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Journal of Alloys and Compounds 444–445 (2007) 292–295

Journal of ALLOYS AND COMPOUNDS

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Magnetic dynamics in correlated electron metals poised between localization and itinerancy

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Received 30 June 2006; received in revised form 28 September 2006; accepted 2 October 2006
Available online 7 November 2006

Abstract

Despite of the impressive range of experimental information on the physical properties of plutonium almost nothing is known on the magnetic dynamics in all plutonium phases. The plausible magnetic spectral response in fcc Pu has been calculated on the basis of the single-ion Kondo model and comparison with a model system CeNi, which is a good analogue of fcc Pu regarding the characteristic Kondo energy scale and partial delocalization of the f-electrons. A broad peak centered at about 40 meV dominates in the spectrum at low temperatures. The most interesting energy transfer range for the inelastic neutron scattering experiments measurements on fcc Pu is 20–150 meV. Magnetic excitations in itinerant systems like Cr and α-Pu are discussed.

Keywords: Rare earth alloys and compounds; Actinide alloys and compounds; Spin dynamics; Inelastic neutron scattering

1. Introduction

Excitation spectra are indispensable experimental data to the understanding of the ground state and the major interactions in plutonium. In particular inelastic neutron scattering (INS) experiments can yield valuable answers with respect to the puzzling question raised over the absence of any evidence of magnetic moments in plutonium [1]. Despite of the impressive range of information which has been attained by measurements of physical properties and theoretical studies the investigation of the dynamic properties of plutonium is by no means complete [2]. INS is very limited in the case of plutonium to say the least and almost nothing is known on the magnetic spectral response in this metal. However, a lot of INS data has been collected for other strongly correlated metals and intermetallics with electrons balanced between itinerant and localized states. Pu is not unique among metallic systems regarding such phenomena as the unit cell volume collapse and the partial delocalization of the f-electrons. Cerium and Ce-based compounds demonstrate many peculiarities of the 4f electron shell similar to the 5f shell in Pu. Cerium-based systems with a wide range of the characteristic Kondo energies have been studied by INS intensively (see [3,4] and references therein). The concept of shifted homology of Ce and Pu is known for a long time [5]. It is based on the electron hole symmetry between the wave functions of the f^n ands f^{6-n} ions. Ce and Pu ions have a similar degree of delocalization of the f-electrons. Thus, Ce compounds could serve as good model systems to judge about the plausible magnetic spectral response in Pu and its compounds. The magnetic spectra of Ce-based compounds contain various contributions. Its is generally assumed that, in the state with large hybridization and relatively high Kondo energies, one broad inelastic peak centered at an energy of several tens to some hundreds of millielectronvolts dominates at low temperatures. The broad peak is a single-ion spectral feature and almost $\boldsymbol{Q}$-independent (except the dependence of the magnetic form factor on the absolute value of $\boldsymbol{Q}$). However, this physical picture is oversimplified, since extra peaks show up in the INS spectra of some Ce-based Kondo systems. These peaks reflect the coherent origin of the ground state in the Kondo lattices. In addition to coherent peaks reflecting dynamic magnetic

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doi:10.1016/j.jallcom.2006.10.002

correlations in the Ce sublattice, other magnetic spectral features have been observed in cerium-based Kondo compounds: inter-multiplet transitions, modified crystal field excitations, magnetic excitations coupled to phonons.

Nothing is known on the magnetic spectral response in α-Pu which is considered as a system where 5f electrons are believed to participate in bonding. Magnetic excitations in itinerant systems are usually very broad extending beyond hundreds milli-electronvolts since the characteristic energy scales are huge and the excitations velocities are provided by the Fermi energy. Elemental Cr is an archetypical itinerant system extensively studied by the INS technique. Investigation of the magnetic excitations in Cr could be useful for the understanding of the magnetic dynamics in α-Pu.

The main goal of the present study was to calculate the plausible magnetic excitation spectrum of fcc Pu on the basis of the INS data collected in Ce-based systems and the analysis of the thermodynamic properties of Pu. We discuss the most interesting neutron energy transfer range to study magnetic excitations in fcc Pu and the feasibility of the INS experiments on ^{239}Pu-based samples.

2. Results and discussion

In order to choose the best model cerium system to understand magnetic dynamics in fcc Pu one should take into account the characteristics Kondo energy scale. Plutonium demonstrates many typical features of Kondo systems in its macroscopic physical properties (specific heat, magnetic susceptibility, resistivity, etc.), so the idea to analyze the magnetic spectral response in Pu on the basis of the Kondo approach looks reasonable at first glance. The value of the Sommerfeld coefficient in fcc Pu $\gamma = 65$ mJ/(mol K^2) [6] is indicative of the moderately heavy fermion or even intermediate valence behaviour. Among Ce-base compounds, CeNi has the same value of the linear specific heat coefficient γ [7]. The ground state in this system is a many-particle non-magnetic singlet. It is worthwhile to note that, very similar to the instabilities of the 5f shell in plutonium, CeNi demonstrates a first order phase transition with a 12% volume collapse [8].

The magnetic excitation spectrum of the 4f analogue of plutonium CeNi have been measured by INS on both single crystal and polycrystalline samples. ^{60}Ni isotope was used to suppress the phonon contribution to the scattering. Details of the experiments are provided in [9]. Figs. 1 and 2 show the magnetic contributions measured on a single crystal and polycrystalline sample, respectively. The spectra can be described by three peaks: one broad with $E_0 = 45$ meV and half-width at half-maximum about 40 meV and two relatively narrow at $E_0 = 18$ and 34 meV. The broad spectral feature is a single-ion peak typical for Ce-based Kondo compounds. Single-ion response is by far the major spectral feature contributing more than 90% to the total magnetic scattering. Two narrow peaks correspond to almost dispersionless collective excitations with intensity strongly dependent on the wavevector $\boldsymbol{Q}$. These peaks somehow reflect the coherent ground state in the system but their exact origin remains unclear.

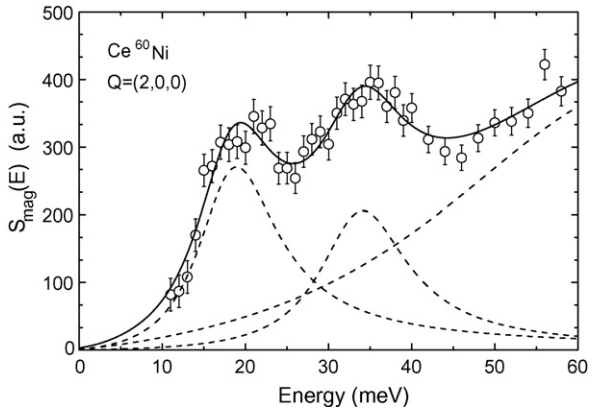

Fig. 1. Magnetic spectral response of the single crystal of $Ce^{60}Ni$ measured at $T = 11$ K at the zone center along **a**-direction $\boldsymbol{Q} = (2, 0, 0)$. Lines: fit of the magnetic response by three inelastic Lorentzians. The magnetic contributions have been normalised by the Ce^{3+} magnetic formfactor to $\boldsymbol{Q} = 2.9$ Å^{-1}.

Now we are coming to the main problem—calculation of the magnetic spectrum in fcc Pu. Coherent spectral features are likely to show up in fcc Pu. Nevertheless, we assume that the broad single-ion peak is the major spectral feature in fcc Pu. The characteristic energy scale of this peak is provided by the value of the Sommerfeld coefficient within the Fermi-liquid approach [10,11]:

$$\gamma = N_A \pi^2 k_B < n_f > \frac{1}{3E_0} \frac{N-1}{N} \quad (1)$$

A reasonable estimate from the specific heat data is $E_0 = 30$ meV assuming the occupancy of the 5f shell $<n_f> = 0.83$ and the effective degeneracy of the ground state N ($2 < N < 6$ since $J = 5/2$ multiplet dominates in fcc Pu). This Kondo energy scale yields the value of the static magnetic susceptibility in fcc Pu at low temperatures $\chi \sim 540$ μemu/mol which is very close to the experimental value obtained for stabilized δ-Pu [12]. Thus, the characteristic energy scale of about 30 meV is consistent with both specific heat and magnetic susceptibility within the Fermi liquid physical picture applied to fcc Pu at low temperatures.

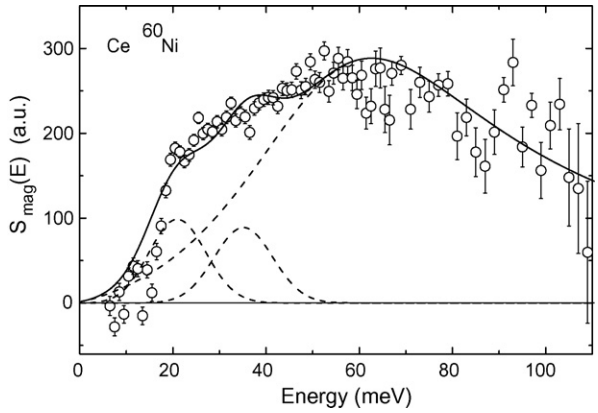

Fig. 2. Magnetic component of the INS spectrum of $Ce^{60}Ni$ polycrystal at $T = 12$ K. Lines: fit by three inelastic Lorentzians, one single-ion peak centered at about 60 meV and two coherent peaks with the energy positions fixed at $E = 18$ and 34 meV.

Another crucial question is the choice of a proper spectral function. Lorentzian is certainly not the best option since the total scattering cross-section diverges. A realistic description of the INS spectra in Kondo systems can be achieved on the basis of the non-crossing approximation solution of the non-interacting Kondo impurities model using the spectral function derived by Kuramoto and Müller-Hartmann (KMH) [13]. The KMH function is a single-ion spectral function for the Anderson impurity:

$$S(Q,E) = \frac{C\chi(Q)F^2(Q)}{(1-\exp(-E/k_BT))}\frac{\alpha E}{u^2(u^2+4\alpha^2)} \times \left[\alpha \ln((1-u^2)^2+4u^2\alpha^2) + |u|\left(\frac{\pi}{2} - \tan^{-1}\left(\frac{1-u^2}{2|u|\alpha}\right)\right)\right] \quad (2)$$

where $u = E/E_0$, $\alpha = \sin(\pi<n_f>/N)$, χ the static magnetic susceptibility and F is the magnetic form factor. The calculated magnetic excitation spectrum is shown in Fig. 3. Since nothing is known on the dynamic magnetic correlations in Pu, possible coherent peaks were not considered at this point. Due to the detailed balance factor (Stokes and anti-Stokes scattering processes asymmetry) the real maximum of the magnetic response is at 40 meV, a bit higher than the Kondo energy scale. If the spectrum is realistic, sizable scattering intensity extends to relatively high energies, much higher than 100 meV. Using the Kramer–Kroenig relation the static magnetic susceptibility was calculated to match the experimental value at $T = 10$ K.

The most interesting energy transfer range to search for the magnetic excitations in fcc Pu is $20\,\text{meV} < E < 150\,\text{meV}$. Such a range implies relatively high incoming neutron energy, much higher than used in [14]. According to Ref. 1[1], Pu magnetic moments do not show up in macroscopic measurements and also in low-energy transfer window in the INS spectra. We would suggest to search for the magnetic excitations in fcc Pu in a broader energy window.

Monoclinic α-Pu is also a very puzzling material. A simple analysis of its properties within the framework of the model we used for fcc Pu failed since no single energy scale is able to provide consistent description of the Sommerfeld coefficient and the low-temperature magnetic susceptibility. In particular, the magnetic susceptibility is very high in α-Pu for the f-electron system with $\gamma = 17\,\text{mJ/(mol K}^2)$. We believe that the magnetic spectral response in α-Pu extends to very high energies, much higher than in fcc Pu. To illustrate the unusual dynamics of a pure itinerant system, we present the magnetic excitations of a chromium single crystal. Cr demonstrates many characteristic features of itinerant electrons [15]. The major difference of Cr and α-Pu is the incommensurate magnetic ordering in chromium due to spin density waves, while α-Pu remains paramagnetic down to very low temperatures. It is clear from the very beginning that the magnon-like modes observed in Cr are not expected in α-Pu. On the other hand, additional spectral features in Cr, which are not directly related to the incommensurate magnetic ordering, may have a counterpart in other itinerant systems like α-Pu. Excitations in itinerant systems are closely related to the topology of the Fermi surface and transitions between the electron and hole pockets in the reciprocal space. Even in high-symmetry chromium (body centered cubic structure) the topology of the Fermi surface is so complicated that the application of the ab initio methods proved to be almost hopeless. In monoclinic α-Pu the topology of the Fermi surface is more complicated, electron correlations are stronger, and difficulties for the ab initio calculations are tremendous. That is why INS is the only tool able to provide reliable information on the magnetic excitations in α-Pu.

The $\boldsymbol{Q}$-dependence of the magnetic excitation in single-$\boldsymbol{Q}$ Cr is shown in Fig. 4. The measurements were performed on the multi-detector triple-axis spectrometer IN3 (ILL). Commensurate scattering (which is called Fincher–Burke modes, see [16] and references therein) dominates in the low energy transfer domain $E < 8$ meV. The energy scale of the commensurate inelastic scattering in Cr is 2 orders of magnitude smaller than the incommensurate one. This is indicative of strong dynamic magnetic correlations in Cr which are not directly related to the

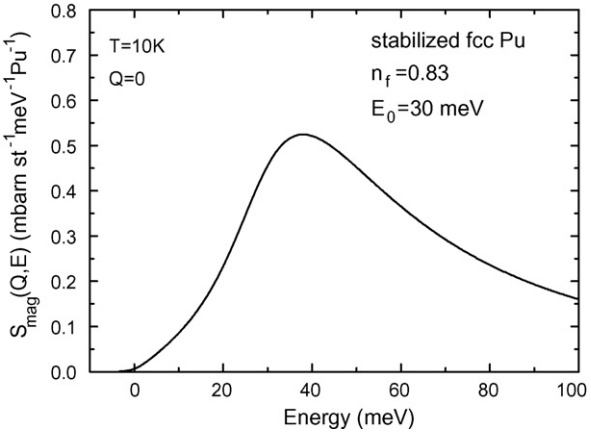

Fig. 3. Calculated magnetic spectral response in fcc Pu at $T = 10$ K. Parameters of the KMH spectral function: Kondo energy $E_0 = 30$, fractional occupation of the 5f shell $n_f = 0.83$.

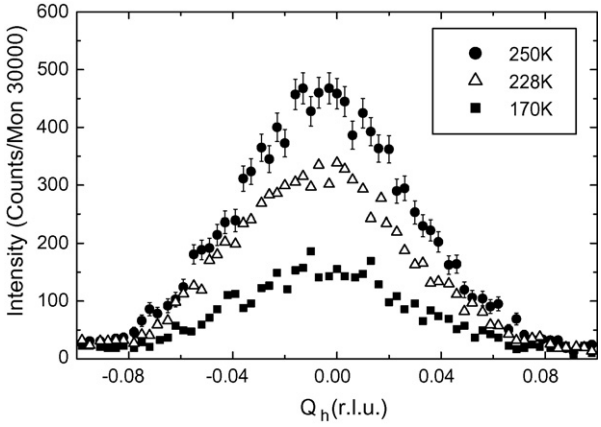

Fig. 4. Magnetic intensity in single-$\boldsymbol{Q}$ Cr crystal measured at $E = 6$ meV around $\boldsymbol{Q} = (1, 0, 0)$.

incommensurate magnetic ordering. Our findings demonstrate that the magnetic ordering is not required in principle to give rise to sizable inelastic peaks in the INS spectrum in an itinerant system. Investigations of the magnetic spectral response on α-Pu single crystal could provide valuable information on the magnetic correlations in this system.

To sum up, the magnetic spectral response of fcc Pu has been calculated based on the model which has been used intensively for 4f electron Kondo systems. Ce-based compounds in many aspects resemble fcc Pu and could be used as good model systems. The energy transfer range to search for the magnetic excitations in Pu is rather high and requires incoming neutron energies $E_i > 100$ meV.

The most promising INS measurements must be done on ^{242}Pu samples. On the basis of our positive experience with highly absorbing samples (like natural boron based MgB_2 with the neutron absorption cross section of about 1500 barn/f.u. and 10-boron reach TmB_{12} [17]) we consider that the INS experiments using the most common ^{239}Pu isotope ($\sigma_{abs} = 1017$ barn) are feasible.

Acknowledgements

This work was performed under the auspices of the Russian Federal Agency of Atomic Energy (State Contract #6.06.19.19.06.988). Financial support by the RFBR (grant #05-08–33456-a) is gratefully acknowledged.

References

[1] J.C. Lashley, A. Lawson, R.J. McQueeney, G.H. Lander, Phys. Rev. B 72 (2005) 054416.
[2] In: N. Cooper (Ed.), Los-Alamos Science, vol. 26, 2000.
[3] E. Holland-Moritz, G.H. Lander, Handbook on the Phys. and Chem. of Rare Earths, vol. 19, in: K.A. Gschneidner Jr., L. Eyring (Eds.), North Holland, Amsterdam, 1994 (Chapter 130, 1).
[4] M. Loewenhaupt, K.H. Fischer, in: K.A. Gschneidner Jr., L. Eyring (Eds.), EBST Handbook on the Phys. and Chem. of Rare Earths, vol. 16, North Holland, Amsterdam, 1993 (Chapter 105, 1).
[5] B.R. Cooper, P. Thayamballi, J.C. Spirlet, W. Müller, O. Vogt, Phys. Rev. Lett. 51 (1983) 2418.
[6] J.C. Lashley, J. Singleton, A. Migliori, J.B. Betts, R.A. Fisher, J.L. Smith, R.J. McQueeney, Phys. Rev. Lett. 91 (2003) 205901.
[7] D. Gignoux, F. Givord, R. Lemaire, J. Less Common Metals 94 (1983) 165.
[8] D. Gignoux, J. Voiron, Phys. Rev. B 32 (1985) 4822.
[9] E. Clementyev, J.-M. Mignot, P.A. Alekseev, V.N. Lazukov, E.V. Nefeodova, I.P. Sadikov, M. Braden, R. Kahn, G. Lapertot, Phys. Rev. B 61 (2000) 6189.
[10] T.V. Ramakrishnan, K. Sur, Phys. Rev. B 26 (1982) 1798.
[11] V.T. Rajan, Phys. Rev. Lett. 51 (1983) 308.
[12] R.H. Heffner, G.D. Morris, M.J. Fluss, B. Chung, S. McCall, D.E. MacLaughlin, L. Shu, K. Ohishi, E.D. Bauer, J.L. Sarrao, W. Higemoto, T.U. Ito, Phys. Rev. B 73 (2006) 094453.
[13] Y. Kuramoto, E. Müller-Hartmann, J. Magn. Magn. Mater. 52 (1985) 122.
[14] R.J. McQueeney, A. Lawson, A. Migliori, T.M. Kelly, B. Fultz, M. Ramos, B. Martinez, J.C. Lashley, S.C. Vogel, Phys. Rev. Lett. 92 (2004) 146401.
[15] E. Fawcett, Rev. Mod. Phys. 60 (1988) 209.
[16] E. Clementyev, P. Böni, F. Demmel, G. Shirane, Physica B 350 (2004) 67.
[17] E. Clementyev, A. Furrer, K. Conder, I. Sashin, Eur. Phys. J. B 21 (2001) 465.