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Spontaneous Relaxation of the Local $4f$ Magnetization in $CePd_3$†

E. Holland-Moritz, M. Loewenhaupt, and W. Schmatz
Institut für Festkörperforschung der Kernforschungsanstalt Jülich, 5170 Jülich, Germany

and

D. K. Wohlleben
II. Physikalisches Institut der Universität zu Köln, 5000 Köln 41, Germany

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Diffuse neutron scattering on the intermediate valence compound $CePd_3$ shows a quasielastic line with Lorentzian shape and very large, nearly temperature-independent width ($\Gamma/2 \simeq 20$ meV). The intensity under this line has $4f$ form factor but the total cross section indicates only 0.5 $4f$ electron per formula unit. These observations are interpreted by spontaneous relaxation of the local $4f$ magnetization due to interconfiguration fluctuation between $4f^1$ and $4f^0$.

In intermediate-valence (IV) rare earth (RE) compounds the incompletely filled $4f$ shell of a given lattice cell may be visualized to move in time back and forth between two configurations with integral occupation numbers n and n-1.[1] It is of central importance to learn more about the temporal motion of the local cells, or, equivalently, about the structure of the local energy spectrum on a scale of order $\Delta E \simeq h/\tau$. The most important question is whether successive transitions on a given cell are correlated in time or not. An uncorrelated motion (spontaneous transition) leads to a simple Lorentzian broadening of the configurational levels ($\Gamma/2 = h/\tau$), while correlated motion, e.g., driven by a strong tendency to magnetic order via the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, should give a more complicated spectrum with sharp lines as $T \to 0$. The lack of structure in the temperature dependence of the macroscopic susceptibility of many IV compounds, especially the absence of magnetic order or crystal-field effects at low temperatures, suggests uncorrelated motion.[2]

So far local measurements have established only upper[3] and lower[4,5] limits to the configurational lifetimes (10^{-15} sec $< \tau < 10^{-11}$ sec). There are reasons to expect τ to lie in the range 10^{-12}–10^{-13} sec for most IV compounds. Obviously, then, thermal neutrons will be a good tool to study the configurational motion on its own temporal as well as spatial scale, as they have been for dilute alloys in connection with the Kondo[6] and spin-glass[7] problems.

In this Letter we report the first direct measurement of the energy spectrum of the local magnetic moment in an IV compound. We have em-

ployed diffuse neutron scattering on $CePd_3$, a classical IV compound with about 0.5 electron in the $4f$ shell.[8] We chose this compound because the extremely small magnetic ordering temperatures of the normal RE compounds[9] XPd_3 make interference of the RKKY interaction with the configurational motion very unlikely.

The double differential cross section of the magnetization $\vec{M}(\vec{\kappa}, t)$ for unpolarized neutrons can be written (for cubic symmetry) as[10]

$$\frac{d^2\sigma}{d\Omega\, d(\hbar\omega)} = \frac{1}{4}(g_N r_e)^2 \frac{k_1}{k_0}\frac{2}{3}\frac{1}{\mu_B{}^2}\frac{1}{2\pi\hbar} \times \int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle \vec{M}(\vec{\kappa}, t)\vec{M}(-\vec{\kappa}, 0)\rangle. \quad (1)$$

Here $\hbar\omega$ and $\hbar\kappa = \hbar(k_0 - k_1)$ are the energy and momentum transfers, $r_e = 2.8\times 10^{-13}$ cm, and $g_N = 1.91$. The integral is related to the imaginary part of the generalized susceptibility $\chi''(\kappa,\omega)$ by the fluctuation-dissipation theorem:

$$\int_{-\infty}^{\infty} dt \langle \vec{M}(\vec{\kappa}, t)\vec{M}(-\vec{\kappa}, 0)\rangle e^{i\omega t} = \frac{2\hbar V 3\chi''(\kappa,\omega)}{1 - e^{-\beta\hbar\omega}}, \quad (2)$$

where V is the volume of the Fourier integration and $\beta = (k_B T)^{-1}$.

We adapt this quite general expression to the case at hand. Since $CePd_3$ does not order magnetically, we take the behavior of a $4f$ metal in the paramagnetic, high-temperature limit as a guideline. In this limit the detectable magnetization is localized in the $4f$ shells and decays exponentially, $\langle \vec{M}(\vec{\kappa}, t)\vec{M}(-\vec{\kappa}, 0)\rangle \sim \exp[-t/\tau(T)]$, with a temperature-dependent time constant $\tau(T)$. From $\chi''(\kappa,\omega)$ we extract the Lorentzian spectral function corresponding to this temporal decay and write in accordance with the Kramers-Kronig relation

$$\chi''(\kappa,\omega,T) = \frac{\hbar\omega\Gamma(T)/2}{[\Gamma(T)/2]^2 + (\hbar\omega)^2}\chi'(\kappa,0,T). \quad (3)$$

Here $\chi'(\kappa,0,T)$ is the real part of the static susceptibility. For sufficiently small momentum transfer ($\kappa^{-1} > r_f$, the radius of the $4f$ shell) it can be factorized to exhibit the $4f$ form factor $F(\kappa)$:

$$\chi'(\kappa,0,T) = \chi'(\kappa\to 0,0,T)F^2(\kappa). \quad (4)$$

If there are no appreciable spatial correlations between cells, $\chi'(\kappa\to 0,0,T)$ can be identified with the static susceptibility $\chi'(0,0,T)$ (as measured in a Faraday magnetometer). Finally

$$\frac{d^2\sigma}{d\Omega\, d(\hbar\omega)} = \frac{1}{4}(g_N r_e)^2 \frac{k_1}{k_0}\frac{2}{\mu_B{}^2}\chi'(0,0,T) \times F^2(\kappa)\frac{\hbar\omega}{1 - e^{-\beta\hbar\omega}}\frac{\Gamma/2\pi}{(\Gamma/2)^2 + (\hbar\omega)^2}. \quad (5)$$

We note that from $d^2\sigma/d\Omega d(\hbar\omega)$ integrated over $\hbar\omega$ for fixed κ one obtains the averaged instantaneous value of $g_J{}^2 J(J+1)F^2(\kappa)$ [$= 6.42F^2(\kappa)$ for $4f^1$]. Equation (5) applies in all simple stable valence RE metals at high temperatures, where one finds Lorentzian energy dependence of the diffuse neutron cross section with the fitting parameters $\Gamma(T) \sim T$ (Korringa behavior) and $\chi'(\kappa\to 0,0,T) \sim T^{-1}$ (Curie law). Normally, with decreasing temperature, when $\Gamma(T)$ has decreased to the order of crystal-field splittings or magnetic ordering energies, the spectrum becomes more complicated. For $CePd_3$ it turns out that Eq. (5) suffices to evaluate the data at *all* temperatures. However, the temperature dependence and magnitude of the fitting parameter $\Gamma(T)$ as well as the total magnetic cross section are quite abnormal.

The neutron scattering cross section was measured with the time-of-flight (TOF) spectrometers DNS at the FRJ-2 reactor in Jülich and D7 in Grenoble. The TOF spectra at D7 were obtained for a neutron energy of 3.3 meV between 15° and 160°. The spectra in Fig. 1 (obtained by transforming the TOF spectra to a scale linear in energy) were taken at 15° from polycrystalline $CePd_3$ and also from the polycrystalline isostructural reference compounds YPd_3 and $TbPd_3$. YPd_3 has no $4f$ electrons and is diamagnetic.[9] $TbPd_3$ has a stable $4f^8$ configuration and orders magnetically at 2 K.[9]

All three compounds show incoherent elastic scattering at $\hbar\omega = 0$ due to nuclear isotopic and/or nuclear spin disorder. This contribution to the cross section is set apart by shading in Fig. 1. For YPd_3 there is also a phonon peak between $\hbar\omega = -20$ and -10 meV at 240 K, which has nearly vanished in the background at 145 K. (In contrast to this noticeable coherent phonon contribution, incoherent phonon scattering, comparable in YPd_3 and $CePd_3$, gives negligible contribution.) Very little scattering is visible above the noise between $\hbar\omega = -10$ and -1 meV in YPd_3. In contrast, $CePd_3$ has considerable intensity in this window and also below the phonon peak. The integrated intensity in the window between -10 and -1 meV decreases with increasing angle (in contrast to coherent phonon scattering) and has the

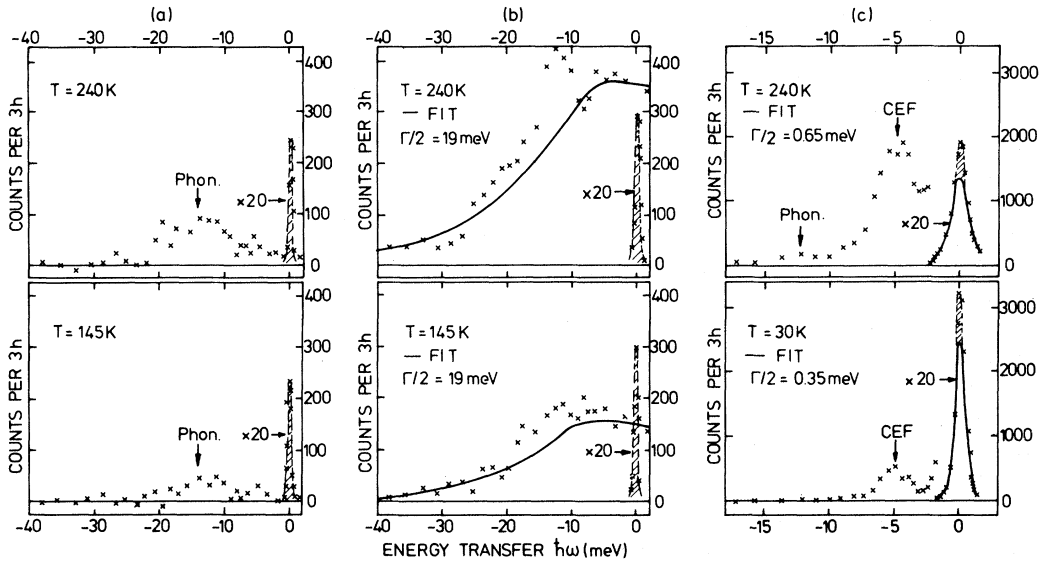

FIG. 1. Neutron inelastic scattering cross section as function of energy for the isostructural intermetallic compounds (a) YPd_3, (b), $CePd_3$, and (c) $TbPd_3$ taken at a scattering angle of 15° at two temperatures.

angular dependence expected from the magnetic $4f$ form factor. Our angular region corresponds to a momentum transfer of 0.5 to 2.5 $Å^{-1}$. At our maximum momentum transfer the $4f$ form factor is 0.85. Within the accuracy we cannot distinguish between $4f$ and $5d$ form factor.

The magnetic scattering in $CePd_3$ is indicated by the solid lines in Fig. 1(b). These lines are fits according to Eq. (5), using the experimental values of the static susceptibility from Ref. (9). (Calibration of the absolute cross section was done with a vanadium standard.) The extra scattering above the fitting curves between -20 and -10 meV can be identified with the coherent single-phonon scattering expected for $CePd_3$ on the basis of the spectrum of YPd_3, with proper scaling due to the differences in mass and scattering length. The fits yield the single parameter $\Gamma(T)$ [Fig. 2(a)]. The errors for $\Gamma/2$ are mainly due to the uncertainty of the phonon contribution between -30 and -10 meV. For comparison, we also show in Fig. 2(b) the quasielastic linewidth of $TbPd_3$ decreases linearly with temperature and extrapolates to the resolution of the spectrometer at $T = 0$. $TbPd_3$ also shows a crystal field transition (CEF).

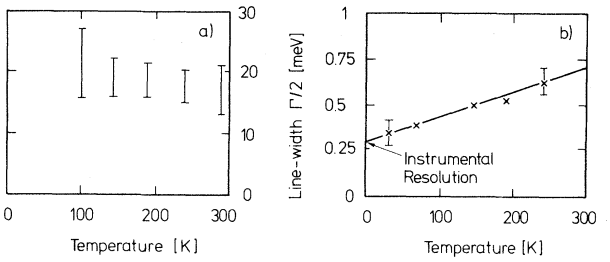

FIG. 2. Temperature dependence of the quasielastic magnetic half-width $\Gamma/2$ for the intermediate (unstable) valence system $CePd_3$ (left) and the stable valence system $TbPd_3$ (right).

Clearly $CePd_3$ is abnormal. It does not show a strong, narrow quasielastic magnetic line like $TbPd_3$, nor any indication of the expected inelastic crystal-field transition (in accordance with the findings of Furrer and Purwins[11]). Nevertheless quasielastic magnetic scattering is present, albeit distributed over an enormous energy range; it is, e.g., the sole contribution to the diffuse cross section in the window between -10 and -1 meV and shows $4f$ or $5d$ form factor there. The integral of $d^2\sigma/d\Omega\, d(\hbar\omega)$ over $\hbar\omega$, using the value of $\chi(0,0,T)$ at $T = 240$ K with an upper limit of the integral at 2 eV, the estimated width of the s band, yields an instantaneous value of $g_J{}^2 J(J+1) \times F^2(\kappa)$ which is about 0.5 times the value for $4f^1$ or about 1.2 times the value of $5d^1$. A $5d$ electron is unlikely in view of the absence of $4f$ scattering in YPd_3 (Fig. 1). It is also inconsistent with the lattice constant of $CePd_3$ and the alloying behavior of $Ce(Pd_{1-x}Rh_x)_3$.[8] On the other hand the diffuse neutron cross section of $CePd_3$ is consistent with the valence 3.45 extracted by Harris,

Norman, and Gardner[8] from the lattice-constant anomaly, assuming fractional occupation of the $4f$ shell. Thus we believe the magnetic diffuse scattering to arise from about 0.5 $4f$ electron per formula unit. This is similar to analogous evaluations in CeTh alloys.[12]

The more interesting aspect of the cross section is the energy spectrum and its temperature dependence. Fits with the *Ansatz* of a single Lorentzian are quite reasonable within the limits given by the background noise. In principle it is also possible to fit a spectrum with two Lorentzians centered at $\hbar\omega = 0$ and two at about $\pm$ 10 meV, but all with widths of order 10–30 meV. Such a fit is guided by the expected crystal-field behavior, i.e., splitting of $J = \frac{5}{2}$ into Γ_7 and Γ_8 of order 10 meV. Since within the present accuracy such a fit (in which the large, temperature-independent widths of all lines remain to be explained) cannot be distinguished from a single Lorentzian, we have chosen to discuss only the latter.

In short, we find a diffuse quasielastic line with a width nearly three orders of magnitude larger than expected on the basis of the normal thermal Korringa-type relaxation of $TbPd_3$. This width is nearly temperature independent between 300 and 100 K, again in contrast to normal Korringa behavior. Note that *below 200 K, the linewidth is actually larger than* k_BT! Therefore, the decay of the local $4f$ magnetization cannot be driven thermally. Moreover, since $\chi'(0,0,T)$ does not change appreciably down to 1 K,[9] the Lorentzian spectral function of the dynamic susceptibility seems to apply with nearly constant Γ down to $T \to 0$. This is in accordance with the local configurational energy spectrum assumed in the earlier phenomenological model.[2,13] With $\Gamma(T)$ found here it is possible, using this model, to fit independently the macroscopic susceptibility and the abnormal temperature dependence of the lattice constant (valence) of $CePd_3$.[14] According to these fits the valence changes from 3.45 at 300 K to 3.55 at 100 K. One also finds $E_{ex} \simeq 40$ meV for the distance between the centers of gravity of the $4f^1$ and the $4f^0$ configurations in the local spectrum.[2]

We conclude by stating that our measurements are consistent with the idea that the projection of the local $4f^1$ magnetization out of the ground state of the IV compound $CePd_3$ decays exponentially in time with time constant $\tau(T \to 0) = 1.8 \times 10^{-13}$ sec. Apparently, this spontaneous decay prevents Curie-Weiss behavior at temperatures smaller than $h/k_B\tau$, as well as magnetic order or the development of crystal-field spectra on an energy scale smaller than h/τ, and is, we believe, a general property of nonmagnetic IV compounds.

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