Evidence for paramagnetic scattering from nonmagnetic Ce sites in the compound Ce$_2$Sn$_5$

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We report the observation of a broad, high-energy single-ion spectral response originating from the ''nonmagnetic'' Ce sites (Ce$_I$) in the compound Ce$_2$Sn$_5$, which supplements earlier findings of two sharp low-energy (<20 meV) crystal-field excitations from the ''magnetic'' Ce sites (Ce$_{II}$). This provides clear *microscopic* evidence for the existence of different *paramagnetic* states of Ce ions on inequivalent crystallographic Ce sites in a compound as well as the dominant role of the local environment in determining their basic character. We have also observed two distinct, high-energy spin-orbit excitations, viz. a well defined peak around $\sim 274(\pm 3)$ meV associated, as expected, with the magnetic Ce$_{II}$ atoms and a broad hump centered on $\sim 350(\pm 10)$ meV arising, quite plausibly, from the nonmagnetic Ce$_I$ sites which suggests that the characteristic energy T_K of the $^2F_{7/2}$ spin-orbit state of Ce$_I$ ion is $\sim 75(\pm 10)$ meV, compared with $T_K \sim 36$ (± 3) meV for its ($^2F_{5/2}$) ground state. [S0163-1829(97)06218-8]

Physical and magnetic properties of Ce$_2$Sn$_5$, the next intermetallic compound after CeSn$_3$ from the Sn-rich end of the Ce-Sn binary series,[1] have received some attention in recent years.[2-7] The compound has the orthorhombic crystal structure with $a \approx c$ (~ 4.6 Å) and an elongated b axis (~ 35 Å). It can be considered[3] as a superstructure of the fcc (AuCu$_3$) compound CeSn$_3$ (lattice parameter $a \sim 4.7$ Å) derived by stacking the basic CeSn$_3$ cells along the **b** direction with ordered anisotropic substitutions of the extra or additional Ce atoms on to some of the Sn sites in the (**a**,**c**) plane. There are thus two distinct crystallographic Ce sites in the lattice, viz. Ce$_I$ ions surrounded by 12 near-neighbor Sn atoms, as in CeSn$_3$, and Ce$_{II}$ ions having 10 Sn and 2 Ce$_{II}$ atoms in the surrounding near-neighbor shell.[3]

Ce$_2$Sn$_5$ orders antiferromagnetically at ~ 2.9 K.[2,4] Spin-density measurements using polarized neutron diffraction[5] as well as magnetic structure determinations[6] show clearly that only Ce$_{II}$ atoms carry well defined magnetic moments and participate in the magnetic order, while Ce$_I$ atoms appear to be nonmagnetic. In a neutron inelastic-scattering study of Ce$_2$Sn$_5$ Bonnet *et al.*[7] observed two well defined crystal-field excitations at low temperatures which were attributed to the ''magnetic'' Ce$_{II}$ atoms. A quantitative crystal-field analysis performed by the authors was found to give an adequate account of the observed magnetic properties of the compound.[7]

The basic nature or the exact magnetic character of the ''*nonmagnetic*'' Ce$_I$ ions in Ce$_2$Sn$_5$ has, however, remained unexplored so far. In a recent paper on compounds with two or more inequivalent Ce sites Gschneidner and Pecharsky[8] have regretted that ''there is no suitable technique, such as NMR or Mössbauer effect to probe the local environment, and so one must rely on an analysis of magnetic, thermodynamic, and electrical property measurements in addition to a crystalline structural analysis to unravel their behavior and to understand their basic nature.''

Neutron-diffraction techniques can be applied to study the crystalline as well as the magnetic structure of a compound. The latter enables us to identify magnetically ordered sites from those that do not order magnetically which appear simply as nonmagnetic. Similarly, spin-density measurements using polarized neutrons, for example on Ce$_2$Sn$_5$ and Ce$_3$Sn$_7$, have permitted to distinguish the magnetic sites (Ce$_{II}$) from the nonmagnetic ones (Ce$_I$), but the basic nature of the latter sites was not resolved from these measurements. The present communication illustrates the usefulness of the neutron *inelastic* scattering as the much needed local probe for providing information on the basic character of the nonmagnetic sites also.

In the following we report on a detailed neutron inelastic-scattering investigation of the compound Ce$_2$Sn$_5$ using epithermal neutrons of incident energy 100 and 200 meV which identify, unambiguously, a broad high-energy magnetic response from the nonmagnetic Ce$_I$ ions with spectral weight, hence the (energy integrated) magnetic moment, comparable to that of the magnetic Ce$_{II}$ ions. Additionally, use of relatively high-energy neutrons ($E_i = 600$ meV) has permitted very interesting observations of two distinct spin-orbit excitations viz., a well defined peak situated on ~ 274 meV, close to the spin-orbit energy of the isolated Ce^{3+} ion and a broad hump, situated on a significantly enhanced energy of ~ 350 meV.

In Fig. 1 we show the results of measurements on Ce$_2$Sn$_5$ with 100 meV neutrons. The two well defined inelastic peaks at 5.3 and 12.1 meV represent the crystal-field excitations which have been studied in detail previously.[7] A closer examination of the energy region above ~ 20 meV indicates the presence of broad, thinly spread scattering whose magnetic origin is evident from the fact that its intensity decreases with increasing scattering angle. We have investigated this higher-energy region using neutrons of incident energy 200 meV. A fit to the magnetic component of the latter data (described below) is superposed on the 100 meV data in Fig. 1, adjusting only the intensity variation via
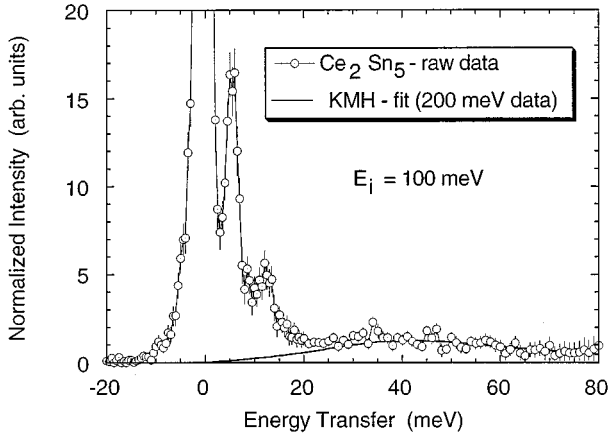
FIG. 1. As-measured low-angle ($\langle 2\Theta \rangle = 5°$) spectrum $S(\Theta,\omega)$ for the compound Ce_2Sn_5 at ~ 20 K. The thick continuous curve is computed for $E_i = 100$ meV using the parameters of the fit to the high-energy response studied with 200 meV neutrons.

the Ce^{3+} form-factor dependence. The close fit illustrates the consistency of the two data sets.

Increasing the incident energy to 200 meV, of course, broadens the energy resolution ΔE significantly (more than proportionately) as can be seen from the width of the zero-energy incoherent elastic peak for the nonmagnetic reference compound $LaSn_3$, Fig. 2(a). Hence the resolution broadened zero-energy nonmagnetic incoherent scattering as well as the
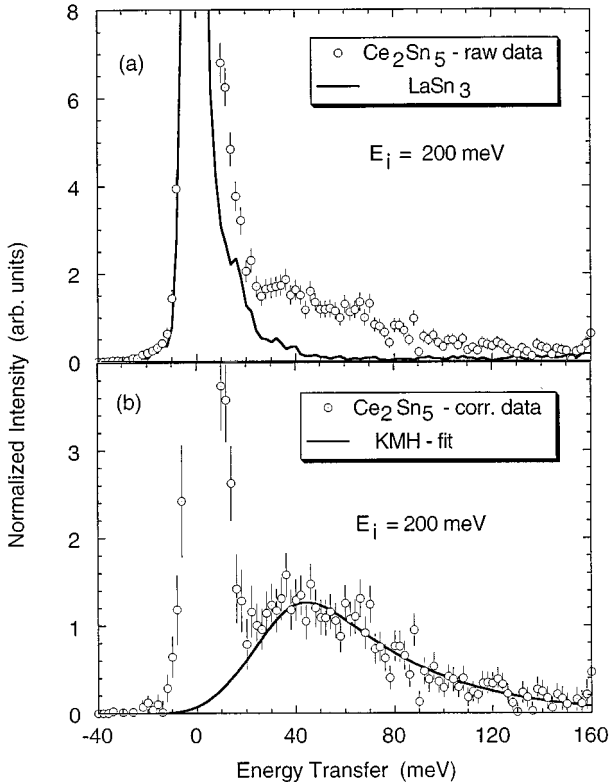

FIG. 2. (a) Normalized intensity of the as-measured inelastic-scattering from Ce_2Sn_5 and $LaSn_3$ compounds. (b) The resultant magnetic response obtained after correction of the nonmagnetic contribution using scattering from $LaSn_3$ as the nonmagnetic reference.

two inelastic crystal-field excitations merge into a broad, low-energy structure which, in view of its spectral extent, also incorporates phononic scattering. The raw data for Ce_2Sn_5, converted from time-of-flight to $S(\Theta,\omega)$, are shown in Fig. 2(a), whereas the data with the nonmagnetic contribution subtracted out, with reference to, scattering from $LaSn_3$, are shown in Fig. 2(b). The thick continuous curve represents a fit using the single-ion spectral function of Kuramoto and Müller-Hartmann[9] for an Anderson impurity, viz.

$$S(Q,\omega) = \frac{C\chi(Q)F^2(Q)}{[1-\exp(-\omega/T)]} \frac{\alpha\omega}{u^2(u^2+4\alpha^2)}$$

$$\times \left\{ \alpha \ln[(1-u^2)^2 + 4u^2\alpha^2] \right.$$

$$\left. + |u|\left[\frac{\pi}{2} - \tan^{-1}\left(\frac{1-u^2}{2|u|\alpha}\right)\right]\right\}, \tag{1}$$

where C is a constant, $\chi(Q)$ is the static susceptibility, $F(Q)$ is the magnetic form factor, and $[1-\exp(-\omega/T)]^{-1}$ is the detailed balance factor. The variable $u = \omega/\omega_0$, where ω_0 is the characteristic energy (or T_K) and $\alpha = \sin(\pi\langle n_f\rangle/N)$, with $\langle n_f\rangle$ the occupancy and N the degeneracy of the $4f$ state. The parameter α has influence mainly on the spectral shape at low energies below the maximum in the spectral response. Since the low-energy region (<20 meV) contains magnetic scattering (crystal-field excitations) from the Ce_{II} sites as well as nonmagnetic scattering, we have excluded it from the fit which was performed fixing the parameter α ($= \sin \pi\langle n_f\rangle/N$) to 0.5, corresponding to degeneracy $N = 6$, and $4f$ occupancy $\langle n_f\rangle \sim 1$. We obtain a characteristic energy of $\sim 36(\pm 3)$ meV, closely similar in magnitude to that for $CeSn_3$.[10]

At first sight the above results may not appear entirely surprising for several reasons such as the fact that the estimated magnetic susceptibility[7] associated with the Ce_I sites in Ce_2Sn_5 is similar to that of $CeSn_3$ and that the linear term γ in the specific heat[7] of Ce_2Sn_5 at temperatures above the strong magnetic ordering peak is similar in magnitude to that for $CeSn_3$. We note however, that the coefficient γ deduced this way in the presence of other strong magnetic contributions does not always constitute entirely reliable information about the basic character of Ce_I ions as seen from the fact that the specific-heat coefficient γ for the compound Ce_3Sn_7 is apparently indistinguishable from zero,[7] although a third of the Ce ions in that compound also occupy Ce_I-type sites. Preliminary neutron inelastic data on this compound indicate that the magnetic response from the Ce_I sites in Ce_3Sn_7 is also similar to that for the other two compounds. While the central result from the present measurements, namely that the magnetic response (hence the basic magnetic character) of the Ce_I ion is determined principally by the local near-neighbor environment of 12 Sn atoms, may appear normal or ''expected,'' its full significance may, however, be rather profound.

In Fig. 3 we show high-energy data obtained using neutrons of incident energy 600 meV where we have again estimated and subtracted out the nonmagnetic contribution with $LaSn_3$ as reference. The continuous curve in Fig. 3 represents a resolution-convoluted fit to the data using the spec-
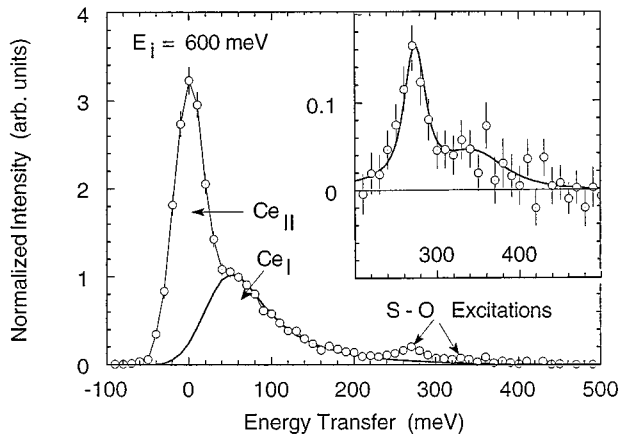
FIG. 3. Normalized magnetic scattering from Ce_2Sn_5 after subtraction of the nonmagnetic contribution using $LaSn_3$ as a reference. The thick continuous curve represents a least-squares fit to data using the single-ion spectral function of Kuramoto and Müller-Hartmann over the energy range $50 < \omega < 200$ meV. The inset shows the residue relative to the fitted curve on an expanded vertical scale. The continuous curve represents a least-squares fit to the residue assuming two Lorentzian spectral components, as described in the text.

tral function of Kuramoto and Muller-Hartmann[9] with the parameter α again held fixed to the value 0.5 ($= \sin \pi \langle n_f \rangle / N$, with $N = 6$ and $\langle n_f \rangle = 1$). The fit was performed over the energy range $50 < \omega < 200$ meV only, and extrapolated outside this range. Existence of some residual signal, relative to the fitted curve, in the energy region ~ 250 to 500 meV is clearly evident in Fig. 3. We associate it with spin-orbit excitations to the higher-lying $^2F_{5/2}$ states. This residual signal is shown on an expanded vertical scale in Fig. 3 where the continuous curve represents a least-squares fit to the data assuming two Lorentzian spectral components to represent the two spin-orbit excitations. The centroids of the excitations are found to be situated on ~ 274 (± 3) and $\sim 350 (\pm 10)$ meV and their half-widths are $\sim 15 (\pm 3)$ and $55 (\pm 15)$ meV, respectively. Due to its large width the latter excitation appears relatively weak but is, nevertheless, statistically significant and meaningful. It is, in fact, very similar in energy and width to the spin-orbit excitation observed earlier in the compound $CeSn_3$ [where despite weak statistical accuracy an evolution in energy and width of the spin-orbit excitation with increasing x in the pseudobinary series $Ce(In_{1-x}Sn_x)_3$ has been clearly observed, Ref. 15]. Its reality is further substantiated by measurements, under identical experimental conditions, and during the same set of measurements hence the same instrumental condition, on the nonmagnetic reference sample $LaSn_3$ which do not show any such structure around this energy.

The well-defined spin-orbit excitation at ~ 274 meV can, quite naturally, be associated with the normal or magnetic Ce_{II} sites and its relatively large half-width of ~ 15 (± 3) meV at 20 K must, therefore, reflect the overall crystal-field splittings of the $^2F_{7/2}$ spin-orbit state. Neither the statistical accuracy of the data nor the broad energy resolution associated with the high incident energy neutrons ($E_i = 600$ meV) necessary for the excitations, of course, per-

mit us to resolve the crystal-field levels. For the Kramer's ion Ce^{3+}, a crystal field of orthorhombic symmetry will lift the sixfold and eightfold degeneracies of the two spin-orbit states $^2F_{5/2}$ and $^2F_{7/2}$ into three and four doublets respectively. The splitting of the ground state into three doublets was confirmed earlier,[7] as well as by the present measurements (Fig. 1). Hence, we conclude that the observed half-width of ~ 15 meV for the spin-orbit excitation is consistent with an overall crystal-field splitting of similar magnitude for the upper $^2F_{7/2}$ state.

However, the energy and width of the spin-orbit excitation associated with the nonmagnetic Ce_I sites in Ce_2Sn_5 represents quite a different phenomenon. In the Anderson single impurity model the ground state for such a strongly hybridized ion is a nonmagnetic singlet[11] so that the observed broad Lorentzian-like spectral response centered on ~ 36 meV represents excitations from this singlet to the $^2F_{5/2}$ state which is renormalized upward by its characteristic energy T_K (~ 36 meV). In general,[11] a state i should be renormalized upward by its characteristic energy $T_K^i \sim D \exp(-\pi |\varepsilon_i| / N_i \Delta_i)$, where the energy ε_i is measured relative to the Fermi level, N_i is the degeneracy, Δ_i is the hybridization parameter, and D is an effective bandwidth parameter (see Ref. 11). Hence, it follows that the characteristic energy of the upper spin-orbit state, $^2F_{7/2}$, should be larger since its degeneracy N_i is larger (8 compared with 6) and $|\varepsilon_i|$ is smaller due to its closer proximity to the Fermi level. Additionally, the latter fact implies that the hybridization parameter Δ_i for the $^2F_{7/2}$ state may also be larger, if at all different from that for the $^2F_{5/2}$ state, again contributing to a larger T_K for that state. In sum, the relatively broad spin-orbit excitation of half-width ~ 55 meV observed at ~ 350 meV suggests that the $^2F_{7/2}$ state is renormalized upwards relative to the ground singlet by its characteristic energy of ~ 75 meV, which is roughly twice that for the $^2F_{5/2}$ ground state.

The present measurements on Ce_2Sn_5 show clearly that the nonmagnetic character of the Ce_I ion evident from the spin-density maps[5] and magnetic structure determinations[6] is related to the large spectral extent of its paramagnetic response, i.e., its large characteristic energy T_K which, according to current theoretical models,[11] imply relatively strong interactions or hybridization with *conduction* electrons. As a consequence, crystal-field splittings are quenched and the ground ($^2F_{5/2}$) and excited ($^2F_{7/2}$) spin-orbit states are broadened and renormalized upwards relative to the low-temperature nonmagnetic singlet[11] by $\sim 36 (\pm 3)$ and ~ 75 (± 10) meV, respectively. *However*, the observed similarity of the form and extent of the magnetic response from $CeSn_3$ with that from Ce_I sites which have the same local environment of 12 Sn near-neighbor atoms, as well as the fact that a Ce ion having two other Ce atoms in the surrounding near-neighbor shell (Ce_{II} sites) behaves as a normal magnetic ion, suggests that interactions involving electrons within the immediate *local environment*, rather than the overall *conduction bands*, as commonly believed, play a very significant role in determining the magnetic character of the Ce ions. A similar phenomenon was reported three decades ago by Jaccarino and Walker[12] for a $3d$ transition metal impurity (e.g., Fe) in a binary, metallic host matrix.

A rather simple criterion for magnetic or nonmagnetic character of a lattice of Ce ions, based on the idea of ''delocalization'' of the $4f$ electron determined by the Ce-Ce separation, has been proposed by Hill.[13] While at first sight, the present observations that the magnetic character of Ce_I ions which are separated from other Ce_I ions by ~ 4.6 Å appear to conform with the Hill criterion that in Ce compounds with Ce-Ce separation greater than 3.5 Å the observed delocalization of the $4f$ electron occurs via hybridization with the neighboring ligands, the fact that for the magnetic Ce_{II} sites which have two other Ce_{II} ions in the near-neighbor shell at a distance of <4.1 Å the increased Ce-Ce overlap apparently *stabilizes* the magnetic moment rather than the contrary clearly argues against its general applicability. Also, it is important to recognize that the *demagnetization* of the Ce_I ion does not involve *delocalization* of the $4f$ electron, as for example in $CeSn_3$, despite the heavy band masses observed in de Haas–van Alphen measurements on this compound,[14] which are sometimes, erroneously, cited as evidence for an itinerant $4f$ band.

Our neutron measurements, on the contrary, show that the magnetic response of Ce_I ions is single-ion-like, being well described by the Anderson single-impurity spectral function.[9] Also, the observations of renormalized but well defined spin-orbit excitations in this and a number of similar compounds[15] can only sustain single-ion descriptions. Although the current theoretical models assume hybridization between the $4f$ and the conduction electrons,[11] very similar formulations should remain applicable even if the mixing interaction is confined to electrons within the near-neighbor environment. The present results clearly demonstrate a truly single-ion phenomenon, proposed for heavy fermion and valence fluctuation systems not only theoretically by many workers (e.g., Refs. 9 and 11) but also on experimental grounds from *magnetic and thermodynamic measurements* in the dilute limit.[16] In the absence of neutron investigations of the expected broad (i.e., thinly distributed over a wide energy) magnetic response in dilute systems, due partly to the difficulty of such investigations in view of the relatively low sensitivity of neutron spectrometers, the present measurements provide clear although indirect evidence that ''moment formation'' even in a regular lattice of Ce ions is essentially a single-ion phenomenon. Finally, we hope that the present investigation has demonstrated the usefulness of neutron *inelastic* scattering as a local probe for the basic nature, i.e., the magnetic character, of ions on different crystallographic sites in multisite systems.

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