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Evolution of the spin-orbit excitation with increasing Kondo energy in $CeIn_{3-x}Sn_x$

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Neutron scattering measurements on $CeIn_3$ show the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ spin-orbit excitation at ~273 meV of half-width $\Gamma \sim 18$ meV, while $CeSn_3$ reveals a broad excitation ($\Gamma \sim 70$ meV) at a significantly higher energy (~345 meV). With increasing Sn content x, hence increasing Kondo energy, the series of compounds $CeIn_{3-x}Sn_x$ show a progressive upward energy shift of the excitation. This is accompanied initially by a collapse of the crystal-field splitting and beyond $x \sim 1$ by a concomitant increase in width.

The intermetallic compound $CeSn_3$ shows many of the unusual properties commonly associated with valence fluctuation systems, in particular an enhanced Pauli susceptibility $\chi(0)$ at low temperatures followed by a shallow maximum and Curie-Weiss behavior above.[1] It has an enhanced magnitude[2] of the linear specific-heat coefficient γ. $CeIn_3$ on the other hand shows the normal Curie-Weiss susceptibility at all temperatures except around and below $T_N(=10.2$ K) where it orders antiferromagnetically.[3]

Magnetic, transport and thermodynamic properties of the pseudobinary isostructural (fcc) compounds $CeIn_{3-x}Sn_x$ ($0 \le x \le 3$) have been investigated by a number of workers.[4–6] Previous neutron measurements of $CeIn_3$ show a broad crystal-field excitation around ~13 meV.[7] At the Sn-rich end measurements[8] on $CeIn_{3-x}Sn_x$, $2 \le x \le 3$ show a broad *inelastic* magnetic response of closely Lorentzian shape (also well described by the Kuramoto–Müller-Hartmann spectral function[9]) centered on a characteristic energy ω_0 (T_0) which varies almost linearly with x from ~40 meV for $x=3$ ($CeSn_3$), to ~9 meV for $x=2$ (i.e., $CeInSn_2$), in good accord with Fermi-liquid relations[10–12] using the literature values of $\chi(0)$ and γ, and assuming integral $4f$ occupancy throughout.

In the following we report measurements of the spin-orbit excitation ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) in the pseudobinary compounds $CeIn_{3-x}Sn_x$, carried out using high-energy neutrons at the spallation neutron source ISIS with the aim to study the evolution of the spin-orbit excitation with increasing characteristic (or Kondo) energy from $CeIn_3$ towards $CeSn_3$. We have also performed measurements at Institut Laue-Langevin (ILL) using thermal energy neutrons to identify crystal-field states within the ground ($^2F_{5/2}$) multiplet of $CeIn_3$ and observe their collapse as the Sn content x, and hence the k-f hybridization, is increased progressively. Such a progressive evolution has so far not been demonstrated experimentally although the absence of well-defined crystal-field states in high-T_K Kondo and/or valence fluctuation systems is well known.

We begin with measurements within the ground manifold ($^2F_{5/2}$) for $CeIn_3$ as well as $CeSn_{1.5}In_{1.5}$, carried out on the IN4 time-of-flight spectrometer at ILL. Figure 1(a) shows the low angle ($\langle 2\theta \rangle = 9°$) data for $CeIn_3$ at 20 K obtained with neutrons of incident energy 50 meV. Phonon contribution, dominated at low angles by multiple scattering (in-plane elastic or inelastic scattering followed by scattering through ~90° into the low-angle detector bank), has been determined and subtracted off with reference to a $LaIn_3$ sample *measured under identical conditions* using a previously described phonon correction procedure.[13] Magnetic multiple scattering from a similar process is expected to be rather weak due to the low magnetic form factor for scattering through large angles (~90°) into the low angle bank. In Fig. 1 the

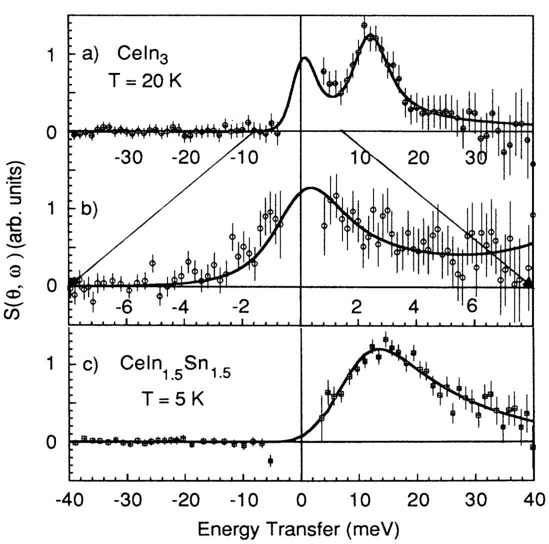

FIG. 1. Magnetic spectral response of $CeIn_3$ at 20 K in the paramagnetic phase (a) measured with neutrons of incident energy 50 meV and (b) with neutrons of 12.5 meV. The smooth curves through both data sets (a) and (b) represent a common two component Lorentzian fit consisting of a crystal-field excitation and a quasielastic distribution. (c) shows the observed magnetic spectrum for $CeIn_{1.5}Sn_{1.5}$ at 5 K including the fit to the Kuramoto–Müller-Hartmann function which closely coincides with the Lorentzian fit, not shown.

continuous curve represents a two component Lorentzian fit which includes a quasielastic part (centered on zero energy) due principally to the Γ_7 ground state (at low temperatures) and an inelastic peak corresponding to the $\Gamma_7 \rightarrow \Gamma_8$ excitation. We have included form-factor variation of intensity with energy transfer and hence Q for fixed scattering angles $\langle 2\theta \rangle$ with the fitted function. The quasielastic region, shown in Fig. 1(b) was studied in greater detail using lower energy neutrons ($E_i = 12.5$ meV), but we have failed to detect the strong Q dependence (of its width and intensity) reported by Lassailly, Burke, and Flouquet[14] for a polycrystalline $CeIn_3$ sample at $6T_N$ (60 K) to temperatures as high as $24T_N$ (240 K). In fact, any Q-dependence of the quasielastic component should also be reflected in the $\Gamma_7 \rightarrow \Gamma_8$ excitation, but Q variation of the intensity of the inelastic peak studied by Lawrence and Shapiro[7] was found to follow the usual ($J = \frac{5}{2}$) Ce^{3+} form-factor dependence. Our results support the latter finding, namely, that measurements on polycrystalline $CeIn_3$ show relatively weak intersite couplings (for both the inelastic and quasielastic components). We also find that a second inelastic magnetic peak around 20–25 meV reported by Lassailly, Burke, and Flouquet[14] is, in fact, phononic in origin suggesting possible influence of residual (uncorrected) phonons in their data analysis. The well-resolved two component fit to the present data allows us to determine the width ($= 3.0 \pm 0.2$ meV) as well as position ($= 11.6 \pm 0.3$ meV) of the crystal-field excitation reasonably accurately yielding the crystal-field parameter $A_4\langle r^4 \rangle = 59$ K, which is close to $A_4\langle r^4 \rangle = 66$ K determined from bulk susceptibility.[15] At 20 K the central quasielastic component has a half-width of 1.8 ± 0.2 meV.

Kondo-lattice and/or heavy Fermion systems often show broad but well-defined crystal-field excitations. The residual widths (as $T \rightarrow 0$ K) of the various crystal-field states represent their characteristic energies given by $T_i = D \exp(-\pi|\varepsilon_i|/N_i\Delta_i)$, with D the conduction electron bandwidth and Δ_i is the hybridization parameter.[12,20] We thus expect the residual width of the Γ_8 state to be larger due to its larger degeneracy ($N_i = 4$) and slightly elevated position (i.e., smaller $|\varepsilon_i|$). In absence of (unresolved) Jahn-Teller splitting of the Γ_8 state the observed width (3.0 ± 0.2) of the crystal-field *excitation* (which represents the convoluted widths of the Γ_7 and Γ_8 states) should be attributed to this mechanism since broadening due to exchange-induced dispersion of the excitation is apparently small as inferred from the fact that $CeIn_{2.5}Sn_{0.5}$ which does not order magnetically (or whose T_N is at least an order of magnitude smaller),[4] shows closely similar widths for both the quasielastic and the inelastic components. From their measurements on $CeIn_3$ Lawrence and Shapiro[7] deduced an overall half-width of ~ 10 meV and a crystal-field splitting of ~ 13 meV, using a *single inelastic peak* of Lorentzian shape to represent the full magnetic response, while Gross *et al.*[16] fitted their data on $CeIn_3$ assuming a *purely quasielastic response* (i.e., a single structure centered on zero energy) and obtained an overall half-width of ~ 15 meV. Both these data sets are compatible with the present results if due allowance is made for the poorer statistical accuracy and energy resolutions of the experiments.

In Fig. 1(c) we show the observed paramagnetic spectral response of $CeSn_{1.5}In_{1.5}$ a composition half-way between $CeIn_3$ and $CeSn_3$, measured under identical conditions. The magnetic response is fairly well described by a broad inelastic Lorentzian centered on $\omega_0 = 11.2 \pm 1$ meV with a half-width Γ of 8 ± 1 meV as well as the Kuramoto–Müller-Hartmann function,[9]

$$\chi''(\omega) = \frac{CN\omega}{\pi\omega_0^2} \frac{\alpha}{u^2(u^2+4\alpha^2)} \times \left\{ \alpha \ln[(1-u^2)^2 + 4u^2\alpha^2] + |u| \left[\frac{\pi}{2} - \tan^{-1}\left[\frac{1-u^2}{2|u|\alpha}\right]\right]\right\} \quad (1)$$

where $u = \omega/\omega_0$ and $\alpha = \sin(\pi\langle n_f \rangle/N)$. This yields the characteristic energy $\omega_0 = 10.6 \pm 1$ meV, and the parameter $\alpha = 0.55 \pm 0.05$. From the latter, assuming integral occupancy ($\langle n_f \rangle = 1$) we obtain the degeneracy $N = 5.4 \pm 0.6$. This result suggests that as the characteristic energy becomes comparable to crystal-field energy (~ 12 meV for $CeIn_3$) the crystal-field splitting essentially collapses (i.e., the $^2F_{5/2}$ state appears to recover its full degeneracy, $N = 6$) and the spectral shape assumes the Fermi-liquid form.[9] In Fig. 1(c) the continuous curve represents the fit to the Kuramoto–Müller-Hartmann (KMH) function which coincides fairly closely with the Lorentzian fit, not shown. We remark that for moderate N (6 or 8) the KMH function [Eq. (1)] closely resembles a Lorentzian, but it deviates markedly from the Lorentzian shape for large N, particularly for $\omega < \omega_0$.

The high-energy measurements were performed at 20 K on the high energy transfer time-of-flight spectrometer at ISIS using neutrons of incident energy 600 meV. Measurements under identical conditions performed on two nonmagnetic reference compounds, namely $LaIn_3$ and $LaSn_3$, were used after appropriate scaling to subtract off the nonmagnetic scattering from the Ce-based compounds. The corrected data are shown in Fig. 2, where the continuous curves represent (resolution convoluted) fits to the data in which energy parameters obtained previously from our lower incident energy (higher-energy resolution) experiments described above or reported previously[8] were held fixed. In the insets to the figures we show the data in the region of the spin-orbit peak on an expanded vertical scale ($\times 5$) where the low-energy magnetic response of the $^2F_{5/2}$ state (represented by the fitted continuous curve) is taken as the "baseline." We have included the $Ce^{3+}(^2F_{5/2})$ form factor variation of intensity with wave vector Q (as a function of the energy transfer ω for a fixed scattering angle $\langle 2\theta \rangle$) for the ground-state response and the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ inelastic structure factor for the spin-orbit excitation.[17]

In Fig. 3 we plot the observed energies and widths of the spin-orbit (SO) excitations against the characteristic energy T_0 (ω_0) of the ground state ($^2F_{5/2}$) obtained from our neutron data where we have defined the characteristic energy as the centroid of the broad inelastic Lorentzian-like distribution (associated with the fully degenerate $^2F_{5/2}$ ground state),[9,12,19,20] while for $CeIn_3$ we take the characteristic energy to be the residual width above T_N(~ 1.8 meV at 20 K) of the quasielastic distribution associated with the ground crystal-field state.[12,20,21] It is interesting that the Kondo energy ω_0 of $CeSn_2In$ is lower than that of $CeSn_{1.5}In_{1.5}$, as also found from bulk susceptibility by Lawrence.[4]

The data in Fig. 3 show that both the energy of the SO excitation and its width increase roughly linearly with T_0, above some constant values Δ_0 and Γ_0, at a rate roughly twice T_0 (ω_0). For $CeIn_3$ and In-rich compounds the low temperature width of the SO excitation is dominated by the crystal-field splitting of the upper (i.e., $^2F_{7/2}$) spin-orbit multiplet. The magnitude of Γ_0 gives a measure of the overall crystal-field splitting of the

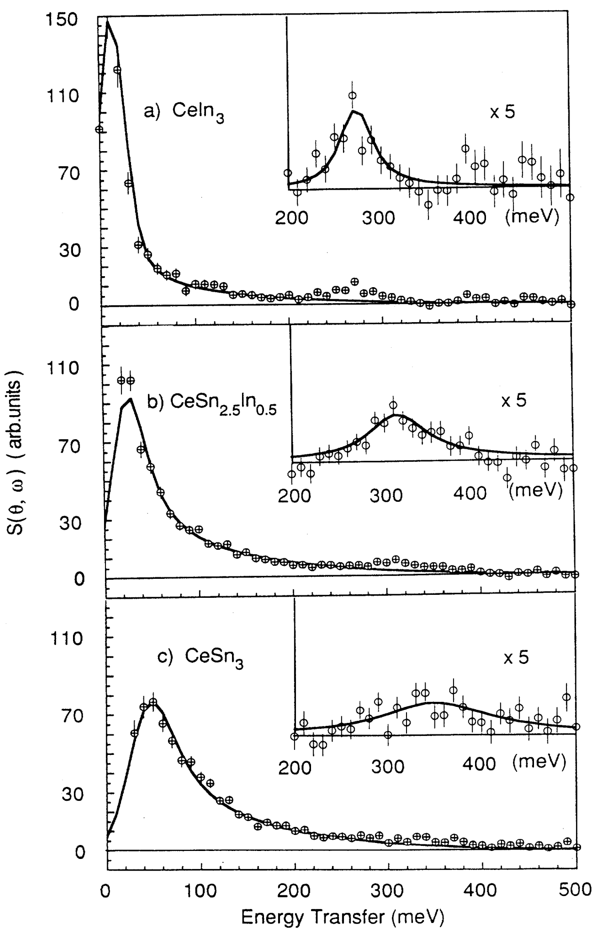

FIG. 2. Magnetic spectral response at 20 K measured with high-energy neutrons of incident energy 600 meV for (a) $CeIn_3$, (b) $CeIn_{2.5}Sn_{0.5}$, and (c) $CeSn_3$. The continuous curves represent least-squares fits to the $^2F_{5/2}$ ground-state response using Lorentzian spectral functions with fixed energy and width parameters obtained from measurements using lower-energy neutrons. The insets show the SO region on an expanded vertical scale (×5) with the fit to the ground-state ($^2F_{5/2}$) response taken as "baseline." The smooth curves through the SO data represent fit to a single Lorentzian.

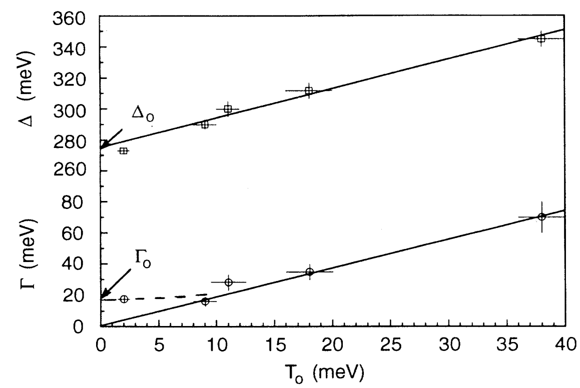

FIG. 3. (a) $^2F_{5/2} \rightarrow {}^2F_{7/2}$ spin-orbit excitation energy Δ and (b) width Γ plotted against the characteristic energy T_0 of the ground $^2F_{5/2}$ manifold.

higher-lying $^2F_{7/2}$ state since at 20 K it represents excitations exclusively from the $\Gamma_7(^2F_{5/2})$ ground state to the three crystal field states Γ_7, Γ_8, and Γ_6 of the $^2F_{7/2}$ manifold. The intercept Δ_0($=275\pm5$ meV) should correspond to the SO energy in absence of the Kondo effect, and is close to the free ion value of 279.4 meV.[18] As mentioned earlier, with increasing hybridization the crystal-field states collapse, i.e., the spin-orbit multiplets become fully degenerate.

The progressive increase in width and energy of the SO excitation is an interesting phenomenon which can be qualitatively understood within the Anderson model.[19,20] Cox, Bickers, and Wilkins[20] have calculated $\chi''(\omega)$ including the SO interaction and show that the *width* Γ of the SO excitation is of the order of the characteristic energy T_{ex} of the upper ($^2F_{7/2}$) state. The present measurements show that the width of the SO excitation increases progressively by an amount roughly equal to $\sim 2T_0$, *once crystal-field splittings are "quenched"* (i.e., beyond $x \sim 1$). Calculations for x-ray photoemission spectroscopy (XPS) and bremsstrahlung isochromat spectroscopy (BIS) (Refs. 19 and 20) indicate that the SO sideband(s) should shift by an amount roughly equal to the characteristic energy T_0 (and T_{ex}, respectively?). The present data show the increase in the SO excitation energy to be $\sim 2T_0$ above a constant value Δ_0(~ 275 meV), i.e., the rate of upward energy shift is similar to that of increase of the width of the excitation. Thus both appear linked to T_{ex}.

In summary, the present data have clearly identified a crystal-field excitation and a quasielastic component, i.e., well-defined crystal-field states within the ground ($^2F_{5/2}$) manifold of $CeIn_3$. With increasing Sn content (increasing k-f hybridization) the crystal field states collapse (i.e., the $^2F_{5/2}$ manifold recovers its full degeneracy) and the spectral shape assumes the Fermi-liquid form.[9] An interesting observation from the present study is that the SO excitation ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) is renormalized upwards and broadens progressively with increasing hybridization from $CeIn_3$ towards $CeSn_3$.

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[21]The residual ($T \rightarrow 0$ K) width of the quasielastic component of a system showing broad but well-defined crystal-field splittings is the best estimate of the ground-state characteristic energy (Refs. 12 and 20). In absence of k-f hybridization-induced spin fluctuations the crystal-field excitations should be sharp (cf. insulators). They broaden as hybridization is "turned on" progressively and eventually the crystal-field states collapse. The magnetic response now assumes the Fermi-liquid form (Refs. 9, 12, 19, and 20) at low temperatures. It is analytically best represented by the KMH function as well as (for moderate degeneracies $N=6$ or 8) by an *inelastic* Lorentzian. The characteristic energy is a parameter of the KMH fit, and is closely equal in magnitude to the centroid ω_0 of the inelastic Lorentzian provided $\omega_0 > \Gamma$, the half-width of the distribution.