Proceedings of the European Conference "Physics of Magnetism '99", Poznań 1999

DYNAMIC CRYSTAL FIELD IN $CePb_3$

S. LIPIŃSKI AND A. SZAJEK

Institute of Molecular Physics, Polish Academy of Sciences
Smoluchowskiego 17, 60-179 Poznań, Poland

The crystal field of valence fluctuating systems is time dependent due to f-electron transfers to the conduction band. We examine the effects of crystal field fluctuations on the neutron spectra, the specific heat and susceptibility of $CePb_3$.

PACS numbers: 75.10.Dg, 75.20.Hr, 75.30.Mb

1. Introduction

The intermediate valence systems can be regarded as a dynamic alloy consisting of sites with two different valencies fluctuating in time [1]. A typical timescale of these fluctuations can be estimated from the quasi-elastic line width (Γ) of the neutron spectra. The low-temperature f-electron transfers into the conduction band are quantum fluctuations and the observed line widths remain finite even for $T \to 0$. Although the f-site occupancy is not sharp the crystal fields (CF) resonances are well identified in many heavy fermion systems (HF) [2]. As a result of valence fluctuations, the crystal field of these systems is time-dependent dynamic crystal field (DCF) [3]. In the following we show that the enormously wide inelastic lines of neutron spectra of $CePb_3$ are mainly determined by the dynamic crystal field disorder.

2. Model

Let us concentrate on a single Ce^{3+} ion, where for a given time interval $0 < t < \tau_f$ ($\tau_f \sim \hbar/\Gamma$) a single $4f$ electron experiences the time dependent crystalline potential

$$H_i(t) = \overline{H}_{\mathrm{CF}} + \Delta H_i(t), \tag{1}$$

where $\overline{H}_{\mathrm{CF}}$ is the average crystal field potential, here assumed to be cubic, and $\Delta H_i(t)$ is a fluctuating part induced by valence fluctuations

$$\Delta H_i(t) = \sum_j c_j(t) V_j. \tag{2}$$

$c_i(t)$ is a fluctuating field taking values 1 or 0 with the site average $\langle c_i(t)\rangle = \nu$ measuring an average deviation of valence from integer. The fluctuations at different sites are assumed to be uncorrelated i.e. $\langle c_i c_j\rangle = \langle c_i\rangle\langle c_j\rangle$. The static CF splits

the $\{|j=\frac{5}{2}\rangle\}$ manifold into Γ_7 doublet and Γ_8 quartet. The non-cubic perturbation V_j can be represented in the lowest order by

$$V_j = A(l)\sum_{m=1}^{5} a_m(j)O_m, \tag{3}$$

where O_m are quadrupolar operators [3], $a_m(j)$ are the geometrical factors, l labels the coordination shell to which belongs site j and $A(l)$ are the DCF parameters. In the following discussion we approximate the effect of time-dependent valence fluctuations by a distribution function of configurations of valence fluctuating centres (VFC) around a given site. Such a simplification is justified if the measuring time is shorter than the lifetime of the considered configurations. It is the case for the neutron measurements discussed below. The use of the quasistatic approximation is also reasonable for the calculation of thermodynamic quantities, because the electron system reaches each new local DCF equilibrium instantaneously (10^{-15} s). The probability of configuration $\{\mu\}$ specified by n VFC's is given by

$$P(\mu) = \nu^z(1-\nu)^{z-n}, \tag{4}$$

where z is a number of neighbouring Ce ion sites taken into consideration.

3. Results

We present the numerical results for the cubic HF system $CePb_3$. The measured half-width of the quasi-elastic line follows $T^{1/2}$ law with a residual width of only 0.17 meV at $T = 0$ and $\Gamma/2 = 1.4$ meV at $T = 128$ K. The inelastic lines are very broad $\Gamma_{\text{in}}/2 = 2.1 \pm 0.4$ meV at $T = 4$ K and $\Gamma_{\text{in}}/2 = 3.5 \pm 0.1$ meV at 128 K [2]. The explicit form of DCF perturbations (3) can be found in Ref. [3]. The crystal field parameters $A(l)$ ($l = 1, 2, 3$) were estimated from the real space integration of charge densities [3, 4] calculated in LMTO-ASA scheme. In the final step of self-consistent cycle the charge densities were computed without the spherical shape restriction. The $4f$ states were treated as open core states [4]. Since local spin density (LSD) calculations overestimate the CF parameters [4] we scaled them by a common factor $\alpha = 0.38$ (for a discussion see Ref. [3]).

In the quasistatic approximation the dipolar spectral function, which determines the magnetic neutron scattering cross-section, can be perceived as a weighted sum of spectral functions for different configurations

$$S(\omega, T) = \sum_{\mu} P(\mu)S_\mu(\omega, T). \tag{5}$$

S_μ is determined by the corresponding dipolar matrix elements and the thermal occupation number of crystal field states for a given configuration μ [3]. The line shape of S_μ is assumed to be Lorentzian with the width taken from the neutron measurements of elastic lines.

Figure 1 presents the spectral function of $CePb_3$ at $T = 128$ K calculated including all the configurations of DCF with one, two, or no VFC's on the first three Ce sublattice nearest neighbor (nn) shells. The result is compared with the static CF curve and with neutron data. We can conclude that the large width of the inelastic line is mainly determined by the spread of crystal field energies corresponding to the different local, temporary crystal fields.

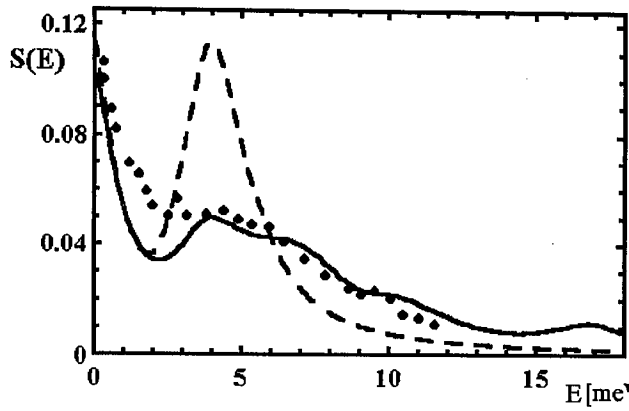

Fig. 1. The dipolar spectral function of $CePb_3$ at $T = 128$ K calculated with $\Delta = 3.8$ meV. Solid line: $\nu = 0.05$ and $A(1) = 0.91$ meV, $A(2) = 0.45$ meV, $A(3) = 0.21$ meV (DCF parameters obtained in LMTO scheme and scaled by a factor $\alpha = 0.38$). Dashed line: static CF model. The circles denote neutron scattering spectra [6].

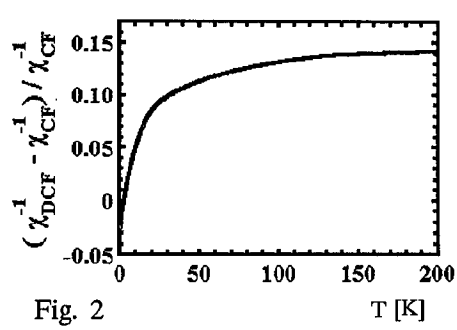

Fig. 2

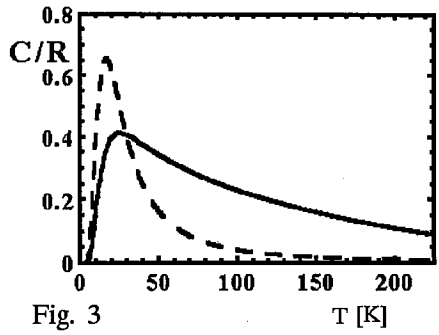

Fig. 3

Fig. 2. Differences between susceptibilities of $CePb_3$ calculated in DCF picture and in the static crystal field model.

Fig. 3. The crystal field contribution to the specific heat of $CePb_3$: solid line — DCF picture, dashed line — static CF model (R is a gas constant).

The dynamic crystal field disorder influences the thermodynamic quantities. Figure 2 presents a comparison of the susceptibility calculated in DCF picture with the one for the static CF model

$$\chi(T) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{S(\omega, T)(1 - \mathrm{e}^{-\beta\omega})}{\omega} \mathrm{d}\omega. \tag{6}$$

The low temperature inverse susceptibility difference $(\chi^{-1}_{DCF} - \chi^{-1}_{CF})/\chi^{-1}_{CF}$ is negative and is of order of 3% and in the high temperature range it reaches 14%. The former reflects the admixture of Γ_8 quartet functions to the cubic ground state functions Γ_7, the effect caused by DCF perturbation. In a consequence, the ground state magnetic moment slightly increases. This phenomenon is masked however by much stronger Kondo effect with the opposite tendency. We do not discuss it here. For high temperatures the slope of $\chi^{-1}_{DCF}(T)$ increases and such a tendency is observed

in experiment [5]. The increase mainly results from the strong reconstruction of Γ_8 manifold. The non-cubic perturbations of DCF split Γ_8 into doublets. The average magnetic moment of the excited states decreases.

Figure 3 shows the specific heat calculated as a weighted sum of the specific heat for different DCF configurations. The wide spread of CF levels caused by DCF manifests in the broadening of the Schottky peak and in the occurrence of the high temperature tail.

Acknowledgments

This work was supported by the Committee for Scientific Research under grant No. 2P03B 118 14. The calculations were performed in the Supercomputer and Networking Centre in Poznań (PCSS).

References

[1] D. Wohlleben, B. Wittershagen, *Adv. Phys.* **34**, 403 (1985).

[2] M. Loewenhaupt, K.H. Fischer, in: *Handbook of Magnetic Materials*, Vol. 7, Ed. K.H.J. Buschow, Elsevier, Amsterdam 1993, p. 503 and references therein.

[3] S. Lipiński, *J. Magn. Magn. Mater.* **192**, 553 (1999).

[4] M. Richter, P.M. Oppeneer, H. Eschrig, B. Johansson, *Phys. Rev. B* **46**, 13919 (1992).

[5] P. Lethmillier, J. Chaussy, *J. Phys. (France)* **37**, 123 (1976).

[6] G. Balakrishnan, D. McK. Paul, N.R. Bernhoeft, *Physica B* **156&157**, 815 (1989).