Magnetic Form Factor of α-Ce: Towards Understanding the Magnetism of Cerium

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A favored interpretation of the $\gamma \leftrightarrow \alpha$ phase transition in cerium postulates the transformation of the localized $4f$ state in γ-Ce to a weakly correlated itinerant $4f$ band in α-Ce. However, results of high-energy neutron inelastic scattering measurements, presented here, show clearly that the magnetic susceptibility response from α-Ce follows the Ce^{3+} form factor despite the large, 30-fold, increase in its spectral width relative to that in γ-Ce. This observation provides, for the first time, indisputable evidence for the localized character of the $4f$ state in the α phase. The present findings appear consistent with recent calculations combining dynamical mean-field theory with the local density approximation that indicate a strongly correlated $4f$ state in α-Ce. The localized $4f$ state is also fundamental to the Kondo volume collapse theories for the $\gamma \leftrightarrow \alpha$ phase transition in cerium.

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Cerium metal, the first member of the $4f$ rare earth series, exhibits an interesting phase diagram as a function of pressure and temperature [1]. One of the phase transitions, from the room temperature γ phase to the α phase by application of pressure ($\geq \sim 0.8$ GPa), was first reported in 1927 by Bridgman [2], followed some years later (1934) by the magnetic susceptibility and dialatometry studies of Trombe and Trombe and Foex [3] which revealed quite a well-defined transition to the α phase on cooling Ce to below $\sim$110 K. The large isostructural volume change of $\sim$15%, as well as the replacement of the normal Curie-Weiss temperature dependence in the magnetic susceptibility of the γ phase, which is indicative of a local moment behavior, by a practically temperature independent susceptibility in α-Ce [1] suggesting a quenched moment state, has intrigued many workers over the years and continues to fascinate us today.

There has, indeed, been a profusion of theoretical effort to understand and explain the $\gamma \leftrightarrow \alpha$ phase transition in Ce. One of the first theories [4], the promotional model, proposed that the $4f$ electron localized on the Ce^{3+} site in γ-Ce is transferred to the conduction band at the transition to the α phase. However, positron annihilation experiments by Gustafson and co-workers [5] detected little change in the number of conduction electrons at the transition. Subsequently, basing on a comparison of cohesive energies of related trivalent and quadrivalent elements, Johansson [6] proposed that the localized $4f$ state in γ-Ce undergoes a Mott-like transition to a narrow $4f$ band in the α phase. This idea has been adopted and developed in a number of theoretical papers, some of which have calculated the P-T phase diagram explicitly [7,8].

Other explanations for the $\gamma \leftrightarrow \alpha$ transition include the Kondo volume-collapse theory based on the single impurity Anderson model, by Allen and co-workers [9], that relates the decrease in the cell volume to the increase in the characteristic energy T_K. A similar theory based on the Kondo Hamiltonian was also proposed by Lavagna *et al.* [10]. However, Johansson *et al.* [7] have criticized the P-T phase diagram obtained from the Kondo volume-collapse calculations of Allen *et al.* [9] in that it shows a marked upward curvature whereas their Mott transition model [7] yields a linear P-T line, consistent with the experimental observations [1].

Further progress in understanding the $4f$ electronic state of α-Ce clearly requires input from other experimental techniques. A very useful probe, particularly for rare earth and actinide ions but largely ignored for α-Ce, is the neutron scattering investigation of the magnetic form factor whose shape depends sensitively on the relative magnitudes of the spin and orbital components of the moment μ. Considering that one of the most pronounced consequences of band formation would be to quench or reduce the magnetic moment significantly, particularly the orbital moment relative to the spin part, the effect of this relative change should be clearly visible from the shape of the magnetic form factor. This can be seen from the dependence on the scattering vector Q of the moment $\mu(Q)$ that can be expressed, in the spherical dipole approximation [11], as

$$\mu(Q) = [\mu_S(Q) + \mu_L(Q)] = [\mu_S + \mu_L]\langle j_0\rangle + \mu_L\langle j_2\rangle, \quad (1)$$

where $\langle j_0\rangle$ and $\langle j_2\rangle$ are Bessel functions of zero and second order that have very different shapes. This is clearly illustrated by the magnetic form factor calculations for α-Ce of Hjelm *et al.* [12] using the linear-muffin tin orbital (LMTO) method and including many body correlation effects via the local density approximation (LDA) which is considerably narrower than the single-ion Ce^{3+} form. The authors [12] have proposed that a measurement of the form factor of α-Ce should enable a clear identification of the electronic nature of the $4f$ state; that is, whether it is localized or itinerant.

Amongst the reasons why the experimental determination of the magnetic form factor of α-Ce has not received adequate attention so far is the difficulty of preparing single crystals of α-Ce normally required for the classic polarized neutron diffraction measurements of $F(Q)$ via the induced moment

$$\mu(Q)]_{q=0} = \chi(Q)H = \chi(0)F(Q)H, \quad (2)$$

where χ is the magnetic susceptibility, H is the applied magnetic field, and $q = 0$ signifies the center of the Brillouin zone, represented by the Bragg peaks. Measurements on Ce alloyed with a relatively high concentration of Th (26 at.%) were, nevertheless, performed on a polycrystalline sample by Moon and Kohler [13] who obtained five data points in the α phase over a limited Q range ($2 \leq Q \leq 6$ Å^{-1}) that do not all lie on the Ce^{3+} form factor curve. As a consequence of this and the relatively high concentration of Th in the sample the results are generally perceived as inconclusive or irrelevant for α-Ce.

Besides the classic polarized neutron diffraction technique the magnetic form factor can also be accessed via neutron inelastic scattering measurements of the magnetic spectral response $S(Q, \omega)$. The latter can be expressed as

$$S(Q, \omega) = s(q)S_q(\omega)F^2(Q), \quad (3)$$

where $s(q)$ incorporates the q dependence due to the intersite correlations, $S_q(\omega)$ represents the spin dynamics at the given q, and $F^2(Q)$ is the square of the magnetic form factor that modulates the overall intensity. For an isotropic system of noninteracting magnetic ions the paramagnetic spectral function $S(Q, \omega)$ reduces simply to $S(\omega)F^2(Q)$, i.e., $s(q) = 1$ and $S(\omega)$ is the same everywhere over all of the (reduced) reciprocal space q. While some neutron scattering measurements of $S(Q, \omega)$ have been reported on γ-Ce there are few studies for α-Ce due, as we now know, to its very large spectral extent and, hence, the difficulty of measuring it with thermal energy neutrons. With the advent of pulsed spallation neutron sources and the associated high-energy time-of-flight spectrometers it became possible to study paramagnetic scattering to relatively high energies. Thus, measurements on a sample of Ce 26 at.% Th were performed at intense pulsed neutron source for energies reaching 900 meV by Loong *et al.* [14] and later at ISIS for several energies up to 2000 meV on a sample of Ce alloyed with 7 at.% Sc [15]. Additions of 7–10 at.% of Sc or Th stabilizes the fcc phase against formation of parasitic double hexagonal close packed β-Ce [1]. Analysis of the constant-angle time-of-flight data from both these investigations assumed single-ion form factor dependence, i.e., $S(Q, \omega) = S(\omega)F^2(Q)$ which could not, however, be verified explicitly from the measurements due to some experimental constraints. The γ phase response $S(\omega)$ for Ce 7 at.% Sc could be interpreted [15] as a Lorentzian quasielastic distribution (i.e., a Lorentzian centered on zero energy) of half-width 5.5 ± 0.5 meV allowing a broadened crystal field excitation Γ_7–Γ_8 in the fit. In the α phase the spectral width was found to have increased almost 30-fold and could be fitted to a very broad Lorentzian centered on ω_0 of $\sim$170 meV representing the characteristic energy T_K in the α phase.

The present measurements were performed on a sample of Ce containing 10 at.% Sc that was prepared by induction melting followed by annealing at 800 K under continuously pumped high vacuum to reduce any hydrogen contamination. We used the MARI spectrometer at ISIS which has a uniform detector coverage over a large range of scattering angles between 3 and 135 degrees. This has permitted the present investigation of the Q variation of intensity over a wide Q range that was not possible in the previous measurements [15] on the high energy transfer spectrometer at ISIS. As in the latter experiment, we have taken advantage of the large hysteresis in the $\gamma \leftrightarrow \alpha$ phase transition to perform measurements at the same temperature in the two phases. The measurements were first performed in the γ phase after cooling the sample from room temperature down to 140 K using neutrons of incident energies 100, 450, 900, and 1500 meV. The sample was then cooled down to 20 K and after a few hours at this temperature during which some brief measurements were performed, the sample was warmed back up to 140 K where measurements were repeated using the same set of incident energies as listed above. The integrated elastic scattering, particularly from the 100 meV data, plotted as a function of the scattering angle, provides diffraction patterns with reasonably good resolution that enabled us to check that almost all of the sample had transformed to the α phase on cooling to 20 K and had remained so on warming back up to 140 K. There was no trace of the double hexagonal close packed β phase, as expected, particularly in the present sample containing 10% Sc [1].

The difference signal (α minus γ) obtained using an incident energy of 900 meV is shown in Fig. 1. The γ phase signal is narrow, resolution limited, and is, of course, negative in the (α minus γ) difference spectrum, hence not represented in the $S(Q, \omega)$ plot, as drawn. The Q variation of the intensity is obtained from constant-ω cuts performed at energies within the range covered. Results from one such constant energy slice centered on the characteristic energy of 170 meV with a width of ± 30 meV is shown in Fig. 2. The continuous curve through the data points represents the Ce^{3+} form factor [11] normalized to unity at $Q = 0$. For comparison, we have also shown the induced magnetic form factor (squared) calculated within the LDA itinerant electron band theory including orbital polarization corrections [12]. It is evident that the latter deviates quite significantly from the single-ion form and cannot at all explain the observed variation of spectral intensity with Q for α-Ce.

The present observation of the Ce^{3+} single-ion-like form factor is one of the most significant findings on α-Ce that provides indisputable evidence for the strongly correlated

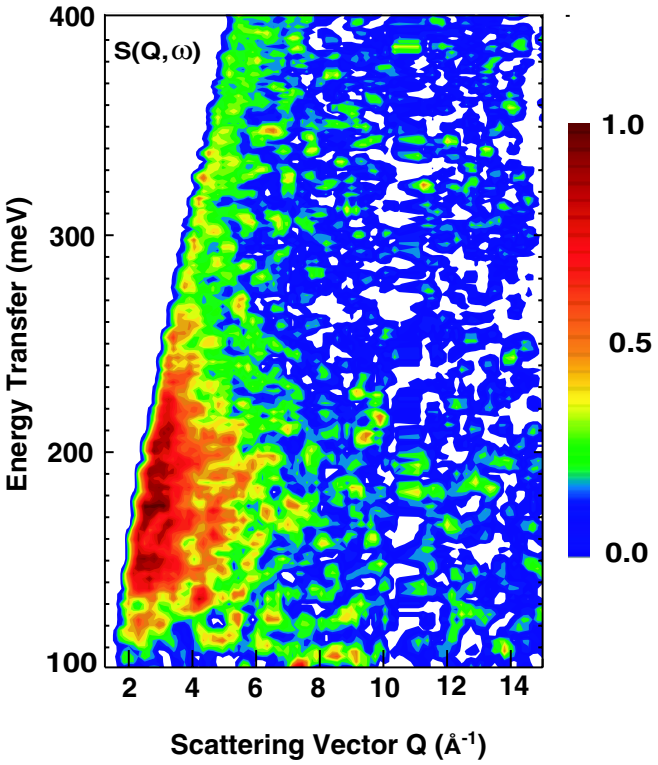

FIG. 1 (color online). The spectral function $S(Q, \omega)$ for α-Ce obtained as the difference spectrum (α-Ce minus γ-Ce). Both α-Ce and γ-Ce spectra were measured at the same temperature of 140 K by taking advantage of the hysteresis in the first order $\gamma \leftrightarrow \alpha$ transition.

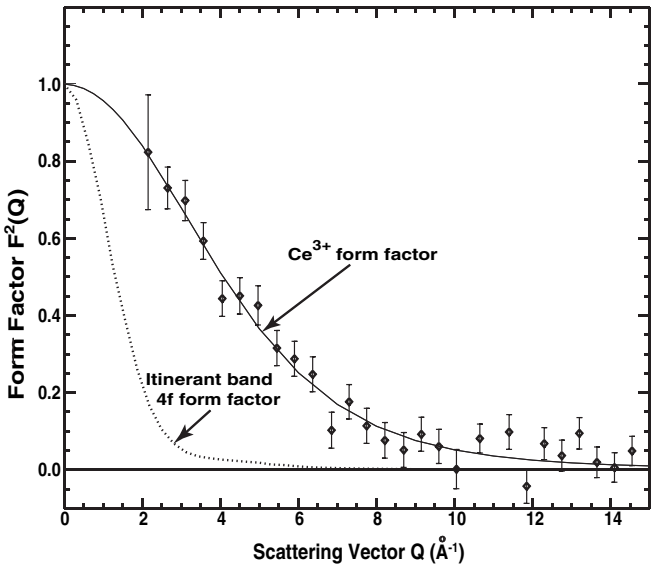

FIG. 2. The magnetic form factor $F^2(Q)$ obtained by constant-ω summation of $S(Q, \omega)$ within an energy bandwidth of ± 30 meV centered on the characteristic energy T_K of 170 meV. The curve through the data points represents the Ce^{3+} form factor [11]. The itinerant electron LMTO-LDA form factor (squared) for α-Ce including orbital polarization (OP) corrections, calculated by Hjelm *et al.* [12], is also shown for comparison.

(localized) character of the $4f$ state in the α phase. It indicates unambiguously that, whatever the nature of the transformation and the resultant magnetic moment, the ratio of the spin to orbital moment in α-Ce remains closely the same as for the free Ce^{3+} ion. It is useful, in this respect, to recall that energy integration of the broad dynamic magnetic susceptibility response in our earlier neutron scattering investigation [15] showed that the α phase moment was at least $\sim 80\%$ of that in the γ phase. As mentioned earlier, in the latter work the analysis of the time-of-flight data taken at constant angles was performed assuming the Ce^{3+} form factor variation of intensity with energy transfer ω (hence Q) which could not, however, be verified explicitly due to some experimental constraints. This is now done quite explicitly, for the first time, in the present study.

Recent calculations based on the dynamical mean-field theory (DMFT) combined with the LDA show that the $4f$ state in α-Ce is not simply a weakly correlated $4f$ band [16,17], as represented in the earlier itinerant electron-LDA treatments, but rather forms a strongly correlated $4f$ state. Analogous DMFT-LDA calculations [18] for fcc δ-Pu and the low temperature monoclinic α phase, which is 25% smaller in cell volume, show that the $5f$ electrons in the low-volume α-Pu also form a strongly correlated $5f$ state, superseding the earlier itinerant electron-LDA descriptions as a weakly correlated $5f$ band. Localized versus itinerant electron description is central to the recurrent debates on the exact nature of the magnetic electrons in a vast number of metallic magnets and paramagnets, the classic example being Fe, a $3d$ element. However, magnetic form factor measurements, although quite incisive for rare earths and actinides, would not so readily reveal the nature of the electronic state of a $3d$ ion since the orbital moment of the $3d$ electrons, the parameter most strongly influenced by band formation, is largely quenched by the strong crystal field experienced by the $3d$ shell in most solid state crystalline lattices.

In conclusion, the present observations of the Ce^{3+} magnetic form factor in α-Ce illustrate the inadequacy of the Mott transition model for the $\gamma \leftrightarrow \alpha$ phase transition in Ce in which the localized $4f$ state in the γ phase is considered to transform to a narrow, weakly correlated $4f$ band in the α phase. In this context the recent theoretical developments [16,17] represent a significant evolution in our understanding of α-Ce, a relatively simple system with only one moment-carrying ($4f$) electron compared with, for example, Pu, an actinide with five electrons in its magnetic ($5f$) shell in the Pu^{3+} state. The situation is also rather complex for the $3d$ magnetic ions such as Fe, Co, Ni with several (> 5) electrons in the unfilled (magnetic) $3d$ shell whose description, in the metallic state, as an itinerant $3d$ band, has often been questioned in the literature.

For α-Ce, it is evident that, thanks to the recent DMFT-LDA theories, the wide disparity between the weakly correlated $4f$-band picture (LDA band calculations) and the single-ion models (Kondo volume-collapse theories) has narrowed significantly. However, whatever the most appropriate theoretical description that might emerge eventually, it must show consistency with the present observations of single-ion Ce^{3+} form factor in α-Ce that provide indisputable evidence for the strongly correlated (localized) $4f$ ground state, an evidence that has been acutely lacking so far.

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