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Magnetic spectral response in the intermetallic compound $CeSn_3$

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Neutron–inelastic-scattering measurements on $CeSn_3$ performed with high-incident-energy neutrons reveal a broad inelastic hump centered around 40 meV at low temperatures, in addition to the usual quasielastic spectrum centered on zero energy. With increasing temperature, the inelastic hump broadens and "melts away," such that around the temperature of the maximum in the susceptibility (~130 K) no observable trace of its presence remains and the full magnetic response can be described by a single quasielastic spectrum.

Many of the anomalous physical properties observed in rare-earth alloys and compounds are believed to represent valence-fluctuation phenomena.[1] Among the rare earths, Ce and Yb compounds show such anomalies most frequently, although several alloys and compounds containing Sm, Eu, and Tm are also known to show valence-fluctuation behavior.[1]

We report neutron–inelastic-scattering measurements on $CeSn_3$ which crystallizes in the $AuCu_3$ structure. The lattice constant as well as anomalously high thermal expansion of $CeSn_3$ compared with $LaSn_3$ suggest a weak intermediate valency.[2] The electronic specific-heat coefficient γ is enhanced[3] and the magnetic susceptibility[4] shows a broad maximum around ~130 K—both characteristic features of intermediate valent as well as Kondo-type systems. Induced magnetic form-factor studies show deviations from the Ce^{3+} form factor at low temperatures.[5] The most commonly adopted description of the low-temperature phase of such system is in terms of paramagnon or Fermi-liquid theories.[6] de Haas–van Alphen measurements on $CeSn_3$ (Ref. 7) indicate strongly hybridized f states at the Fermi level with large effective masses suggesting possible itinerant character of the f electrons. A clear evidence for the change in the nature of the $4f$ state at low temperatures is provided by the NMR Knight shift[8] in $CeSn_3$, which shows deviations from its linear dependence on the susceptibility below the temperature of the maximum in the latter.

The neutron scattering measurements were performed on the IN4 thermal beam time-of-flight spectrometer at the Institut Laue-Langevin with use of neutrons of incident energy 50.4 and 81.8 meV. In Fig. 1 the spectral response $[n(\omega)+1]^{-1}S(Q,\omega)$ measured with neutrons of incident energy 50.4 meV at constant scattering angles 2θ is shown for the $CeSn_3$ and the $LaSn_3$ samples. We note that at low angles ($2\theta=7.2°$) the spectral response for $CeSn_3$ contains both magnetic and phonon scattering contributions, whereas at the highest scattering angle ($2\theta=135°$) which corresponds to $Q=9$ Å^{-1}, the magnetic contribution is negligibly small. The observed extent of the phonon energy range ($|\omega|\lesssim 20$ meV) is in good agreement with the phonon dispersion curves measured on single-crystal samples.[9] Furthermore, because the compounds are polycrystalline the phonon scattering is sampled over many Brillouin zones and spatially averaged and can be scaled over the whole energy range for any two fixed scattering angles θ and θ' by a simple scaling function $C_\theta^{\theta'}(\omega)$.

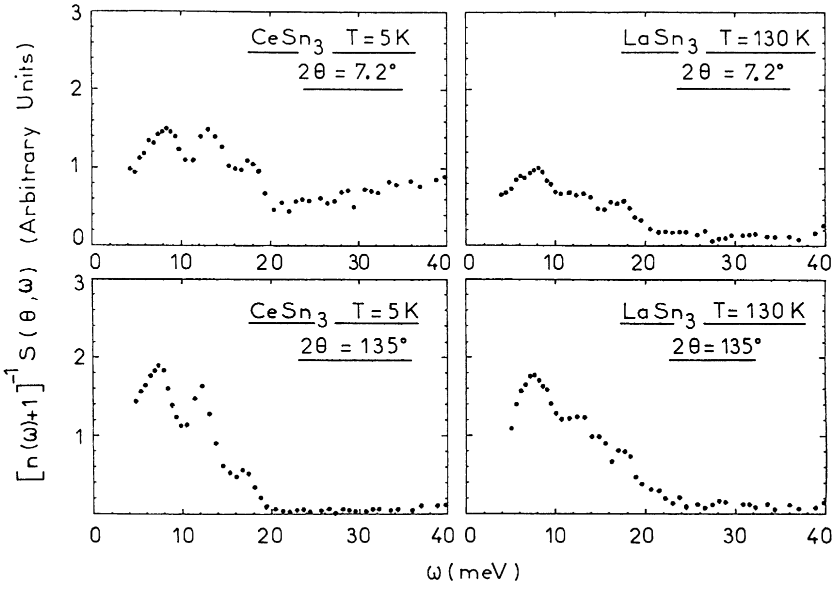

FIG. 1. Low-temperature spectral response $[n(\omega)+1]^{-1}S(Q,\omega)$ for fixed scattering angles 2θ, representing the low-angle (phonon and magnetic) and the high-angle (phonon only) spectra for the $CeSn_3$ and $LaSn_3$ samples.

Such a scaling provides a simple way to subtract out phonons from the low-angle data for the magnetic sample, using the same function $C_\theta^{\theta'}(\omega)$ between a pair of high- and low-angle spectra as for the LaSn$_3$ alloy, since phonon frequencies are closely similar in both alloys. Thus having obtained $C_\theta^{\theta'}(\omega)$ for the LaSn$_3$ sample the same function is used to scale the phonon scattering observed in the corresponding high-angle data for the CeSn$_3$ sample, which is then subtracted out from the low-angle data to obtain the purely magnetic contribution.

The scattering cross section for an isotropic paramagnet can be expressed as[10]

$$\frac{d^2\sigma}{d\Omega\, d\omega} \propto \frac{k'}{k_0} S(Q,\omega,T) \propto \frac{k'}{k_0}[n(\omega)+1]\chi''(Q,\omega,T) \ . \qquad (1)$$

Since the low-temperature data in Fig. 1 clearly indicate the presence of both a quasielastic and a broad inelastic scattering hump we express the susceptibility $\chi''(Q,\omega,T)$ in terms of Lorentzians centered about $\omega=0$ and $\omega=\pm\omega_1$. Thus

$$\chi''(Q,\omega,T) = F^2(Q)\omega\left[\frac{a_0(T)\Gamma_0(T)}{\omega^2+\Gamma_0^2(T)} + \frac{a_1(T)\Gamma_1(T)}{(\omega-\omega_1)^2+\Gamma_1^2(T)} + \frac{a_1(T)\Gamma_1(T)}{(\omega+\omega_1)^2+\Gamma_1^2(T)}\right] \ . \qquad (2)$$

Hence the Kramers-Kronig relation yields

$$\chi(Q,T) = [a_0(T)+2a_1(T)]F^2(Q) \ ,$$

where $\Gamma_0(T)$ and $\Gamma_1(T)$ are the widths of the central quasielastic and inelastic peaks and $a_0(T)$ and $a_1(T)$ are the amplitude factors. We have proceeded to fit the data to Eq. (2) taking $a_0(T)$, $a_1(T)$, $\Gamma_0(T)$, $\Gamma_1(T)$, and ω_1 as free variable parameters. However, having determined ω_1 reasonably accurately from the low-temperature data we have subsequently kept it fixed, thus reducing the number of variables to four.

In Fig. 2 we show the inelastic spectra (corrected for the variation of intensity with Q for fixed scattering angles 2θ, using the Ce^{3+} form-factor dependence)[11] together with solid curves representing the best fit to the data. The fitted parameters permit us to compute the static susceptibility $\chi(Q)$, which is plotted in Fig. 3 together with the measured bulk susceptibility, where the neutron data have been scaled to the bulk measurements. We note that the measured $\chi(Q)$ follows reasonably closely the bulk susceptibility $\chi(0)$ except at low temperatures, where the bulk susceptibility shows the well-known Curie-type upturn, often attributed to extrinsic effects such as impurities, although the induced magnetic form-factor measurements[5] suggest it to be at least partly intrinsic.

The linewidths of the broad quasielastic and inelastic spectral peaks are shown in Fig. 4. The quasielastic linewidth is found to be 11 ±1 meV at 5 K and increases to about 30 ±6 meV at 130 K, beyond which it shows a tendency to saturate out (or to decrease slightly). The linewidth of the broad inelastic hump also increases with temperature, but its spectral weight decreases rapidly. This is illustrated in Fig. 4(b), where the ratio $a_1(T)/a_0(T)=\alpha(T)$ is plotted as a function of temperature.

This inelastic hump in CeSn$_3$ with its unusual temperature dependence is a new feature which has previously not been observed. The earlier neutron-inelastic-scattering measurements on CeSn$_3$ (Ref. 12) show a broad quasielastic spectrum of width ~22–25 meV at all temperatures. These measurements were, however, performed in upscattering (neutron energy gain) using low-incident-energy neutrons ($E_i=3.5$ meV). Hence, at low temperatures, as the thermal population decreases the energy range of measurements in upscattering becomes progressively more restricted. Now,

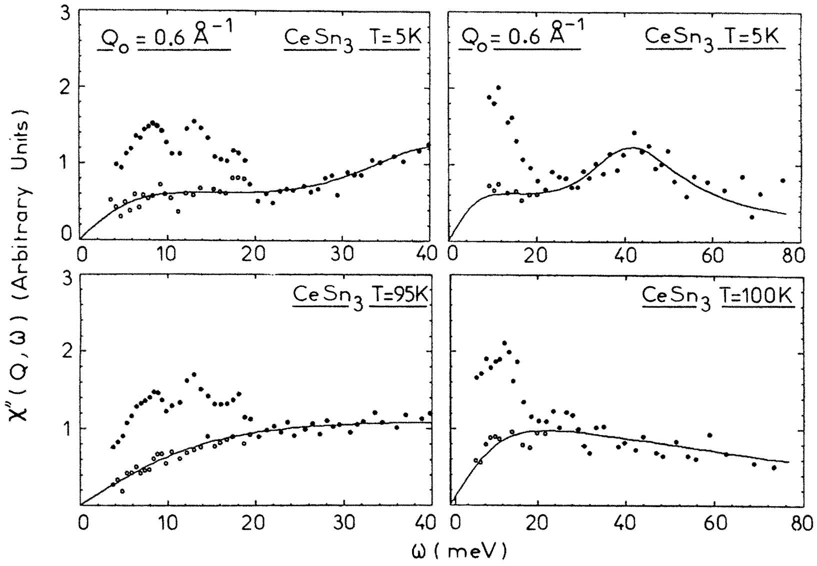

FIG. 2. Spectral response $\chi''(Q,\omega)$ for CeSn$_3$ obtained with the use of 50.4- and 81.8-meV neutrons. The data have been corrected for intensity variation as a function of Q for fixed scattering angles 2θ with use of the Ce^{3+} form-factor dependence (Ref. 11). The solid points give the measured spectra and the open circles the data after phonon subtraction. The solid curves represent the best fit to the data to the spectral function given by Eq. (2). Note the different scales in the abscissas of the two sets of figures.

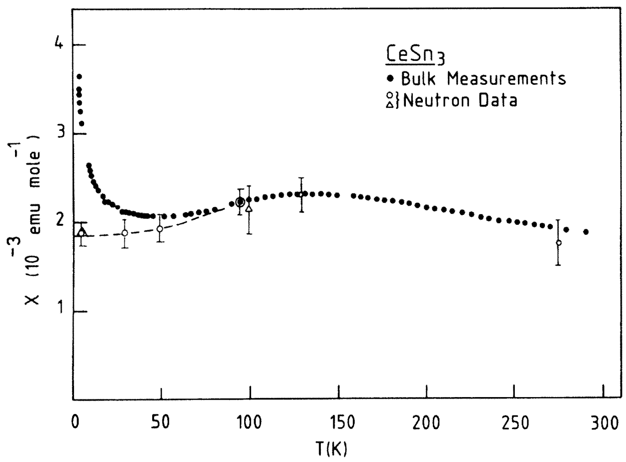

FIG. 3. Static susceptibility χ for $CeSn_3$. The solid points give the results of the bulk measurements and the open circles and triangles are the static susceptibility determined from the inelastic scattering measurements with the use of 50.4- and 81.8-meV neutrons, respectively. The dashed curve represents the bulk susceptibility after correction of the Curie upturn in the susceptibility.

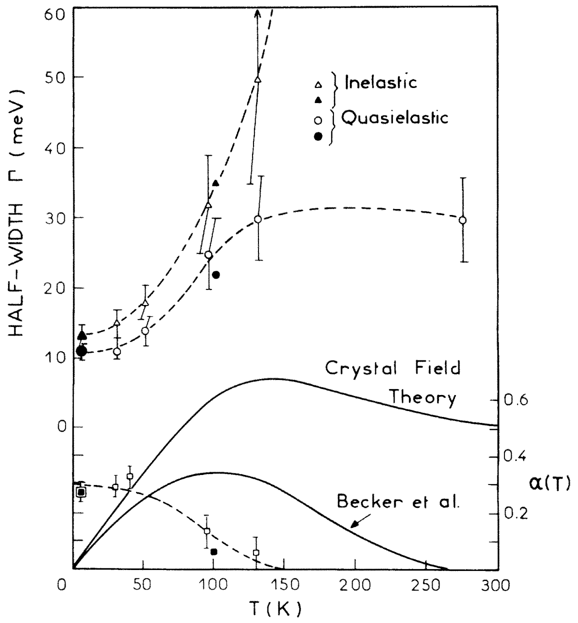

FIG. 4. (a) Half-width Γ of the inelastic and the quasielastic parts of the spectra as a function of temperature. The open symbols represent the results of fits to the 50.4-meV data and the filled symbols those for the 81.8-meV incident energy measurements. (b) Relative weight $\alpha(T)$ of the inealastic (van Vleck) and the quasielastic (Curie) parts of the spectral response as a function of temperature. The dashed curve indicates the trend of points. The solid curves represent the expected behavior in the simple crystal-field model and qualitative expectations from the theory of Becker, Fulde, and Keller (Ref. 16).

since the high-energy inelastic peak occurs only at low temperatures, it would evidently be difficult to observe in an upscattering experiment. More recently Holland-Moritz, Wohlleben, and Loewenhaupt[12] have reanalyzed their data on $CeSn_3$ allowing for a possible crystal-field excitation at $\Delta = 10$ meV. In contrast, the present results show a broad but well-defined excitation at $\Delta = 40$ meV. The origin of this hump, however, is not entirely clear. Apparently several different mechanisms could plausibly account for such a magnetic response, as discussed below.

Crystal-field excitation. As the simplest interpretation, the inelastic hump could be considered as a form of crystal-field excitation with, however, several distinctive features: (i) large residual linewidths for both the inelastic and the quasielastic peaks as $T \to 0$ K; (ii) a rather high-energy (40-meV) excitation in a (cerium-based) metallic system, corresponding to an abnormally large magnitude for the fourth-order crystal-field parameter $|A_4\langle r^4\rangle|$ (compared with the neighboring $PrSn_3$ and $NdSn_3$ compounds); (iii) the relative intensity of the van Vleck and Curie susceptibility terms abnormal compared with that expected for Ce^{3+} ions in a cubic crystal field; (iv) anomalous temperature dependence of the intensity of the inelastic peak, in particular its rapid disappearance around 130 K.

Disregarding intensity considerations we may estimate the crystal-field parameter $|A_4\langle r^4\rangle|$ simply from the position of the inelastic hump and obtain $|A_4\langle r^4\rangle| \simeq 200$ K, which is much larger than for $NdSn_3$ ($A_4\langle r^4\rangle = -16$ K) (Ref. 13) and $PrSn_3$ ($A_4\langle r^4\rangle = \sim +10$ K).[14] For the light rare-earth compounds, Lethuillier and Chaussy[13] have demonstrated the progressive enhancement of the fourth-order term $A_4\langle r^4\rangle$ towards more positive values as one goes from Nd to Pr to Ce in RPb_3 and RIn_3 compounds, which is attributed to increasing coupling of the 4*f* moment with the conduction electrons. The enhancement of the $A_4\langle r^4\rangle$ term is, however, much larger (by almost an order of magnitude) in $CeSn_3$, compared with the neighboring RSn_3 compounds, than expected from the observed trend in RPb_3, RIn_3, and RMg_3 compounds.

Inasmuch as an identification of the broad quasielastic and inelastic spectra in $CeSn_3$ with the Curie and van Vleck terms in the susceptibility has any meaning, we may attempt to compare the ratio $a_1(T)/a_0(T) = \alpha(T)$ with predictions of the simple crystal-field theory. For Ce^{3+} ions in a cubic crystal field it can be shown that

$$\alpha(T) = \frac{1-\exp(-\Delta/T)}{(\Delta/T)} \frac{2|\langle\Gamma_7|J_z|\Gamma_8\rangle|^2}{2|\langle\Gamma_7|J_z|\Gamma_7\rangle|^2+4|\langle\Gamma_8|J_z|\Gamma_8\rangle|^2\exp(-\Delta/T)} , \tag{3}$$

where Γ_7 is assumed to be the ground state. A similar expression can be obtained for the Γ_8 ground state. Here Δ is the energy separation between the two levels and $|\langle\Gamma_i|J_z|\Gamma_j\rangle|^2$ are the matrix elements tabulated by Birgenau.[15] In Fig. 4 we have plotted this ratio as a function of temperature, assuming $\Delta = 40$ meV. At low temperatures $\alpha(T) \to 0$ as $T \to 0$ K simply because the Curie term for a normal magnetic system varies as $1/T$.

In a recent theory Becker, Fulde, and Keller[16] have shown how inclusion of a coupling between the local 4*f* moment and conduction electrons modifies the simple crystal-field description. In particular, they show that with increasing temperature the spectral weight from the inelastic peak is transferred to the quasielastic part until above some temperature only a single quasielastic spectrum remains. In Fig. 4 we have included a qualitative curve to illustrate the modification from the simple crystal-field model suggested by the theory. It is evident that although the predicted behavior at high temperatures could reproduce the observations in $CeSn_3$, the low-temperature behavior is in conflict, being similar to the simple crystal-field model, namely, $\alpha(T) \rightarrow 0$ as $T \rightarrow 0$ K.

Excitation across a hybridization gap in the f band. Another intermediate valence system which shows an inelastic as well as a quasielastic peak in its spectral response is TmSe. Early measurements on this compound by Loewenhaupt and Holland-Moritz[17] revealed an inelastic peak at about 10 meV at low temperatures which they interpreted as a crystal-field excitation. Later measurements on single-crystal samples by Grier and Shapiro[18] have shown an abnormal q dependence of the intensity of the peak and confirmed the observation that the peak progressively disappeared by about 100 K. This effect has been interpreted by Fedro and Sinha[19] in the Anderson lattice model as resulting from excitations across the hybridization gap in the $4f$ band at low temperatures.

In more recent measurements on a dilute alloy of Tm, namely, $Tm_{0.5}Y_{0.95}Se$, Holland-Moritz and Prager[20] have again found a single inelastic magnetic peak which the authors suggest represents a localized excitation between two f states proposed by Mazzaferro, Balseiro, and Alascio.[21]

Excitation of the f electron to the conduction band. Other theories of mixed-valence phenomena which also predict inelastic humps in the magnetic response function include those by Balseiro and López[22] and Schlotmann[23] based on the Anderson single impurity model with orbital degeneracy in the $U \rightarrow \infty$ limit. Both the resultant charge and spin susceptibilities in this model show bumps at low temperatures, at an energy corresponding to that needed to promote an f electron to the conduction band. The calculated results for the spin susceptibility, both static and dynamic, are similar to the present experimental observations on $CeSn_3$. In particular, the dynamic susceptibility shows a broad hump at low temperatures which disappears completely at higher temperatures. The static susceptibility similarly shows a broad maximum qualitatively similar to that observed in $CeSn_3$. Another result of the theory which bears some resemblance to the experimental observations concerns the temperature dependence of the spin relaxation rate. The present results show that the quasielastic linewidth initially increases with temperature and then saturates out or even decreases slightly at higher temperatures, in qualitative accord with the theory.

Finally, the observed evolution of the inelastic hump below the temperature of the maximum in the bulk susceptibility is closely correlated with the anomaly in the Knight-shift data[8] which indicate a breakdown of its linear dependence on the susceptibility below the temperature of the maximum. Similar deviations have been observed in other intermediate valence compounds such as $YbAl_3$ and YbCuAl.[8]

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