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Diffuse-Neutron-Scattering Measurements of the Fractional Occupancy of the Localized $4f^1$ Configuration in Ce-Th and $CeAl_3$ †*

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Diffuse-neutron-scattering measurements at $2 < T < 300$ K have been employed to determine the fractional occupancy η of the localized $4f^1$ configuration. For $CeAl_3$, $\eta = 0.9$–1.0 at 11 K. For $Ce_{0.8}Th_{0.2}$, $\eta = 0.4 \pm 0.1$ at 11 K. No evidence of a compensating conduction-electron polatization was observed.

The collapsed phase of some systems, e.g., SmS under pressure, $Sm_{1-x}M_xS$ (M = Gd, Y, La), and $SmAs_xS_{1-x}$, are believed to be configuration-fluctuation (CF) systems. These are systems which exist an appreciable fraction of time in more than one electronic configuration; e.g., in SmS under pressure, both the $4f^5$ and $4f^6$ configurations are occupied. X-ray photoemission measurements[1] have determined the fractional occupancy of these two configurations in anion-substituted SmS. Inelastic-neutron-scattering measurements[2] have established an upper bound of 10% on the amount of valence mixing in the black phase of SmS. It has been suggested that $CeAl_3$, α-Ce, and the α phase of CeTh alloys may be CF systems. Here we present evidence based upon diffuse-neutron-scattering measurements which show that the α phase of $Ce_{1-x}Th_x$ alloys ($x = 0.2$, 0.266, 0.29) and possibly $CeAl_3$ are CF systems. No evidence of a compensating conduction-electron polarization was observed in either system.

The square of the effective moment $\mu_{\text{eff}}^2 = 3kT\chi/A$ of Ce can be reduced by (1) crystal fields, (2) a small value for the spin correlation time τ, (3) a compensating conduction-electron polarization, and (4) a small value for the fractional occupancy of the localized $4f^1$ configuration, η. Using the fluctuation-dissipation theorem and the Kramers-Kronig relations, one can show that susceptibility measurements average $\langle J(0)\, J(t)\rangle$ over a time proportional to T^{-1}. The susceptibility at low temperatures is determined by both η and τ. In contrast, diffuse-neutron-scattering measurements with sufficiently energetic neutrons determine η and are insensitive to τ provided that τ is large compared to the neutron measuring time which is the transit time 10^{-12}–10^{-13} sec. Neutron-scattering measurements also provide information about the spatial distribution of the moment. Such measurements on dilute *Cu*Fe [3] and *Al*Mn [4,5] have provided evidence for a spin-compensating conduction-electron polarization. NMR[6,7] measurements on *Cu*Fe samples more dilute than those used in the neutron studies indicate that if such a compensating polarization exists it does not extend out as far as the first nearest Cu neighbor. Mössbauer-effect measurements[8] of the local susceptibility do not provide any evidence of a large compensating polarization. Gurgenishvili, Neresyan, and Kharadze[9] predict a negative conduction-electron polarization localized around dilute Kondo impurities. Recent renormalization-group theory has not yet been applied to this question. Boyce and Slichter[6] discuss this matter further. Since our systems are not dilute it is not clear that these theories are applicable.

The α-γ phase transformation in Ce under pressure and in Ce-Th alloys[10] is analogous to a liquid-gas transformation in that a phase change occurs without a change in the symmetry of the system and there is a line of first-order phase transitions ending in a second-order transition. Both the α and γ phases are fcc but the lattice parameter is smaller in the α phase. Below a critical concentration $x_c = 0.265$ of Th in $Ce_{1-x}Th_x$ at zero pressure, these systems undergo a first-order phase transition with decreasing temperature from the γ to the α state. Lawrence, Croft, and Parks[11] have inferred that the forces involved in the transformation are very long range, since measurements show that the critical exponent for the density δ is 3.0 ± 0.2.

Samples used in the present study were initially arc melted. The $CeAl_2$ samples were annealed for two weeks at 100°C and then powdered. Some of the Ce-Th alloys were filed into a powder and then annealed for one day at 500°C. Others were prepared in the form of slabs. The structure of the alloys was determined by x-ray and neutron measurements to be fcc while $CeAl_3$ was a hexagonal DO_{19} structure. Two double-axis spectrometers, one with $\lambda = 1.005$ Å and the other with $\lambda = 4.4$ Å, at the Oak Ridge reactor were employed. At a fixed scattering angle 2θ we detected neutrons at all allowed energies; i.e.,

$$d\sigma/d\Omega = \int_{-\infty}^{\omega_0} (d^2\sigma/d\Omega d\omega) d\omega, \qquad (1)$$

where $d^2\sigma/d\Omega d\omega$ is the diffuse cross section per unit solid angle $d\Omega$ and per energy lost by the neutron, and $\hbar\omega_0$ is the energy of the incident neutron. Though the momentum transfer $\hbar \mathbf{Q}$ is not precisely determined, for $|\omega/\omega_0| < 0.2$ and $\theta < 20°$, Q is still approximately given by the elastic result $Q = 4\pi \sin\theta/\lambda$. In order to interpret our data we employ asymptotic results for $d\sigma/d\Omega$ in the limit that $\hbar\omega_0 >> |E_\lambda - E_{\lambda'}|$ for all eigenstates E_λ and $E_{\lambda'}$ in the ground-state J manifold. In this limit and for $n = 1$, Gurgenishvili, Neresyan, and Kharadze[9] have included the conduction-electron polarization in their calculation of $d\sigma/d\Omega$. We shall consider the same limit for general η but for $\mathbf{Q}$ sufficiently large that we can neglect conduction-electron effects. With the above conditions and for a polycrystalline sample containing uncorrelated spins in zero magnetic field one can derive

$$d\sigma/d\Omega = \tfrac{2}{3} p_0{}^2 g^2 J(J+1) F^2(Q)\eta, \qquad (2)$$

where η is the fractional occupancy of the localized $4f^1$ configuration, $p_0 = \gamma e^2/2m_e c^2$, and F is the magnetic form factor. Equation (2) determines η as the ratio of the observed paramagnetic diffuse cross section to $\tfrac{2}{3} p_0{}^2 g^2 J(J+1)F^2$ provided that F is independent of η.

We determine η for $CeAl_3$ and Ce-Th using this result.

(1) $CeAl_3$.—Values of $d\sigma/d\Omega$ per Ce atom for $\lambda = 1$ and 4.4 Å as a function of temperature are plotted in Fig. 1. These values have not been

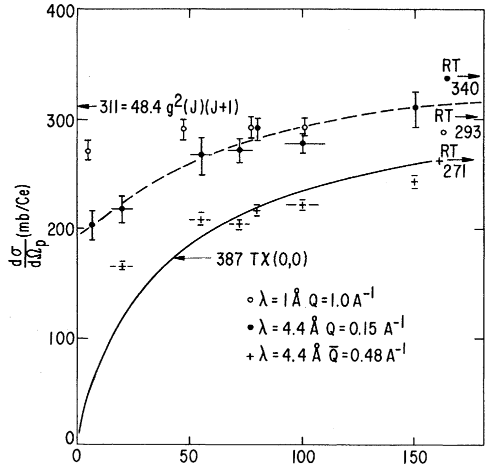

FIG. 1. Paramagnetic diffuse cross section $d\sigma/d\Omega_p$ in millibarns per Ce atom per steradian for $CeAl_3$ versus T. The data denoted by + represent an average for $0.25\ Å^{-1} \leq Q \leq 0.7\ Å^{-1}$. Room-temperature values are denoted by RT.

corrected for nuclear disorder of thermal diffuse scattering. The nuclear disorder scattering is very small since CeAl$_3$ is a well-ordered compound and the diffuse scattering from Ce and Al is less than 10 mb. At these Q values the thermal diffuse contribution is less than 10 mb. Also shown in Fig. 1 is the elastic result $d\sigma/d\Omega_{el} = 387T\chi \propto \mu_{eff}^2$, in millibarns, for χ measured on the same sample.[12] The previous diffraction[13] results for F based upon scattering off the 201 planes ($Q = 2.60$ Å^{-1}) show a 30% decrease between 81 and 5 K and at 5 K are in approximate agreement with the Ce^{3+} atomic form factor.[14]

For $\lambda = 1$ Å, $d\sigma/d\Omega$ is approximately equal to the value 311 mb predicted by Eq. (5) for $F = 1$, $J = \frac{5}{2}$, $g = \frac{6}{7}$, and $\eta = 1$. This is possible since $\hbar\omega_0$ is probably larger than nearly all energies within the $J = \frac{5}{2}$ manifold. If F is assumed to be temperature independent for $Q < 1$ Å^{-1}, then the decrease in $d\sigma/d\Omega$ observed at 11 K implies that η has only decreased to about 0.9 and hence cannot cause a large decrease in μ_{eff}^2. From our measurements we conclude that any negative conduction-electron polarization contribution to F greater than approximately 20% must be confined to distances greater than 5 Å or it would have been observed as a decrease in the cross section at small Q. Since there is no evidence of a large compensating conduction-electron polarization and since μ_{eff}^2 decreases more than one would expect from crystal-field effects alone if the ground state[15] is $J_z = \pm\frac{3}{2}$, μ_{eff}^2 must also be reduced by the value of τ.

(2) Ce$_{0.8}$Th$_{0.2}$.—The susceptibility above the transition can be fitted with $\chi = A(2.66 \pm 0.2\mu_B)^2/3k(T+132)$. Since this μ is approximately equal to $2.54\mu_B$, the value predicted by Hund's rules, one can infer $\eta = 1.0$ at high temperatures. The θ value is probably primarily due to a small value for $\tau \propto \theta^{-1}$ since θ is larger than one would expect from magnetic interactions in this system or from the crystal-field splitting.[16]

The nuclear disorder cross section is equal to 46.6 mb under the reasonable assumption for this system that there is no chemical short-range order. If $\hbar\omega_0$ is great enough to excite all multiphonon processes, the thermal diffuse cross section $d\sigma/d\Omega_T$ is given by $\bar{b}^2(1 - e^{-2W})$ where $\bar{b}$ is the average scattering amplitude and e^{-2W} is the Debye-Waller factor which we determine from measuring the intensities of Bragg peaks. Subtracting the nuclear disorder and $d\sigma/d\Omega_T$ from the total cross section, we obtain the values of the paramagnetic cross section $d\sigma/d\Omega_p$ for $x = 0.2$ plotted versus Q in Fig. 2(a). The values of $d\sigma/d\Omega_p$ in Fig. 2(b) have not been corrected for $d\sigma/d\Omega_T$ which is less than 10 mb at these Q values. The values of $d\sigma/d\Omega_T$ are sufficiently large ($\simeq 100$ mb) for $Q \geq 3$Å^{-1} at 293°K that their subtraction decreases the precision of our measurements at high Q but they have negligible effect on our determination of η at small Q. The data in Fig. 2(a) are consistent with an atomic Ce^{3+} form factor. From the data of Fig. 2(b) one can infer that any negative conduction-electron polarization must be confined to distances greater than 5 Å. If there were a conduction-electron cloud whose spatial extent was similar to a 6s electron, one would observe a decrease at small Q.

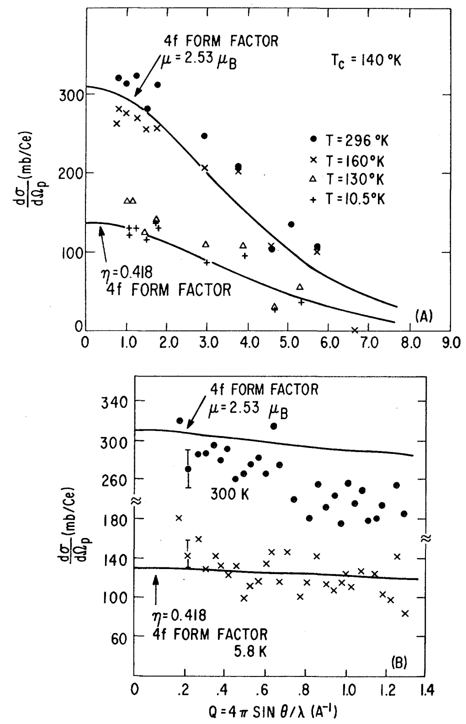

FIG. 2. Paramagnetic diffuse cross section $d\sigma/d\Omega_p$ in millibarns per Ce atom per steradian for Ce$_{0.8}$Th$_{0.2}$ at several temperatures versus Q for (a) $\lambda = 1.0$ Å, and (b) $\lambda = 4.4$ Å.

The temperature dependence of $d\sigma/d\Omega_p$ shown in Fig. 3. The points at 1 Å are extrapolations to $Q = 0$. The points at 4.4 Å are averages of $d\sigma/d\Omega_p$ from 0.25 Å^{-1} $\leq Q \leq 0.7$ Å^{-1}. From the 1-Å data, one sees that $\eta \simeq 1$ at room temperature. The fractional occupancy η decreases 10% above the transition, decreases 40% at the transition, and decreases another 10% below the transition. Approximately 0.4 of a localized 4f electron remains at 11 K. We have obtained qualitatively

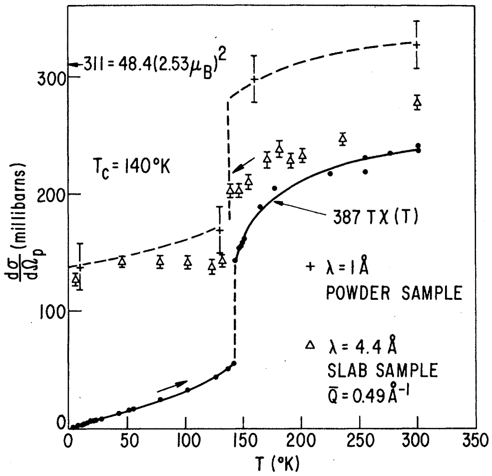

FIG. 3. Paramagnetic diffuse cross section $d\sigma/d\Omega_p$ in millibarns per Ce atom per steradian for $Ce_{0.8}Th_{0.2}$ versus T.

similar data for $x = 0.266$ and 0.29. Since there is no evidence of a large conduction-electron compensating polarization, the small value of μ_{eff}^2 at 11 K is due to the small value of η, a small value of τ, and possibly crystal-field effects.

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Observation of Two-Dimensional Phases Associated with Defect States on the Surface of TiO_2 †

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Surface electronic states associated with defects produced by Ar-ion bombardment of TiO_2 crystals have been studied by ultraviolet-photoemission, electron-energy-loss, and Auger spectroscopy and low-energy-electron diffraction. Evidence is given for three distinct phases dependent upon the extrinsic surface-defect concentration. Phase I contains isolated surface states 0.7 eV below the conduction band, phase II is associated with the creation of Ti^{3+} pairs, and phase III consists of a surface layer of ordered Ti_2O_3.

The importance of transition-metal oxides in a wide range of catalytic and electrocatalytic applications has spurred a great deal of research on their surface properties and on the role of surface defects in their catalytic activity. For example, surface states on TiO_2 have recently been shown to play a central role in the TiO_2-catalyzed photoelectrolysis of water.[1] Previous