Evidence for localized $4f$ states in α-Ce

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(Received 15 July 1993)

Paramagnetic spectra of γ and α-Ce measured at the *same temperature* using high-energy neutrons ($\sim$2 eV) yield a $4f$ occupancy of $\sim$0.8 in α-Ce. This phase of Ce also shows single-ion magnetic response but with a high Kondo energy of $\sim$1800 K. In γ-Ce we observe the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ spin-orbit (SO) excitation at $\sim$260 meV. Remarkably, α-Ce also reveals a broad SO excitation shifted to a higher energy ($\sim$450 meV). These observations reinforce the idea of *localized* $4f$ states in α-Ce and k-f hybridization as the driving mechanism for the $\gamma \leftrightarrow \alpha$ transition.

The $\gamma \rightarrow \alpha$ phase transition in cerium metal has been the subject of a large number of investigations. Fcc γ-Ce stable at room temperature shows the normal Curie-Weiss magnetic susceptibility. On application of pressure ($\gtrsim$6 kbar) or on cooling (below 110 K), it undergoes an abrupt $\sim$14% volume change maintaining the same fcc structure (α-Ce).[1] The phase transition is accompanied by a marked drop in the magnetic susceptibility which shows enhanced Pauli paramagnetism.[2,3]

The first theories of the transition associated it with transfer of the localized $4f$ electron to the conduction bands. Certain experiments,[4] however, showed that the valence did not alter significantly at the transition, and triggered new ideas based on the Mott transition model (localized f electron in γ-Ce$\rightarrow$ delocalized f band in α-Ce).[5] Other theories, based on the Kondo-lattice[6] and Anderson impurity models[7] have put forward the idea of the Kondo volume collapse due to increased Kondo energy, or k-f hybridization, in the α phase.

We report results of a neutron inelastic-scattering study of the temperature-induced $\gamma \leftrightarrow \alpha$ phase transition in Ce, which we believe could aid our choice of the most appropriate model to describe the phase transition. We have performed measurements on Ce alloyed with 7 at. % Sc to stabilize the fcc phase against ($d$hcp) β-Ce formation. Gschneidner, Elliott, and McDonald[1] have reported that addition of about 7 at. % Sc suppresses the formation of β-Ce almost completely ($<1\%$), and (unlike Th or other additives) additions of up to 10 at. % Sc has negligible effect on the volume change $\Delta V/V$ at the transition compared with pure Ce.[1]

Previous neutron-scattering work on Ce includes the measurements in the thermal energy range by Rainford, Buras, and Lebech,[8] induced magnetic form-factor measurements on single-crystal Ce 26 at. % Th by Moon and Koehler[9] and a neutron inelastic-scattering study by Loong *et al.*[10] on a polycrystalline alloy of the same nominal composition. Polarized neutron inelastic-scattering measurements on α-Ce performed by Fillion *et al.*[11] show a marked increase in the cross section around $\sim$200 meV, consistent with the present results, but in (resolvable) *disagreement* with the observed maximum at 138$\pm$6 meV by Loong *et al.*[10] for their alloy containing 26 at. % Th, a relatively high concentration where the character of the transition changes from a first-order to a second-order type.[12]

We begin with the data for $S(Q,\omega)$ obtained using neutrons of the highest optimal incident energy (2100 meV) currently practicable on a time-of-flight spectrometer. The $\gamma \rightarrow \alpha$ transition occurs at $\sim$110 K on cooling and the reverse transition at $\sim$170 K on warming.[1,2] We therefore chose to work at 125 K, first performing measurements in the γ phase then cooling the sample to 20 K (α phase), and finally warming up again to 125 K (α phase) where measurements were repeated under identical conditions. A one to one subtraction between the two eliminates all nonmagnetic contributions due to phonons, multiphonons as well as traces of hydrogen. The resultant difference signal measured with two different resolutions is shown in Fig. 1 where the positive intensity structure is predominantly the γ-phase response, while the extended "negative intensity" tail is mainly the α-phase signal. In the diagram the continuous curve represents the higher statistical accuracy (poorer resolution) data corrected for the Ce^{3+} form-factor variation (see below).

For a *normal, well behaved* isotropic paramagnet

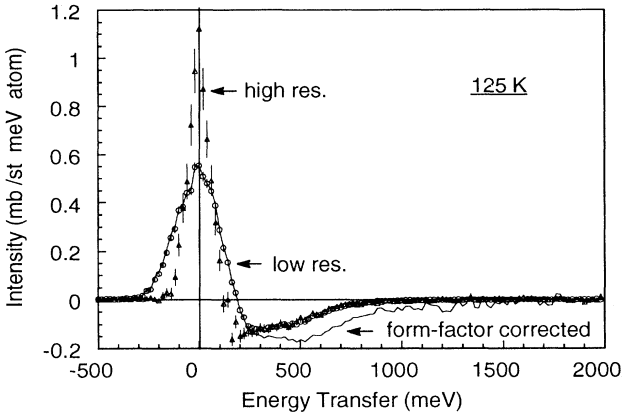

FIG. 1. Spectral intensity difference between γ and α-Ce at 125 K measured using neutrons of incident energy 2100 meV with two different energy resolutions. The continuous curve shows the low resolution (higher statistical accuracy) data corrected for variation of intensity with ω (hence Q) for fixed scattering angle $\langle 2\theta \rangle$, assuming the Ce^{3+} form-factor dependence.

$$\int_{-\infty}^{\infty} S(Q,\omega)d\omega \propto \langle M_Q^Z M_{-Q}^Z \rangle \propto \mu_Q^2 , \quad (1)$$

where

$$S(Q,\omega) \propto \left[1-\exp\left[-\frac{\omega}{T}\right]\right]^{-1} \chi''(Q,\omega)$$

with $\chi''(Q,\omega)$ representing the imaginary part of the magnetic susceptibility and ω and T in units of energy. Although not strictly justified, we *assume* in the following that for a valence fluctuation system with $4f$ occupancy $\langle n_f \rangle$ the integral of $S(Q,\omega)$ can be represented by $\mu_Q^2=\mu_0^2F^2(Q)\langle n_f \rangle$, where $F^2(Q)$ is the form factor. If the integration was limited to the energy region of the ground multiplet ($^2F_{5/2}$) then $\mu_0^2=g_J^2J(J+1)\mu_B^2$ with $J=\frac{5}{2}$. We are, however, performing an energy integration well beyond the energy range of the upper spin-orbit state ($^2F_{7/2}$), so that μ_0^2 should be proportional to the cross section of all excitations from the ground multiplet, which we assume to remain constant between the two phases. Under these assumptions the change in the $4f$ occupancy $\Delta\langle n_f \rangle$ relative to γ-Ce can be expressed as

$$\Delta\langle n_f \rangle = \int_{-\infty}^{\infty} \left\{ [S(Q,\omega)]^{\gamma} - [S(Q,\omega)]^{\alpha} \right\} \times d\omega \Big/ \int_{-\infty}^{\infty} [S(Q,\omega)]^{\gamma} d\omega . \quad (2)$$

In the present experiment, despite the use of a high incident energy (2100 meV), the magnetic signal becomes indistinguishable from noise beyond $\sim$1500 meV as Q becomes progressively very large with ω (for fixed scattering angle $\langle 2\theta \rangle$). We have applied corrections to the data for intensity variation with Q using the Ce^{3+} form-factor dependence, which appears quite justified.[9] Numerical integration of the form-factor corrected data (shown in Fig. 1) up to 1500 meV yields $\Delta\langle n_f \rangle = 0.2\pm0.1$, from which, assuming $\langle n_f \rangle = 1$ for γ-Ce, we obtain $\langle n_f \rangle = 0.8\pm0.1$ for α-Ce, consistent with positron annihilation[4] and Compton scattering[13] measurements, which indicate close to integral occupancy. The latter measurements, however, did not distinguish between localized and bandlike $4f$ states, while the present neutron data, which span the Q range $3 \rightarrow 15$ Å^{-1} and, as discussed below, show a single-ion-like magnetic response for the $^2F_{5/2}$ ground state as well as the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ spin-orbit (SO) excitation, suggest that $\sim$0.8 electrons remain *localized* in α-Ce.

In Fig. 2 we show the observed scattering $S(Q,\omega)$ (magnetic + phonons) for both α and γ phases at 125 K using neutrons of incident energy 450 meV. The inelastic peak at $\sim$260 meV in γ-Ce represents the spin-orbit excitation $^2F_{5/2} \rightarrow {}^2F_{7/2}$, while the "structure" around $\sim$160 meV in α-Ce forms part of the broad maximum in the magnetic response, which is more clearly seen in the difference signal. As discussed below, the centroid of the broad inelastic response yields a measure of the Kondo temperature T_K so the shift of the magnetic intensity from low to high energies between γ and α-Ce signals a large change in T_K.

Low-temperature (20 K) magnetic scattering in α-Ce (extracted with La as the nonmagnetic reference) using neutrons of $E_i=600$ meV are presented in Fig. 3 in the form $\chi''(\omega)/\omega$, where the continuous and the dashed curves show the best fits to a Lorentzian and the Kuramoto-Müller-Hartmann (KMH) spectral function for an Anderson impurity,[14] yielding $\omega_0 \sim$ 170 and 156 meV, respectively. The other parameter of the KMH fit $\alpha(=\pi n_f/N)$, found to be 0.43 ± 0.03, yields $n_f=0.83$ (assuming $N=6$), in good accord with the result obtained from the integrated spectral intensity. We remark that the Kondo energy obtained from the neutron data $\sim$170 meV (or $\sim$156 meV from the KMH fit) is about twice the value of $T_K \sim 82$ meV obtained from a reanalysis of the photoemission data for α-Ce,[15] which reevaluates upwards by a factor >3 the T_K determined by the original authors.[16] This convergence of the photoemission and

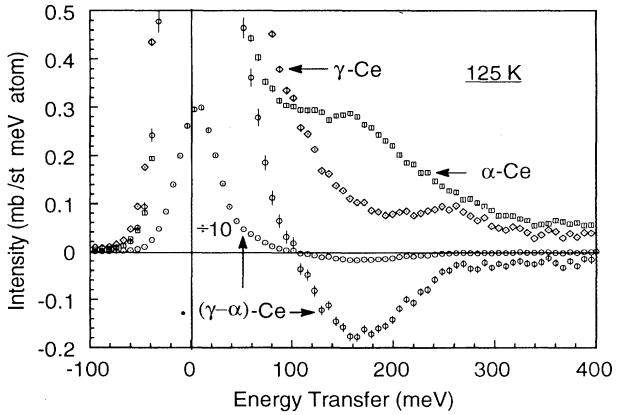

FIG. 2. (a) Observed scattering (magnetic + phonons) from γ and α-Ce at 125 K using neutrons of incident energy 450 meV. The circles represent the difference signal (magnetic) plotted on two different vertical scales.

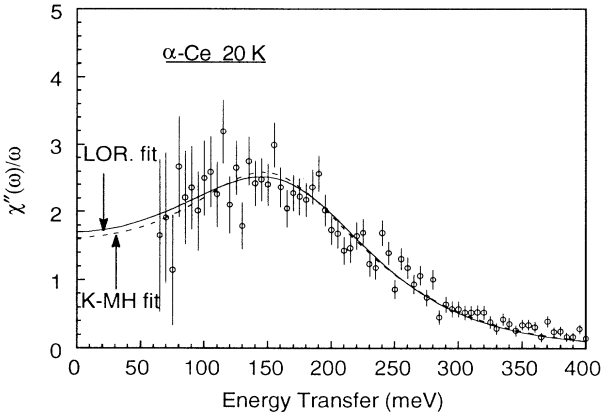

FIG. 3. Low-temperature (20 K) dynamic susceptibility response of α-Ce represented as $\chi''(\omega)/\omega$. The continuous curve represents the Lorentzian spectral fit and the dashed curve shows the fit to the Kuramoto-Müller-Hartmann function (Ref. 14). Form-factor variation has been included in the fits.

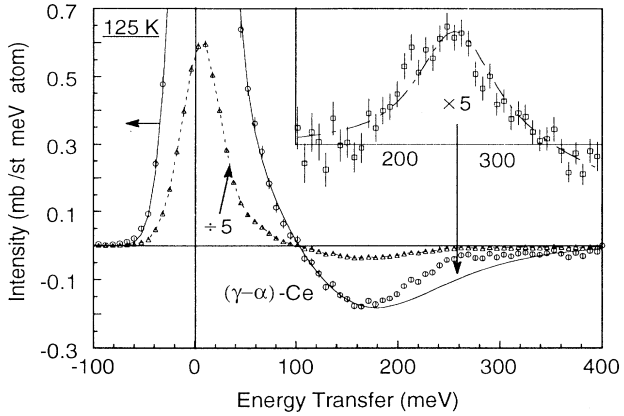

FIG. 4. Two component least-squares fit to the γ-α difference signal ($E_i = 450$ meV) in the energy range $-100 < \omega < 200$ meV. The continuous and short dashed curves represent the Ce^{3+} form-factor corrected overall fit. The residue is plotted on an expanded vertical scale in the inset where the long dashed curve parametrizes the SO excitation, taking into account the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ structure factor (Ref. 19) as well as the SO excitation in α-Ce.

the neutron results is, of course, encouraging and may improve as new experimental data allowing better evaluation of surface contributions become available.[17]

It is interesting that the Kondo temperature T_0 (T_K) for α-Ce obtained from our neutron data is fairly close to that predicted from the linear specific-heat coefficient γ via the Fermi-liquid relation[18] $\gamma = \pi^2 k_B^2 \langle n_f \rangle / 3\omega_0$, where $\omega_0 = T_0$. Finite U (~ 6 eV) corrections to these relations are of the order of ~ 2–3% (cf. the estimated f^2 occupancy for Ce in Ref. 15, for example) and dwarfed by uncertainties in ω_0 (170 ± 10 meV) and $\langle n_f \rangle$ (0.8 ± 0.1). We obtain $\gamma = 10.5 \pm 1.5$ mJ mol^{-1} K^{-2}, which compares reasonably well with 12.8 mJ mol^{-1} K^{-2} obtained from specific-heat measurements,[3] allowing for some (s,p,d) conduction-electron contribution. A similar evaluation for the susceptibility via the relation $\chi(0) = \mu^2 \langle n_f \rangle / 3\omega_0$, yields $\chi(0) = (3.1 \pm 0.4) \times 10^{-4}$ emu mol^{-1}. This is smaller than the bulk susceptibility of 5.32×10^{-4} emu mol^{-1} *at 50 K (its minimum value).*[3] The discrepancy could in part be due to an enhancement of the moment μ via hybridization induced admixture between the $^2F_{5/2}$ and $^2F_{7/2}$ states.[20] However, we suspect the main source to be impurity contamination evident in the susceptibility data in the form of a Curie-Weiss tail at low temperatures.[3] At 50 K the β-phase contribution to the bulk susceptibility, given by $\chi \sim C/(T+12)$, could be ~ 30 times that of α-Ce, $\chi \sim C/2000$. Hence, presence of $< 2\%$ β-Ce could account for most of the discrepancy.

The γ minus α difference signals shown in Figs. 1 and 2 have been analyzed assuming a narrow *quasielastic* response for γ-Ce,[10] or broadened crystal-field states,[9] Γ_7 and Γ_8, giving rise to quasielastic and inelastic components. For the α phase we have assumed a broad *inelastic* Lorentzian spectral response (cf. Fig. 3). We have included form-factor variation of intensity with energy transfer ω (and hence Q) with the fitted functions. For γ-Ce the simple quasielastic fit yields a width of 7.5 ± 0.5 meV, while the crystal-field fit yields a quasielastic width of 5.5 ± 0.5 meV (at 125 K), consistent with $T \rightarrow 0$ K characteristic (Kondo) energy of ~ 5 meV.[16] In Fig. 4 the thick continuous curve (and the short dashed curve) represents the overall best fit to the 450-meV data. The residue in the region of ~ 260 meV represents the spin-orbit excitation. This is shown in the inset together with a curve (dashed) which parametrizes the spin-orbit excitation (width 40 ± 5 meV, position 260 ± 10 meV), taking into account the SO excitation in α-Ce (see below) and the appropriate form factor for the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition.[19]

Results for $E_i = 2100$ meV are reproduced in Fig. 5 where the continuous curve represents the overall fit. The final fits are obtained for *the same parameters for both the 450- and 2100-meV data.* Only the vertical scale is adjusted by the factor 1.12 between the two data sets,

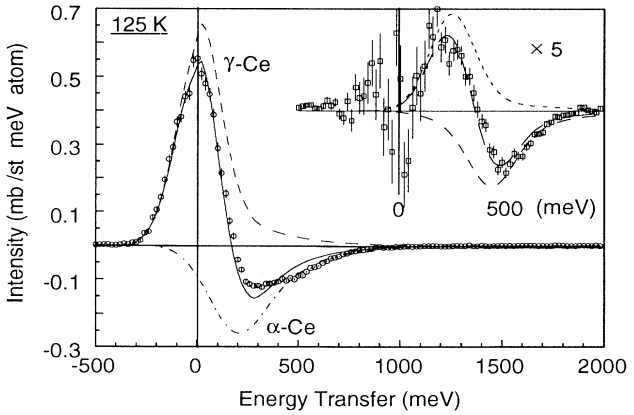

FIG. 5. Model fit to the γ-α difference intensity for $E_i = 2100$ meV (for the same parameters as the 450-meV data, see text). The two components of the fit are shown by the dashed (γ-Ce) and the dash-dotted (α-Ce) curves. The residue is shown on an expanded vertical scale in the inset, together with a fit assuming SO excitations in both phases, shown by the dashed curves.

which can be accounted for by possible systematic errors in the vanadium calibration and uncertainty in the scattering angle, ($\pm 0.5°$ at 4.5°). The dashed and dash-dotted curves represent the ground ($^2F_{5/2}$) state components for the γ and α phases. The residual intensity is shown on an expanded vertical scale in the inset together with the curve obtained for the same parameters (components are shown dashed) as used to fit the SO region in the lower-energy data, Fig. 4. We believe the peak at ~ 450 meV represents the SO excitation in the α phase. Although its relatively high energy as well as broad width (~ 100 meV) may appear rather unusual, they are not entirely unexpected in view of theoretical considerations for x-ray photoemission spectroscopy and bremsstrahlung isochromat spectroscopy spectra.[20,21] We emphasize that the SO excitation evidenced in α-Ce is *not an artifact* of the fit or the fitted spectral forms, although its exact position, shape and width may depend on the spectral functions (Lorentzian or KMH) chosen to represent the ground-state response. In fact, the SO excitation is *clearly observable* in the *as-measured* difference signal in Fig. 1, particularly in the form-factor corrected data (continuous curve). Its relatively small intensity compared with the main response is in good quantitative accord with theory, taking into account the respective form factors.[19]

In conclusion, we have identified a single-ion spectral response in α-Ce, well described by the KMH spectral function ($T_K \sim 1800$ K) or an inelastic Lorentzian ($T_K \sim 2000$ K). Numerical integration of the difference signal between the γ and α-Ce measured with high-energy neutrons at the same temperature and over the same Q range thus suggests that the $4f$ electron remains *localized* in α-Ce to the extent of around 8 parts in 10. Further evidence for localized $4f$ states in α-Ce is provided by the observation of broad, higher-lying, but well-defined spin-orbit excitation at finite Q's. These results together with the observed magnitudes of the characteristic (Kondo) energies of α and γ-Ce ($T_K \sim 60$ K) provide strong support to the "Kondo volume collapse" theories of the $\gamma \rightarrow \alpha$ transition.

The samples were prepared at the Laboratoire Louis Néel, Grenoble. We thank R. Raphel and B. Gorges for their assistance in the preparation work. Helpful discussions with B. R. Coles, B. Coqblin, S. W. Lovesey, C. Lacroix, M. Lavagna, K. Matho, and D. Nunez-Regueiro are also acknowledged.

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