observed relationship between x and T_0 is given by

Fig. 2. Temperature dependence of static magnetic susceptibility for $\text{Ce}_{0.9-x}\text{La}_x\text{Th}_{0.1}$ of three compositions. Dashed line: measured susceptibility; solid line: corrected susceptibility after subtraction of impurity contribution.

$$\chi(0) = \frac{515 \times 10^{-6} (\text{emu-deg}) / (\text{gm-Ce})}{T_0} = \frac{C}{11.2 T_0} \quad (1)$$

where C is the Curie constant for non-interacting Ce atoms. It is interesting to compare this result with the result $\chi(0) \approx C/2T_{\text{SF}}$ for a large class of Ce- and Yb-based compounds which exhibit non-magnetic ground states, but for which spin fluctuations appear to dominate charge fluctuations, and mixed valence effects are absent: T_{SF} is the spin fluctuation temperature (see, e.g., Ref. 4 and the references cited therein).

For the purpose of the intended neutron scattering study, the $\text{Ce}_{0.9-x}\text{La}_x\text{Th}_{0.1}$ system is ideally suited, since as seen in Figs. 2 and 3 it is possible to vary the energy parameter $k_B T_0$, which we identify as the charge fluctuation energy E_C , by over a factor of ten. Inelastic neutron scattering measurements were made on the two samples with the smallest values of T_0 , viz., $x = 0.14$, $T_0 = 24\text{K}$ and $x = 0.20$, $T_0 = 12\text{K}$. The experiments were carried out on a triple-axis spectrometer at the Brookhaven High-Flux Beam Reactor,

Fig. 3. Asymptotic susceptibility in $T = 0$ limit as function of valence transition temperature T_0 . Circles: $\text{Ce}_{0.9-x}\text{La}_x\text{Th}_{0.1}$; Triangle: pure fcc Cerium (from Ref. 5).

operated in the constant-Q mode with a fixed analyzer energy and varying incident energy. The inelastic neutron spectra for the $x = 0.14$ sample are shown in Fig. 4. The data have been corrected for the phonon contribution by subtracting the inelastic neutron spectrum from an almost identical size ($\sim 15\text{g}$) sample of $\text{La}_{0.9}\text{Th}_{0.1}$, which is non-magnetic but expected to have similar phonon properties to the Ce-based samples. The latter spectrum exhibits a broad peak at about 8 meV and its intensity at all measured frequencies is smaller than the magnetic scattering.

In fcc Cerium the $J = 5/2$ ground state multiplet is split by the cubic CEF into a Γ_7 doublet ground state and Γ_8 quartet. Hence, when interpreting the inelastic neutron spectra, it is necessary to consider quasielastic scattering from each of the two levels and inelastic scattering between them. The starting point for the generation of a fitting equation for the neutron spectra is the general formula⁶ for the magnetic neutron-scattering cross-section

$$\frac{d^2\sigma}{d\Omega d\omega} = \text{const} (1 - e^{-\beta\hbar\omega})^{-1} \chi''(q, \omega, T) \quad (2)$$

Fig. 4. Inelastic neutron spectra of $\text{Ce}_{0.76}\text{La}_{0.14}\text{Th}_{0.1}$ taken at $q = 1.5 \text{ \AA}^{-1}$. Background and phonon contributions have been subtracted (see text). Solid lines: least squares fit of Eq. (5); dashed lines: quasielastic (EL) and inelastic (INEL) contributions.

where the constant term includes instrumental and other factors of no concern in the present study, the second term is required for detailed balance and $\chi''(q, \omega, T)$ is the dynamical susceptibility. If the moments are localized and mutually independent, $\chi''(q, \omega, T)$ may be factored into a frequency (and temperature)-dependent part and a local form factor $F(q)$

$$\chi''(q, \omega, T) = \chi''(0, \omega, T) |F(q)|^2. \quad (3)$$

In the case of a single level system, if the spin dynamics are characterized by a single relaxation channel, then, in accordance with the Kramers-Kronig relation

$$\chi''(0, \omega, T) = M \frac{\hbar\omega}{kT} \frac{\gamma}{(\hbar\omega)^2 + \gamma^2} \quad (4)$$

where M is the scattering amplitude and γ the energy width at half maximum of the Lorentzian function (hereafter called the linewidth). This relaxation Ansatz, which is commonly used, is pathological in the high frequency limit, since the presence of the Lorentzian function leads to a divergence in the integrated scattering cross-section. However, this difficulty is conveniently skirted by introducing a high frequency cut-off outside the region of experimental interest.

In the case of two levels split by a CEF energy Δ , it is a simple matter to generalize Eq. (4), by taking into account the temperature dependent populations of the two levels and the scattering amplitudes both for quasielectric scattering from the individual levels and inelastic scattering between the levels. The inelastic scattering would be manifested as two Lorentzians centered at $\omega = \pm\Delta$. However, this procedure has validity only if $\gamma \ll \Delta$, when there is negligible overlap between the quasielastic peak(s) [Eq. (4)] and the inelastic peak. When there is appreciable overlap, viz., $\gamma \sim \Delta$, a proper treatment necessarily entails the inversion of the complete dynamical matrix.⁷ Moreover, in Anderson lattice systems, of which the system under study is an example, when the spin fluctuation, charge fluctuation and CEF spin fluctuation lifetimes are comparable, all three must be treated on an equal footing. This, of course, is tantamount to completely solving the Anderson lattice problem.

As evident in Fig. 4, $\Delta \sim \gamma$; thus, in view of the aforementioned difficulties in formulating $\chi''(0, \omega, T)$ for that regime, we are forced into using a rather generalized fitting formula, namely,

$$\chi''(0, \omega, T) = \frac{\hbar\omega}{kT} \left\{ A(T) \frac{\gamma}{(\hbar\omega)^2 + \gamma^2} + B(T) \left[\frac{\gamma}{(\hbar\omega - \Delta)^2 + \gamma^2} + \frac{\gamma}{(\hbar\omega + \Delta)^2 + \gamma^2} \right] \right\} \quad (5)$$

An attraction of Eq. (5) is that quantities such as the population factors and scattering amplitudes of individual levels are not specified, nor should they be for the case $\gamma \sim \Delta$, where the hybridization effects between the two levels (Γ_7 and Γ_8 for the system under study) cannot be treated perturbatively. As seen in Fig. 4, this fitting formula works well at all temperatures. The term EL (for quasi-Elastic) and the term INEL (for INELastic) refer to the first and second terms of Eq. (5) respectively. The values for $\gamma(T)$ and $\Delta(T)$ corresponding to the fits shown in Fig. 4 are given in Table 1 and plotted in Fig. 5. Shown also in Table 1 are the

Table 1. Linewidths (γ) and CEF Energies (Δ)

T(K)	$\text{Ce}_{0.76}\text{La}_{0.14}\text{Th}_{0.10}$		$\text{Ce}_{0.70}\text{La}_{0.20}\text{Th}_{0.10}$	
	$\gamma(\text{meV})$	$\Delta(\text{meV})$	$\gamma(\text{meV})$	$\Delta(\text{meV})$
4.5	—	—	7.1 ± 0.4	15.5 ± 0.4
5.5	11.7 ± 1.8	20.9 ± 0.9	—	—
20	10.1 ± 1.3	17.2 ± 1.1	—	—
27.5	8.9 ± 0.6	15.0 ± 0.7	—	—
35	8.2 ± 0.4	14.2 ± 0.5	—	—
50	7.5 ± 0.4	14.0 ± 0.5	5.5 ± 0.2	13.6 ± 0.2
110	7.6 ± 0.4	14.4 ± 0.4	—	—

Fig. 5. Linewidth and CEF energy versus temperature from data in Table 1.

preliminary results obtained at only two temperatures for an $x = 0.20$ sample. A consistency check on the above procedure is obtained by calculating the static susceptibility via the Kramers-Kronig relation

$$\chi'(0,0,T) = \int_{-\infty}^{\infty} \frac{\chi''(0,\omega,T)}{\omega} d\omega \quad (6)$$

Using Eq. (5) for $\chi''(0,\omega,T)$ yields.

$$\chi'(0,0,T) = \frac{\pi}{kT} [A(T) + 2B(T)] \quad (7)$$

In Fig. 6, $\chi'(0,0,T)$ from Eq. (7), using for $A(T)$ and $B(T)$ the fits in Fig. 4, is compared with the static susceptibility measured on a Faraday balance. The two curves have been shifted into alignment by multiplying one of them by an arbitrary constant, since no attempt was made to obtain a quantitative calibration of $d^2\sigma/d\Omega d\omega$. The goodness of the fit in Eq. (7) is not only an overall measure of the goodness of the fits in Fig. 4; it also implies that the form of Eq. (5) is a reasonable approximation.

A determination of the valence $N \equiv 4 - \langle n_{4f} \rangle$, where $\langle n_{4f} \rangle$ is the average occupancy of the 4f level, can be made for the $x = 0.14$ sample from lattice constant measurements (Fig. 7) obtained from the neutron scattering study. Note that the inflection point in the curve coincides approximately with the value $T_0 = 24K$ determined from the magnetic susceptibility studies (see Fig. 3). Using Vegard's law,⁸ it is possible to estimate from the alloy data the lattice constants for an equivalent pure Ce sample: this gives

Fig. 6. Solid curve: static susceptibility measured with Faraday balance; data points: static susceptibility calculated by Eq. (7).

$a_{\text{Ce}}(293\text{K}) = 5.160 \text{ \AA}$ and $a_{\text{Ce}}(5\text{K}) = 5.080 \text{ \AA}$. Using the frequently used, but untested, hypothesis that the valence linearly tracks the lattice constant, we can arrive at the valence by interpolating between the values for trivalent and hypothetical tetravalent Ce: $a_{\text{Ce}+3}(293\text{K}) = 5.221 \text{ \AA}$ and $a_{\text{Ce}+4}(293\text{K}) = 4.661 \text{ \AA}$.² This yields $N(293\text{K}) = 3.11$ and $N(5\text{K}) = 3.25$. Correcting for the effects of ordinary thermal expansion, assuming that Ce in the absence of Anderson lattice effects would mimic the behavior of metals with similar melting points, gives for the ground state valence $N_{\text{Cor}}(5\text{K}) = 3.20 \pm 0.02$. It is of interest to compare this value with that of systems with $x \leq 0.09$ which exhibit either second or first order transitions with concomitant large changes in the lattice constant. In the latter case $N \geq 3.6$ in the ground state.^{2,3}

In conclusion, we present hypotheses for the physical origin of the observed linewidths and the temperature dependence of the linewidth and CEF energy. If, as discussed above, we identify kT_0 as the charge fluctuation energy E_c , then, clearly, this energy is too small to explain the observed linewidths: e.g., for $x = 0.14$, $T_0 = 24\text{K}$, $E_c = 2.1 \text{ meV}$; for $x = 0.20$, $T_0 = 12\text{K}$, $E_c = 1.0 \text{ meV}$. Thus, we are led into the assumption that the lines are broadened by spin fluctuations (Kondo-like). As inferred in the previous discussion generated by the results in Fig. 3, it is tempting to write, in the $T \rightarrow 0$ limit, $T_{\text{SF}} \sim 5.6 T_0$. Hence, we would predict a line broadening of 11.6 meV for the $x = 0.14$ sample and 5.8 meV for the $x = 0.20$ sample. The observed linewidths in the low temperature limit are 11.7 meV and 7.1 meV for the two samples respectively-- remarkably close to the predicted spin fluctuation energy. The increase in γ with decreasing temperature (Fig. 5), which mimics the shape of the volume contraction (Fig. 7), reflects presumably the increase in T_{SF} with decreasing lattice constant, which is commonly observed in both dilute and concentrated rare earth systems which exhibit Kondo-like behavior.

Fig. 7. Lattice constant versus temperature for $\text{Ce}_{0.76}\text{La}_{0.14}\text{Th}_{0.10}$ measured by neutron diffraction.

The measurement of the crystal field energy reported herein is probably the first such measurement for fcc Cerium. For pure fcc Cerium (also, for $\text{Ce}_{0.74}\text{Th}_{0.76}$), the crystal field peaks, if they exist, are too broad to be seen.² Within the spirit of the above discussion this is expected because of the larger interaction parameters implied by the large values of T_0 , and hence T_{SF} , for the latter systems. The importance of local environment effects (due to the presence of Th and La) in the present study, in either altering Δ or broadening the excited level, remains an open question. The fact that the temperature dependence of Δ approximately tracks that of γ is also unexplained; however, a possible tenant is that charge fluctuations, because they produce local electric multipole fields, can increase the CEF. This is particularly easy to visualize for the case where the charge fluctuations are slower than the CEF spin fluctuations.

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