Kondo resonance energies in $CePd_3$

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We have determined characteristic Kondo energies of the $^2F_{5/2}$ and $^2F_{7/2}$ spin-orbit states of Ce in the compound $CePd_3$ using epithermal neutrons. They are ~ 50 and ~ 90 meV, respectively. Kramers-Kronig and moment sum-rule integrals together help to ascertain that the low-temperature magnetic response for the ground state ($^2F_{5/2}$) is closely (and almost wholly) represented by a single-ion spectral form with the characteristic energy of ~ 50 meV. Additional or deviational low-energy magnetic scattering (at energies above ~ 2 meV) which could be associated with possible low-temperature coherence or other phenomena is estimated to be at a level below $\sim 2\%$ of the integrated single-ion spectral intensity.

Physical properties of Kondo lattice and/or valence fluctuation systems are governed by a characteristic (Kondo) energy scale which is relatively low, typically ~ 10 to ~ 100 meV for most systems amenable to theoretical descriptions within the single-ion models, valid in the limit of large degeneracy and with conduction electron hybridization dominating over intersite (spin-spin) correlations. Neutron scattering can yield direct information about the Kondo energy of such a system via its paramagnetic spectral response.[1]

Low-temperature paramagnetic scattering from $CePd_3$ was investigated by Galera and co-workers using polarized neutrons on a three-axis spectrometer with a coarse energy resolution as well as the conventional time-of-flight technique.[2,3] Both indicated a broad, single-ion magnetic spectral response centered on the characteristic or Kondo energy of ~ 55 meV. However, a subsequent investigation by Shapiro, Stassis, and Aeppli[4] on a single crystal using a three-axis spectrometer with unpolarized neutrons claimed to find magnetic scattering only at low energies. The authors interpreted their data in terms of a quasielastic and an inelastic Lorentzian spectral components corresponding to *two low-energy scales* of ~ 3 and ~ 16 meV which, they argued, correlate reasonably well with the coherence energy T_{coh} of ~ 40 K [suggested by electrical resitivity[5] and magnetic susceptibility of $CePd_3$ (Ref. 6)] and the spin-fluctuation energy $T_{sf} \sim 240$ K (deduced from the relation $T_{coh} \sim T_{sf}/N$, where N is the degeneracy of the $4f$ state) (Ref. 7).

A comparative neutron time-of-flight investigation reported recently[8] on the same single crystal of Shapiro *et al.*[4] and a polycrystalline powder of $CePd_3$ packed into a cylindrical form of similar dimensions has demonstrated how the low-angle, low-energy scattering (below ~ 30 meV) is dominated by nonmagnetic (phononic) multiple scattering in large samples used (necessary) in the neutron measurements. We report here results of a neutron-scattering investigation on polycrystalline $CePd_3$ performed on the pulsed source time-of-flight spectrometer HET at ISIS where we have attempted to minimize multiple scattering by subdividing the polycrystalline samples, of $CePd_3$ and the nonmagnetic reference YPd_3, into small elements separated by neutron absorbing slats.[9] The measurments performed using neutrons of incident energy 200 meV under very low background conditions give excellent agreement with earlier findings of Galera *et al.*[2,3]

In the second part of the present investigation we have used high-energy neutrons ($E_i = 900$ meV) to study the magnetic response over a much wider energy range with a view to ascertain the lower incident energy data and to search for the spin-orbit excitation to the $^2F_{7/2}$ state of Ce. We report a broad inelastic structure around ~ 360 meV, well above the spin-orbit energy of ~ 270 meV for the free ion, and argue below that it represents excitations from the low-temperature Kondo singlet to the $^2F_{7/2}$ state renormalized upwards by its characteristic energy of ~ 90 meV.

The results for the ground ($^2F_{5/2}$) state response are shown in Fig. 1. The data were converted to $S(\Theta, \omega)$ without empty-cell (background) corrections, which were negligible, and converted to absolute units relative to a vanadium standard. In Fig. 1(a) the squares represent the low-angle $\langle 2\Theta \rangle = 5°$ scattering from the nonmagnetic reference compound YPd_3. The observed scattering is confined mainly to energies below 30 meV where its intensity increases with increasing angle as shown by the dashed curve which represents data for $\langle 2\Theta \rangle = 136°$ scaled down by a factor 11.8 to match the low-angle scattering. This scaling factor, however, is much smaller than the ratio of ~ 400 expected from the Q^2 variation of intensity between the two scattering angles of 5° and 136°, for single-phonon processes, and illustrates clearly the role of multiple scattering which contributes dominantly to the observed nonmagnetic inelastic scattering at low angles in measurements on large samples. Thus, despite the steps taken to reduce multiple scattering in the present experiment there remains significant nonmagnetic contributions in the low-angle data whose origin is mainly in

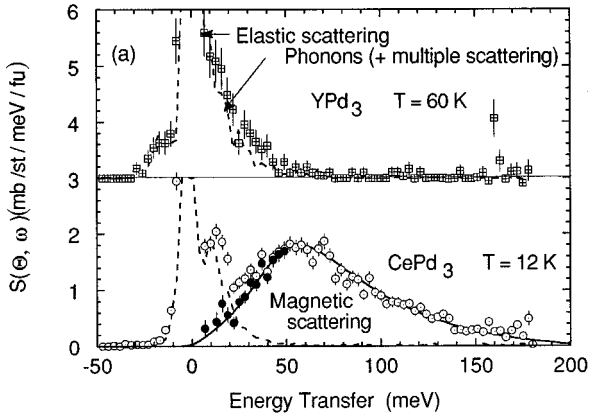

FIG. 1. Scattering cross sections of (a) YPd_3 at 60 K and (b) $CePd_3$ at 12 K, measured with neutrons of incident energy 200 meV. The data points represent low-angle data, $\langle 2\Theta\rangle = 5°$, while the dashed curves correspond to high-angle scattering, $\langle 2\Theta\rangle = 136°$, scaled down by a factor of 11.8. The thick continuous curve represents a least-squares fit using the KMH spectral function, to data above 30 meV. The black circles represent "phonon" corrected data (open circles minus the dashed curve) which fall closely on the fitted curve.

such processes. For our $CePd_3$ sample the inelastic scattering below 30 meV at low angles, shown by open circles in Fig. 1(b), is closely similar to that in YPd_3 and increases with increasing scattering angle. It represents a cross section of only ~ 28 mb st^{-1} fu^{-1} which is about 17% of the total as measured inelastic signal. The bulk of the signal is peaked on $\sim 50-60$ meV and decreases with increasing angle, as expected for magnetic scattering, such that for $\langle 2\Theta\rangle = 136°$ there is no measurable intensity in this energy region. The dashed curve in Fig. 1(b) shows the high-angle data scaled down by the same factor (viz. 11.8) as for YPd_3. It represents the estimated nonmagnetic contribution for $CePd_3$ assuming that the *ratio* of the nonmagnetic scattering at a given low angle for $CePd_3$ relative to a high angle (where magnetic contribution is negligible) is the same as the ratio of the observed scattering for the same two angles for an isostructural nonmagnetic reference,[10] in the present case YPd_3. This method does not require that phonon frequencies be the same for the two compounds, only the total cross sections, particularly the absorption coefficients, should not be too different. Its validity has been tested with two nonmagnetic isostructural samples, one against another, and has also been confirmed by Monte Carlo simulations performed more recently.[11]

However, even a *large* error of as much as 20% in the nonmagnetic contribution estimated by this method corresponds to a cross section of only ~ 6 mb sr^{-1} fu^{-1} (i.e., 20% of ~ 28 mb) which is $\sim 3\%$ of the total as measured signal (~ 170 mb sr^{-1} fu^{-1}) or $<2\%$ of the form-factor corrected integrated magnetic cross section (~ 280 mb sr^{-1} fu^{-1}). In Fig. 1(b) the black dots show the data below 50 meV obtained by subtracting out the nonmagnetic contribution. The fact that the corrected data fall closely on the curve representing the single-ion spectral fit to data above 30 meV (discussed below) gives us confidence that our method of estimating nonmagnetic contribution is much more accurate than 20% error, quoted above.

The continuous curve in Fig. 1(b) represents a least-squares fit to the *as-measured* data (open circles) *above* 30 meV using the *single-ion* spectral function for the Anderson impurity derived by Kuramoto and Müller-Hartmann (KMH).[12] It yields a characteristic or Kondo energy of 47 ± 3 meV while a similar fit to a Lorentzian, which is practically indistinguishable over the measured energy range, suggests a characteristic energy of 49 ± 3 meV and a half-width $\Gamma = 36\pm 2$ meV. The second parameter of the KMH fit yields $\langle n_f\rangle = 0.97\pm 0.05$ assuming the degeneracy N is 6 $= 2J+1$, with $J = \frac{5}{2}$.

An evaluation of the integrated, form-factor-corrected cross section for the magnetic response yields 280 ± 30 mb sr^{-1} Ce^{-1}, which corresponds to $\langle n_f\rangle = 0.9\pm 0.1$. As shown previously,[8] the "magnetic" signal in the data of Shapiro *et al.* represents a cross section of only ~ 33 mb sr^{-1} Ce^{-1} if the integration is limited to 80 meV, i.e., the measured energy range, or ~ 54 mb sr^{-1} Ce^{-1} if the integral is extended to 500 meV. Even the latter corresponds to only $\sim 1/6$th of the full cross section of Ce (314 mb st^{-1} Ce^{-1}) or, equivalently, a low $4f$ occupancy $\langle n_f\rangle$ of ~ 0.17 only.

The Kramers-Kronig integral of our magnetic response yields $\chi(0) \sim (1.6\pm 0.15)\times 10^{-3}$ emu mol^{-1} which compares well with the temperature-independent bulk susceptibility $\chi(0) = 1.4\times 10^{-3}$ emu mol^{-1}, neglecting the low-temperature Curie-Weiss upturn.[13] Shapiro *et al.* also found that the static susceptibility from their two low-energy components together gave good agreement with the bulk susceptibility. The reason why both the present data and those of Ref. 7 yield similar values for the susceptibility but give markedly different moments (cross sections) is simply that the moment integral is $\int S(\omega)d\omega$ while the Kramers-Kronig integral at low T is proportional to $\int [S(\omega)/\omega]d\omega$. Thus, low-energy spectral components contribute more weight (proportional to $1/\omega$) to the susceptibility compared with the moment integral.

Similarly, although the Curie-Weiss upturn (or "tail") in $CePd_3$ (as well as many other valence fluctuation compounds) at low temperatures often respresents quite an appreciable fraction of the temperature-independent susceptibility $\chi(0)$, i.e., that $\chi_{\rm tail} \sim \int [S(\omega)/\omega]d\omega$ is fairly significant ($\sim 30\%$ for $CePd_3$ at 10 K), the *spectral weight* $\int S(\omega)d\omega$ associated with the "tail" *need not be so large* if its origin is in low-energy processes such as those due to "stable" (or low Kondo temperature) magnetic moments. From our neutron data it appears that the spectral widths of the bulk of such low-energy processes in $CePd_3$ (whether intrinsic or extrinsic) must be below ~ 2 meV, and that their total spectral weight does not exceed a few percent. It is, of course, not excluded that the low-temperature coherence phenomenon suggested by the electrical resistivity[5] as well as the bulk susceptibility,[6] which may possibly be linked to formation of "quasiparticle bands," (Ref. 7) should be reflected in the inelastic magnetic response in some manner. While there does appear to be a correlation between the susceptibility upturn and the low-temperature anomaly in the induced magnetic form factor,[14] the present data do not show any significant manifestation (above the $\sim 2\%$ level) of *inelastic* magnetic scattering related to this effect in the mea-

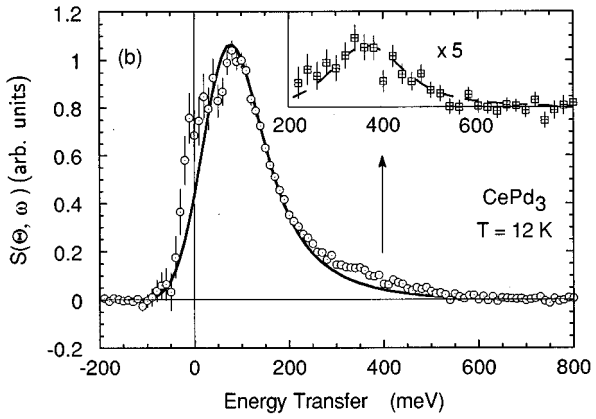

FIG. 2. High-energy *magnetic* scattering in $CePd_3$ obtained using YPd_3 as the nonmagnetic reference measured under identical conditions with neutrons of incident energy 900 meV. The data over the energy range $100<\omega<250$ meV were fitted to the KMH function fixing the parameters T_K and α to the values determined from the best fit in Fig. 1. The residue is shown on an expanded vertical scale in the inset, where the dashed curve represents a least-squares fit to a Lorentzian of half-width 60 ± 10 meV, centered on 360 ± 10 meV.

sured response above ~2 meV. It is evident, however, that the broad high-energy scattering characterizes the bulk (almost the whole) of the spectral response of $CePd_3$ and that any additional contributions or deviations from the single-ion spectral form at energies above ~2 meV due to other processes would be at the few percent ($<2\%$) level represented by the uncertainty in estimating the nonmagnetic contribution.

In Fig. 2 we show the results of high-energy measurements on $CePd_3$ using neutrons with incident energy 900 meV. These data are corrected for nonmagnetic scattering using YPd_3 as the nonmagnetic reference measured under identical conditions. A small relatively sharp peak of spurious origin at ~380 meV observed for both samples as well as in the ''empty'' measurement subtracts out completely in the difference signal. We have fitted the resultant response (over the range $100<\omega<250$ meV) to the KMH spectral form fixing the parameters T_K and α to their values determined more accurately from the low-energy data and varying only the vertical amplitude. The resultant fit, shown in Fig. 2, describes the high-energy data extremely well except for the broad residue in the energy region between ~200 and ~600 meV, which we believe represents the excitation to the $^2F_{7/2}$ state. In the inset we show the rebinned residue on an expanded vertical scale together with the Lorentzian fit which helps to parameterize the excitation (half-width $\sim60\pm10$ meV, centered on $\sim360\pm10$ meV).

The observation of the broad ''spin-orbit'' excitation at ~360 meV may appear a little surprising considering that the spin-orbit energy for the isolated Ce^{3+} ion is only ~270 meV.[15] Strictly, the ''ground'' magnetic response represents excitations from the low-temperature singlet (Kondo) state to the $^2F_{5/2}$ state. Similarly, the observed SO excitation represents the transition from the ''Kondo singlet'' to the $^2F_{7/2}$ state. Both SO states should renormalize upwards relative to the ''Kondo singlet'' by their respective Kondo energies given by $T_K^i=D\exp(-\pi|\epsilon_i|/N_i\Delta_i)$, where D is the conduction electron bandwidth and Δ_i the hybridization parameter.[1] Since the ''bare'' energy of the $^2F_{7/2}$ state $|\epsilon_i|$ is smaller (by ~270 meV) and the degeneracy N_1 higher (8 compared with 6) it is reasonable to expect its Kondo energy to be higher (even if Δ_i did not also increase).

We recall that in the interpretation of the inverse photoemission (BIS) data[16] on $CePd_3$ both spin-orbit levels are assumed to be shifted above the Fermi energy E_F by the same rather low Kondo energy of ~24 meV. With the currently practicable energy resolutions of BIS measurements it is, presumably, not possible to resolve the two spin-orbit ''peaks'' and determine their Kondo energies directly with the required precision. Existing photoemission data[17] on $CePd_3$ were taken with much poorer resolution than is now possible to achieve. However, Ce-based valence fluctuation systems for which high-resolution photoemission data are available appear to show the $^2F_{7/2}$ spin-orbit ''sideband'' at a fairly constant energy closely equal to the free-ion spin-orbit splitting. This is indeed surprising since the centroid of the $^2F_{7/2}$ spin-orbit ''peak'' should shift closer to E_F by an amount equal to the difference between the Kondo energies of the two spin-orbit states.[1] One possible reason for this may be the low Kondo energies of many of the systems investigated with high resolution, and the fact that the widths of the ''peaks'' are large, hence the effective shifts may not be easy to discern. On the other hand, if the photoemission data imply that the two spin-orbit states are renormalized by roughly the same amount then the observations are contrary to our finding.

In conclusion, we have shown that the ground state ($^2F_{5/2}$) magnetic response of Ce in the compound $CePd_3$ can be closely, and almost wholly, represented by a single-ion spectral function with a characteristic Kondo energy of ~50 meV. The spectral integral of the magnetic response suggests a $4f$ occupancy $\langle n_f\rangle$ of 0.9 ± 0.1. The observed excitation to the $^2F_{7/2}$ state situated on ~360 meV suggests a Kondo energy of $\sim90(\pm10)$ meV for this state. Thus we find that the two spin-orbit states have *different* characteristic energies, in possible contrast with the apparent lack of observable energy dependence of the centroid of the $^2F_{7/2}$ sideband in the photoemission investigations of Ce-based Kondo and/or valence fluctuation systems reported to date.

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