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Neutron-spectroscopy study of the heavy-fermion compound $CeCu_6$

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Inelastic-neutron-scattering experiments have been performed on the canonical heavy-fermion compound $CeCu_6$ over a wide range of energy transfers (up to 100 meV). We find evidence for two inelastic crystal-field transitions from the ground state at 7.0 and 13.8 meV, in addition to substantial quasielastic scattering. The crystal-field-level scheme (0–7–13.8 meV) determined by neutron spectroscopy is compared to estimations based on macroscopic measurements and optical reflectivity.

Heavy-fermion materials are characterized by a low-temperature scale, the Kondo temperature T_K, typically about 10 K, below which the f electrons display Fermi-liquid properties. The Kondo temperature is a measure of the strength of the interactions between the localized f electrons on the rare-earth or actinide ions and the conduction electrons and is therefore central to the development of heavy-fermion behavior. However, there are other important energy scales in heavy-fermion systems and it is the balance between these, e.g., between intersite and single-site fluctuations, which will determine what the ground state is, i.e., whether it is magnetically ordered, heavy fermion, or mixed valent. One of the most important energy scales is the crystal-field (CF) potential, which splits the Hund's-rule ground-state multiplet and manifests itself in practically all measurable properties as well as determining the symmetry and degeneracy of the ground state.

$CeCu_6$ is one of the canonical heavy-fermion intermetallic compounds with a huge value of the electronic specific-heat coefficient $\gamma=1.53$ J/mol/K^2 and an enhanced Pauli susceptibility at low temperatures.[1] There have been a number of investigations of the CF-level scheme using specific heat,[2,3] single-crystal magnetic susceptibility,[4] and inelastic neutron scattering (INS).[5] While these studies have provided useful estimates of the energies of the CF transitions, there have been no direct observations of both the allowed transitions. The earlier INS measurements were performed with low incident energy in order to study the magnetic quasielastic scattering;[5] the data gave some evidence of a CF transition at 5.5 meV, but any higher-energy transitions would have been outside their range. There have also been extensive single-crystal INS studies of the low-frequency response of $CeCu_6$ in which two different components were identified, one of which was inelastic below 1.5 K with a peak at 0.2 meV and gave evidence for antiferromagnetic correlations.[6,7] The second was Q independent and so was associated with single-site fluctuations defining a Kondo temperature of 5 K. Rossat-Mignod *et al.*[7] conclude that the antiferromagnetic correlations only persist up to about 10 K, above which only a single-site response is seen. No effects due to CF excitations could be seen in this energy range.

We report INS results over a wide energy-transfer range on $CeCu_6$ in which the magnetic scattering has been separated from the nuclear (phonon) contribution by a scaled subtraction of $LaCu_6$ spectra. The analysis establishes the existence of two broad inelastic transitions at 6.4 and 12.7 meV at 20 K, whose energies are temperature dependent, and magnetic quasielastic scattering with widths consistent with the earlier high-resolution measurements.[5]

The samples of $CeCu_6$ and $LaCu_6$ were prepared by arc melting of the constituent elements with no measurable weight loss. Both x-ray- and neutron-diffraction measurements confirmed that the samples were single phase. Sets of INS spectra were taken on two different time-of-flight spectrometers: MARI is a direct-geometry chopper spectrometer on the pulsed spallation neutron source ISIS (Rutherford Appleton Laboratory, U.K.), and KDSOG is an inverse-geometry spectrometer on the pulsed reactor IBR-2 (JINR, Dubna, Russia). In the case of the MARI measurements, 100-g samples were mounted in a thin-walled aluminum can on the tail of a closed-cycle refrigerator and cooled to 20 K. Spectra were taken with fixed incident energies of 40 and 70 meV, giving energy-transfer (ε) resolutions of 1.0 and 1.8 meV, respectively, at the elastic position. The resolution improves with energy transfer. The KDSOG experiments used 300-g samples also mounted in aluminum cans in a helium cryostat. Measurements were made at 10 and 77 K with a fixed scattered energy of 4.9 meV. The resolution is 0.6 meV at the elastic position, but becomes worse than MARI at high-energy transfer.

MARI has continual detector coverage from 3° to 140°. At the highest angles, there is negligible magnetic scattering because of the Ce^{3+} form factor. These spectra show that the phonon spectra of $CeCu_6$ and $LaCu_6$ are nearly identical as anticipated since the compounds are isostructural and the cross section of the Ce sample is 94.7% of the La sample at high wave-vector transfer Q. Nevertheless, we have not performed a direct subtraction of the low-angle spectra to obtain the magnetic scattering since there are small shifts in the two phonon spectra. Instead, we have used a scaling procedure first described by Murani[8] and successfully used to analyze the CF excitation spectra in $CeCu_2Si_2$.[9] The La spectra are used to define a scaling function $R(\phi,\phi',\varepsilon)=S(\phi,\varepsilon)/S(\phi',\varepsilon)$ that maps the high-angle spectra on to the low. The high-angle $CeCu_6$ spectra are then multiplied by this function, which has been smoothed by a spline. Figure 1(a) shows the result of this procedure (solid circles) where it is compared to the measured low-angle spectrum (open circles). The difference between these two energy distributions represents the estimated magnetic scattering of $CeCu_6$, shown in Fig. 1(b).

The KDSOG data are used to provide an independent check on this analysis. Figure 2 shows both $CeCu_6$ and $LaCu_6$ spectra measured at 10 and 77 K. The data are plotted as measured rather than transformed to the more usual scattering law since this shows the distribution of intensity with energy transfer and gives a clearer idea of the relative weights with which the different scattering contributions are determined. When transformed to $S(\phi,\varepsilon)$, the spectra look similar to the MARI data. There is additional scattering above 50 meV which occurs in a region of very high incident flux [see Fig. 3(a)] and is identical in the two samples. The origin of this background is not known, since it occurs well above the single-phonon density of states, but may represent multiphonon scattering or scattering from trace hydrogen impurities. Figure 3 shows the difference spectra obtained by a direct subtraction procedure, after correcting for the different nuclear cross sections and absorptions. Note that the scattering above 20 meV coincides with strong phonon scattering; small shifts between the two compounds lead to anomalous subtractions. This region has not been included in the fits.

The neutron-scattering law for unpolarized neutrons in the dipole approximation is[10]

$$S(Q,\varepsilon)=f^2(Q)\left\{\frac{\varepsilon}{1-\exp(-\varepsilon/kT)}\right\}\left[\sum_m \chi_C^m F(\varepsilon,\Gamma_{mm})+\frac{1}{2}\sum_{m\neq n}\chi_{VV}^{mn}\left\{1-\exp\left[-\frac{\varepsilon_{mn}}{kT}\right]\right\}F(\varepsilon-\varepsilon_{mn},\Gamma_{mn})\right],$$

where $f^2(Q)$ is the dipole Ce^{3+} form factor, χ_C^m and χ_{VV}^{mn} are the Curie and Van Vleck magnetic susceptibilities where m and n label the CF states (see Ref. 10 for more detailed definitions), and $F(\varepsilon,\Gamma)$ is a normalized function characterizing the line shape of the transition. The results of fitting Lorentzian line shapes to the magnetic

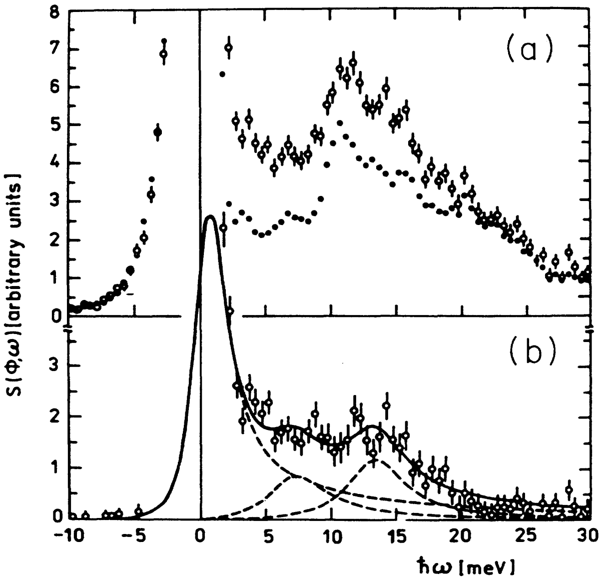

FIG. 1. (a) Neutron energy spectra from $CeCu_6$ at 20 K measured on MARI at 7° with an incident energy of 40 meV (open circles). The solid circles show the phonon contribution estimated by multiplying the high-angle data by the $LaCu_6$ scaling function. (b) The magnetic response of $CeCu_6$ estimated by subtracting the phonon contribution. The solid line is a fit to three Lorentzians centered at 0, 7.0, and 13.8 meV, shown individually as the dashed lines.

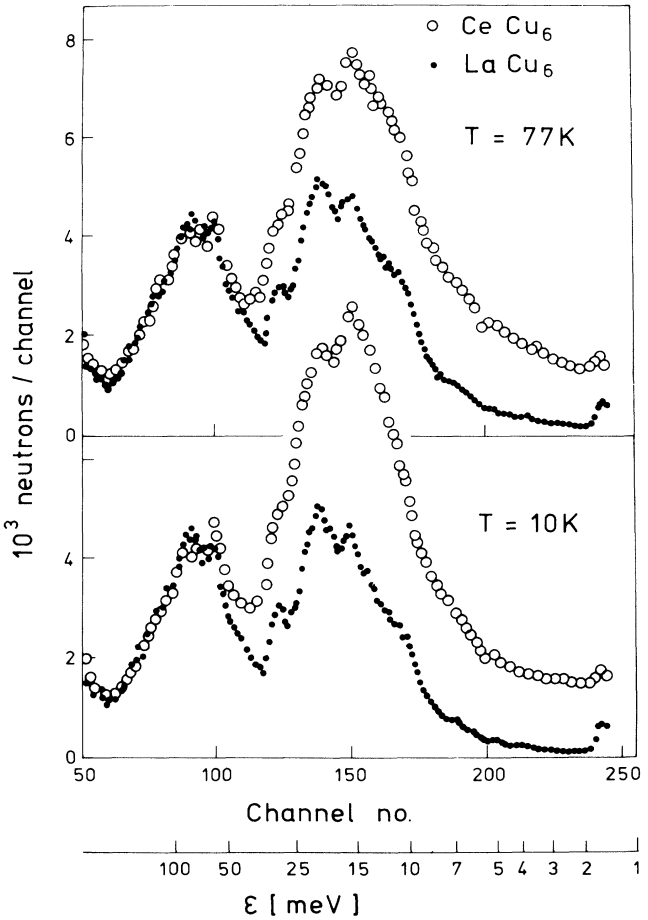

FIG. 2. Neutron time-of-flight spectra from $CeCu_6$ (open circles) and $LaCu_6$ (solid circles) at 10 and 77 K measured on KDSOG.

spectra are shown as the solid lines in Figs. 2 and 3. The individual components are plotted as the dashed lines.

Both sets of measurements require three peaks, one quasielastic and two inelastic, to provide an adequate description of the data. The biggest uncertainty is in defining the quasielastic scattering on MARI because of the strong elastic nuclear scattering. We have fixed the width of this contribution to the value reported by Walter, Wohlleben, and Fisk[5] for 20 K. Two inelastic components are essential to obtain a good fit, although the intensity of the lower-energy peak is very dependent on the amplitude of the quasielastic component and could only be estimated with an accuracy of about 20%. In the case of the KDSOG data, the quasielastic component is very well defined with widths $\Gamma(10\ \mathrm{K})=1.2(0.1)$ meV and $\Gamma(77\ \mathrm{K})=3.9(0.4)$ meV, in reasonable agreement with the earlier investigation.[5] Once again two inelastic transitions are required to explain the observed energy distribution.

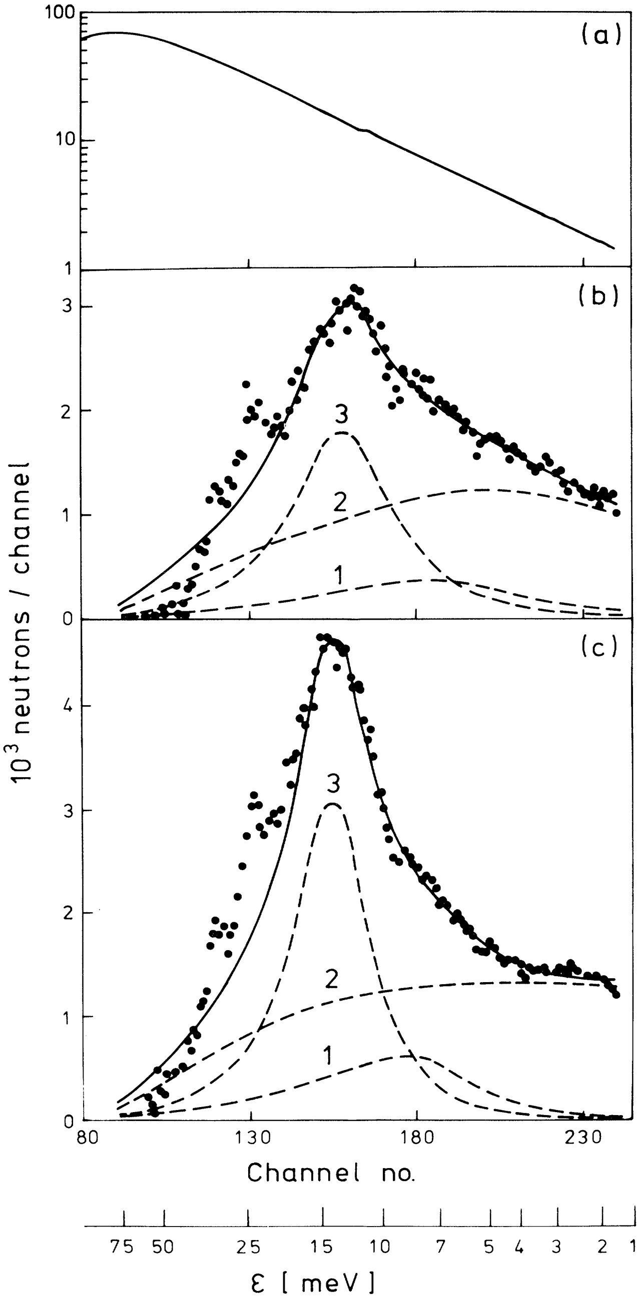

FIG. 3. (a) Energy dependence of the incident neutron flux on KDSOG. The magnetic contribution to the neutron time-of-flight spectra at (b) 77 K and (c) 10 K measured on KDSOG determined by subtracting $LaCu_6$ data from $CeCu_6$ data. The dashed lines show the three Lorentzian components centered at 7.0 meV (1), 0.0 meV (2), and 13.8 meV (3).

The energies of the inelastic transitions show a weak temperature dependence, being roughly equally spaced at all temperatures: At 10 K, they are at 7(1) and 13.8(0.3) meV, at 20 K, 6.4(0.7) and 12.7(0.4) meV, and at 77 K, 5.7(0.7) and 12.5(0.5) meV. The position of the first excited level is consistent with the earlier estimate of Walter, Wohlleben, and Fisk.[5] The linewidths of the two transitions cannot be individually determined, but when constrained to be equal, they increase with temperature as expected from 3.8(0.7) meV at 10 K to 5(1) meV at 77 K. The MARI data at 20 K are narrower [$\Gamma=2.7(0.4)$ meV] than the KDSOG data at 10 K, and so there must still be some systematic error from the subtraction procedure probably because of the difficulty in estimating the quasielastic scattering. Even at 10 meV, this is an appreciable component in the total magnetic scattering [Fig. 1(b)] and the other peak parameters are strongly correlated to its intensity. Such discrepancies are to be expected given the relative strengths of the magnetic and nuclear scattering [Figs. 1(a) and 2], but do not affect our general conclusions.

It is not possible from these results to define the parameters of the CF Hamiltonian because of the low (orthorhombic) symmetry of this structure. We can only make comparisons with other estimates of the CF-level scheme. On the basis of single-crystal magnetic-susceptibility measurements, a similar scheme with two equidistant doublets has been proposed.[4] The two transitions were predicted to be at 9.2 and 20.8 meV, slightly greater than our observations, probably because of uncertainty in their estimates of the fourth-degree parameters. Two specific-heat studies proposed two different level schemes. Fischer *et al.*[2] estimated transition energies of 3.6 and 6.8 meV, whereas Rietschel *et al.*[3] estimated 5.2 and 6.9 meV. The energy of the lower transition is in good agreement with the latter study. However, the full splitting is underestimated in both works, reflecting the difficulty of estimating the Schottky contribution at high temperatures. Our calculations show that the position and value of the maximum in the Schottky specific heat is consistent with the neutron-derived level scheme. Our final comparison is with optical reflectivity measurements[11] which show structure at 5 and 15 meV with intensities characteristic of hybridized intra-*f*-shell transitions. These can now be assigned to CF transitions.

Although the data define a CF-level scheme, the measurements do not support a standard CF model. First, the peaks are very broad, indicating that there is either strong dispersion or single-site spin fluctuations. Since the antiferromagnetic correlations observed by Rossat-Mignod *et al.*[7] only persist to 10 K, they are probably too weak to account for the observed widths. We were also unable to observe any Q dependence to the magnetic response, although dispersion effects could have been masked out by the powder averaging. Although the linewidths are broader than the Kondo temperature, the most likely origin of the CF linewidths is still quantum fluctuations induced by the hybridization of the f electrons with the conduction band. It is common for the CF peaks to be broader than the fluctuations of the ground-state doublet in CF-split heavy-fermion compounds, such as $CeCu_2Si_2$ and $CeAl_3$,[9,12,13] because of the increased number of hybridization channels associated with the excited levels.[14] Second, the intensity of the quasielastic scattering is more than an order of magnitude greater than the intensity of the CF peaks, as also noted by Walter, Wohlleben, and Fisk.[5] This is much larger than expected from conventional CF models and implies a partial suppression of the localized CF response.

In conclusion, inelastic-neutron-scattering experiments on two different spectrometers and using two different methods of estimation of the magnetic response have been performed on the heavy-fermion intermetallic compound $CeCu_6$. Both sets of measurements find evidence for two inelastic transitions as well as substantial quasielastic scattering. The CF potential therefore splits the ground-state multiplet of the Ce^{3+} ion into three doublets at 0, 7.0, and 13.8 meV at the lowest measured temperature of 10 K. As has been observed in other Ce heavy-fermion compounds, the CF transitions are very broad, indicating the influence of f-electron hybridization with the conduction electrons. This direct observation of the CF-level scheme is consistent with the microscopic properties measured by other experimental techniques.

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