Possible Anisotropic $s - f$ Hybridization in a Cubic Heavy-Fermion Compound: $CeIn_1Sn_2$

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Polarized neutron scattering measurements on a single crystal of composition $CeIn_1Sn_2$ show a broad, single-ion, spectral response centered on a characteristic energy of $\sim 9 \pm 1$ meV at the zone boundary point (0 0 1.5). The zone center spectral response is closely similar in form but has a slightly reduced amplitude, smaller by some 20%. Constant-ω scans show that these intensity modulations, of amplitude $\sim 10\%$, resembling intersite antiferromagnetic correlations, are superimposed on a mean variation that follows the Ce^{3+}, $4f^1$, single-ion form factor, and are tentatively attributed to $\mathbf{q}$-dependent hybridization of the localized $4f$ state with the conduction electrons.

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The intermetallic compounds $CeIn_3$ and $CeSn_3$ represent an interesting pair of Ce-based systems having the same, $AuCu_3$, structure. Indium (In) and tin (Sn), constituents of the partner sublattice of cerium (Ce), are near-neighbors in the periodic table, with Sn, to the right of In, having an extra electron in its outer shell. $CeIn_3$, classed a heavy-Fermion system, shows a central quasielastic distribution (i.e., broadened magnetic scattering centered on $\omega = 0$) and a broad but well-defined crystal field excitation at ~ 12 meV [1]. It becomes antiferromagnetically ordered below ~ 10.2 K [2].

Like all the so-named valence fluctuation systems, $CeSn_3$ can also be classed as a heavy-Fermion system since hybridization of the $4f$ electron with the outer shell electrons of the neighboring ions in the lattice, in general the conduction electrons, is the common physical mechanism influencing the magnetic and thermodynamic properties of all these systems. This hybridization process is apparently stronger for $CeSn_3$ compared with $CeIn_3$. Hence, in contrast to the latter compound, $CeSn_3$ shows a broad spectral response with a characteristic energy of ~ 35–40 meV [3]. Furthermore, the compound also remains paramagnetic down to very low temperatures. Progressive replacement of some of the In by Sn to form the pseudobinary intermetallic compounds $Ce(In_{3-x}Sn_x)$ suppresses the antiferromagnetic order found in $CeIn_3$ when the Sn content x is increased to above ~ 0.5. Further evolution of the physical properties with x, hence increasing hybridization, has been shown to follow a well-defined scaling behavior [4] particularly in the range $2 < x < 3$. Neutron scattering measurements on the series of compounds $Ce(In_{3-x}Sn_x)$ show the merger of the crystal field excitation and the quasielastic response into a broad spectral response for $x > 0.5$ which is centered on a finite energy ω_0, identified as the characteristic energy $T_K (= \omega_0)$. Over the concentration range $2 < x < 3$ the characteristic energy increases progressively with x, from a value of $\sim 9 \pm 1$ meV at $x = 2$ reaching $\sim 40 \pm 5$ meV for $x = 3$, i.e., for the compound $CeSn_3$ [3].

A large majority of the investigations on Ce and Yb-based heavy-Fermion systems, particularly those with cubic crystalline structures have been performed on polycrystalline samples with the assumption that the physical properties of these cubic heavy-Fermion systems can be considered to be isotropic, to a good approximation. A reasonable verification of this assumption is provided by the data on a single crystal sample of $CeIn_1Sn_2$ [5]. This compound forms part of the series $Ce(In_{3-x}Sn_x)$ in which In and Sn ions are dispersed randomly on the B sites. These data showed a magnetic response that was very similar in *spectral form* both at the zone boundary (ZB) and at the zone center (ZC), except that the intensity of the response was stronger by $\sim 20\%$ at the ZB relative to the ZC. In view of the fact that one of the end-members of the series, viz. $CeIn_3$, orders antiferromagnetically and also that antiferromagnetic correlations are suggested as intrinsic to heavy-Fermion systems [6] the observed correlations in the magnetic response of $CeIn_1Sn_2$ were given this interpretation [5]. The relatively small ($\sim 10\%$) modulations in intensity, and possibly also in the *spectral form*, demonstrate that the magnetic spectral response from a cubic polycrystalline sample provides a reasonably good overall representation of its dynamic magnetic susceptibility. Similar conclusions about polycrystalline and single crystal data were also reached by Lawrence *et al.* [7] from their measurements on a single crystal of $YbInCu_4$ based on the similarity of the magnetic spectral response at the ZB and the ZC, with, however, a small $\sim 10\%$ increase in intensity at the ZB.

Another aspect of the measurements on polycrystalline heavy-Fermion systems of Ce and Yb is that they were mostly performed with the use of unpolarized neutrons on time-of-flight spectrometers where the separation of magnetic and nonmagnetic (mainly phononic) contributions is often performed with reference to a nonmagnetic isostructural sample [8]. Although this method has proved quite successful and has been widely used in the analysis of time-of-flight data on magnetic systems, there are occasions when results obtained with this technique have en-

countered disagreement. For example, basing on measurements on a single crystal sample of $CePd_3$ using a three axis spectrometer (and also unpolarized neutrons) Shapiro *et al.* [9] have claimed to observe significant magnetic scattering at very much lower energies than reported by the time-of-flight studies on this compound [10]. Recent measurements by Lawrence *et al.* [11] on a single crystal sample using the time-of-flight spectrometer MAPS with position sensitive detectors are now attempting to address this controversy. Very interestingly, the latter study on $CePd_3$ has also brought into evidence modulations in intensity of ~10% (about the mean variation) in the magnetic response between the ZC and ZB that are apparently similar, or equivalent, to our earlier observations on the $CeIn_1Sn_2$ single crystal [5]. Similar measurements to those on $CePd_3$ were also reported earlier on $YbAl_3$ [12].

In this Letter we report the results of a neutron polarization analysis study of the same $CeIn_1Sn_2$ single crystal sample as used in our previous investigation [5]. This technique enables one to access the magnetic scattering directly as can be seen readily from two equations relating the spin-flip cross section (σ^{SF}) measured with neutron spins parallel and perpendicular to the scattering vector $\mathbf{Q}$:

$$\sigma^{\mathrm{SF}}_{\parallel \mathbf{Q}} = \sigma_{\mathrm{mag}} + \tfrac{2}{3}\sigma_{\mathrm{inc}} + \text{background}$$
$$\sigma^{\mathrm{SF}}_{\perp \mathbf{Q}} = \tfrac{1}{2}\sigma_{\mathrm{mag}} + \tfrac{2}{3}\sigma_{\mathrm{inc}} + \text{background}.$$

Hence, a subtraction of the two cross sections yields the magnetic scattering ($\frac{1}{2}\sigma_{\mathrm{mag}}$) directly, eliminating incoherent scattering (σ_{inc}) and background, as well as other nonmagnetic contributions, e.g., phonons, which do not appear in the spin-flip (SF) channels, except for some ''leakage'' of nonmagnetic scattering due to finite beam polarization ($p = 0.8$ in these measurements). However, since our flipping ratios were isotropic in the three orthogonal directions (x, y, z) these nonmagnetic contributions appear equally in the two SF channels and, thus, cancel out to a very good approximation.

The present investigation was performed on the IN20 spectrometer at the ILL, with the outgoing neutron wave vector k_f kept fixed at 4.1 $\mathrm{Å}^{-1}$ and using a graphite filter in the outgoing beam. The flipping ratio measured on a Si (111) Bragg peak was ~12 and isotropic. It was found to reduce isotropically to ~8 ($p \sim 0.8$) with the $CeIn_1Sn_2$ sample placed inside the cryostat.

In Fig. 1 we show the magnetic scattering observed at the ZB as a function of energy transfer ω. The data are closely similar to those obtained earlier using unpolarized neutrons [5]. In view of the limited amount of available beam time we did not attempt to measure the magnetic response at the ZC also, but our previous data using unpolarized neutrons have shown the similarity in the spectral form at the two principal reference points in the Brillouin zone. Within the statistical precision of the data, hence the resultant error bars in the parameters of the fits, we were

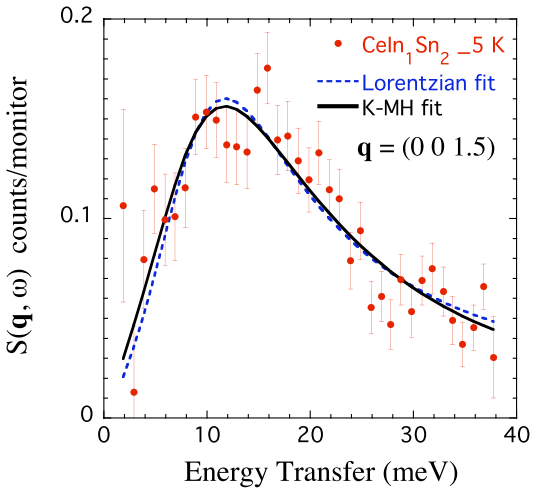

FIG. 1 (color online). Paramagnetic spectral response from the $CeIn_1Sn_2$ sample at 5 K at the ZB point (0 0 1.5). The continuous curve represents a fit to the Kuramoto and Müller-Hartmann spectral function [13] and the dashed curve represents the Lorentzian spectral fit. Parameters resulting from the fits are given in the text.

unable to ascertain small changes (~10%) in the width or the centroid of the magnetic response that may be expected on the basis of the moment sum rule. The continuous curve through the data in Fig. 1 represents a least-squares fit to the analytic function of Kuramoto and Müller-Hartmann [13] calculated for the single impurity Anderson Hamiltonian, viz.,

$$f(\omega) = \frac{C_1\alpha}{u^2(u^2+4\alpha^2)}\Big[\alpha \ln((1-u^2)^2 + 4u^2\alpha^2) + |u|\Big(\frac{\pi}{2} - \tan^{-1}\frac{1-u^2}{2|u|\alpha}\Big)\Big],$$

where $u = \omega/\omega_0$ and $\alpha = \sin(\pi\langle n_f\rangle/N)$, with ω_0 the characteristic energy, $\langle n_f\rangle$ the $4f$ occupancy, N the degeneracy of the $4f$ state and C_1 is a constant. It is perhaps useful here to recall that the scattering cross section for a single-ion can be expressed as

$$S(Q,\omega) = C_2(1-\exp(-\omega/T))^{-1}\omega f(\omega)F^2(Q),$$

where the Q dependence is contained within the form factor $F^2(Q)$ only. Parameters obtained from the spectral fit to the data are $\omega_0 = 9.4 \pm 0.3$ meV and $\alpha = 0.69 \pm 0.08$ from which we deduce the ground state degeneracy $N = 4.1 \pm 0.85$, assuming the $4f$ occupancy $\langle n_f\rangle = 1$. This is close to the ground state degeneracy $N = 6$ for the $J = 5/2$ state. Indeed, the precision of the data, with their error bars, is such that an almost equally good fit (with only slightly different χ^2) is obtained with N held fixed to the value 6. This yields $\omega_0 = 9.6 \pm 0.3$ meV. An alternative fit to the data using the Lorentzian form of the spectral response, viz.,

$$f(\omega) = \frac{\Gamma/2\pi}{\Gamma^2 + (|\omega| - \omega_0)^2}$$

yields $\omega_0 = 8.0 \pm 0.8$ meV and the spectral half-width $\Gamma = 8.7 \pm 0.4$ meV.

The magnitudes of the characteristic energies ω_0 of 9.4 ± 0.3 meV and 8.0 ± 0.8 meV obtained from the two types of fits are reasonably close to the characteristic energy $T_K = 8.6$ meV obtained from the low temperature susceptibility data [14] $\chi(0) = 8.0 \times 10^{-3}$ emu mole^{-1} via the Fermi liquid relation $\chi(0) = \mu^2\langle n_f\rangle/3T_K$ of Ramakrishnan and Sur [15] for the single-ion Anderson model. The latter is equivalent, in the limit of large degeneracy N, to the relation $\chi(0) = N\mu^2 \sin(\pi\langle n_f\rangle/N)/3\pi T_K$ obtained by Kuramoto and Müller-Hartmann [13], also from the single-ion Anderson Hamiltonian.

In Fig. 2 we show constant-ω scans at 13 meV as well as at 18 meV along the $[00\xi]$ direction. These scans show modulations in intensity between the ZC and the ZB with an amplitude of ~10% about the mean, or overall, variation that is well represented by the Ce^{3+} single-ion $4f^1$ form factor. The observed intensity modulations are very similar for both energies, and also with those at 25 meV studied earlier [5] using unpolarized neutrons. Similar

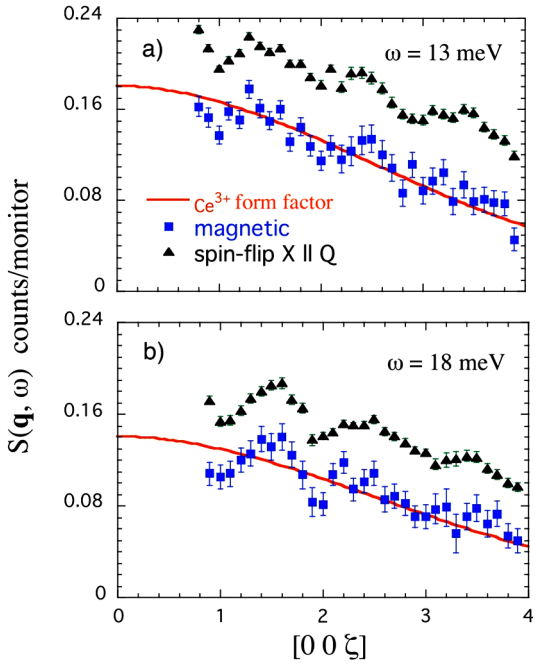

FIG. 2 (color online). Constant-energy scans along $[00\xi]$ at (a) $\omega = 13$ meV and (b) $\omega = 18$ meV, performed on the $CeIn_1Sn_2$ single crystal sample at 5 K. The data also show the as-measured spin-flip scattering ($\sigma^{SF}_{\|Q}$) parallel to the scattering vector Q (triangles) which consists of the magnetic cross-section, plus incoherent and background scattering contributions. The continuous curve is the Ce^{3+} form factor through the data representing the magnetic scattering (squares) given by $2(\sigma^{SF}_{\|Q} - \sigma^{SF}_{\perp Q})$.

modulations in intensity, of amplitude ~10%, have also been seen in $CePd_3$ [11] in the two dimensional intensity-map in the K-L plane obtained by integrating the scattering within a narrow energy range, of $50 < \omega < 70$ meV, around the maximum in the magnetic response, and well above the phonon cutoff. The latter investigation did not include constant-ω scans similar to those presented here. However, the data represented by the two dimensional intensity-map for $CePd_3$ are equivalent to the present observations on $CeIn_1Sn_2$ in that, along $[00\xi]$, they both indicate a higher magnetic scattering intensity at the ZB compared to the ZC by about the same amount, ~20%. A similar investigation to that on $CePd_3$ was reported earlier for $YbAl_3$ [12], whose magnetic spectral response is rather complex [8,12,16]. Also, as mentioned earlier, neutron scattering measurements on a single crystal of $YbInCu_4$ [7] show a single-ion spectral response with a ~10–15% higher intensity at the ZB, in its low temperature phase.

Limiting our considerations, for the present, to $CePd_3$ [11] and $CeIn_1Sn_2$ it is evident that for these two cubic heavy-Fermion systems, despite their significantly different characteristic energies of ~9 and ~55–60 meV [5] the spectral response is qualitatively quite similar, showing weak modulations of intensity of similar amplitude (~10%) between the ZC and ZB, along the $[00\xi]$ direction. These modulations of spectral intensity observed for $CePd_3$ have been interpreted [11] as due to transitions across a gap formed by hybridization between the conduction electrons and $4f$ bands. In the present case of $CeIn_1Sn_2$ we have seen that the mean, overall variation follows the $4f^1$, Ce^{3+} single-ion form factor and this clearly implies that the hybridized state has the localized single-ion character. For, if the intensity modulations were associated with hybridization between the conduction electrons and a $4f$ band, the mean structure factor (i.e., overall intensity variation as a function of Q) would be very different from the single-ion form. This is because band formation involves a substantial quenching (reduction) of the spin as well as the orbital moment, the reduction relative to their single-ion values being, in general, much larger for the orbital component, as demonstrated for the actinides [17]. This would, therefore, yield a significantly narrower form-factor comparable, quite possibly, to that calculated for α-Ce assuming an itinerant $4f$ band [18].

Observations of intensity modulations of very *similar amplitude* at roughly the same temperature in two heavy-Fermion systems with characteristic energies differing by almost an order of magnitude rules out simple antiferromagnetic intersite correlations as a possible mechanism. This is because the strength of the intersite correlations should vary in some inverse relation to the characteristic energy. We believe, however, the observed phenomenon could be due to the significant **q**-dependence in the hybridization process which is, necessarily, **q**-dependent for non-cubic heavy-Fermion systems where the low temperature

susceptibilities $\chi(0)$ are often markedly different along the principal crystallographic axes. It is, however, an open question whether such modulations as observed here would be seen in dilute systems also, or whether the coherence resulting from scattering from (or hybridization with) a periodic lattice of single-ions is a necessary requirement.

In this context it is interesting that disorder due to the random distribution of Sn and In on the B sublattice of $CeIn_1Sn_2$ has practically no influence on the magnetic properties of the compound since, as shown by Lawrence [4], the system $Ce(In_{3-x}Sn_x)$ evolves homogeneously with x, particularly in the range $2 < x < 3$. Neutron data on the series of compounds $Ce(In_{3-x}Sn_x)$ [1] also bear this out in that the characteristic energy ω_0 increases almost linearly with increasing x, while maintaining its ratio with respect to the spectral width Γ roughly constant and equal to that for the pure compound $CeSn_3$. On the other hand disorder in the Ce sublattice, by dilution with La, has a very significant impact on the form of the spectral response [19] which becomes highly distorted transforming into a very broad quasi-elastic-like structure for La substitutions of $\sim 40\%$.

Finally, there is the question of the possible Q dependence of spectral response related to the observed coherence in many physical properties; electrical resistivity, de Haas–van Alphen oscillations showing highly renormalized masses at the Fermi surface, etc. In several theoretical treatments, for example [20], the imaginary part of the susceptibility response is shown to be qualitatively divided into two parts; one due to the f states, which in the present case are localized and energy broadened, and the other representing the itinerant band states (conduction electrons) which are renormalized due to the hybridization with f electrons. However, the susceptibility response associated with these itinerant states is expected to be relatively weak, extending over a large energy range (~ 2 eV) and confined to very low Q. Both these are well outside the Q-ω range covered in the present investigation.

In conclusion, using neutron polarization analysis to access the magnetic scattering directly, we have found that small modulations of intensity with an amplitude of $\sim 10\%$ between the zone boundary and zone center, resembling antiferromagnetic correlations, are superimposed on an overall variation, with Q, that is intrinsically single-ion-like, following closely the Ce^{3+} form factor for the localized $4f^1$ state. The results thus demonstrate that the $4f$ state in this system maintains its single-ion character. Additional evidence for the single-ion character of the $4f$ state of $CeIn_1Sn_2$ is provided by the *spectral form* of the magnetic scattering that is well described by the analytic function for the single-ion Anderson Hamiltonian. Furthermore, the characteristic energy ω_0 obtained from a fit to the data to the latter function is in good accord with the single-ion Fermi liquid relation relating the low temperature susceptibility $\chi(0)$ with the characteristic energy T_K. The observed modulations in intensity are tentatively attributed to $\mathbf{q}$ dependence in the hybridization. Clearly some theoretical input is needed to help us reach a proper understanding of this very interesting phenomenon.

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