

Neutron scattering from α -Ce at epithermal neutron energies

A P MURANI

Institut Max von Laue Paul Langevin, 6 Rue Jules Horowitz, 38042 Grenoble, France
E-mail: murani@ill.fr

Abstract. Neutron scattering data, using neutrons of incident energies as high as 2 eV, on α -Ce and α -Ce-like systems such as CeRh₂, CeNi₂, CeFe₂, CeRu₂, and many others that point clearly to the substantially localized 4f electronic state in these systems are reviewed. The present interpretation is contrary to the widely held view that the 4f electrons in these systems form a narrow itinerant electron 4f band.

Keywords. Neutron scattering; α -Ce-like systems; heavy fermions.

PACS Nos 71.27.+a; 71.20.Eh; 75.20.Hr

1. Introduction

The γ - α phase transition in Ce has remained enigmatic ever since its initial observation in 1927 by Bridgman [1]. A well-illustrated experimental observation of the γ - α phase transition in Ce, as a function of pressure, is provided by the data of McPherson *et al* [2]. These show a large, \sim six-fold, drop in the susceptibility as pressure is increased to above \sim 9 kbar when the metal transforms from the γ - to the α -phase. This phase transition involves a 14% volume reduction, although the crystalline structure remains unmodified, being fcc in both phases [3]. The transition is first order showing a large hysteresis, as the reverse transition to the γ -phase is achieved only when the pressure drops to below \sim 6 kbar. A similar observation of the dramatic change in the magnetic susceptibility of the metal (alloyed with a small concentration of Sc or Th to prevent β -phase formation) is seen as a function of temperature also. The Curie-Weiss susceptibility in the γ -phase drops suddenly on cooling below 110 K by roughly the same amount as in the pressure study, becoming practically temperature independent at lower temperatures. Such constant low-temperature susceptibilities, resembling Pauli paramagnetism, have been observed in a number of Ce-based alloys and compounds, which are, thus, considered as α -Ce-like systems, and also classified as valence fluctuation systems.

In a review entitled '*Neutrons and rare earth magnetism*' published in the *Neutron News* in 1995 [4] the author, A R Mackintosh, made the following remarks:

"In the early 1960s, the generally accepted model of the γ - α phase transition in Ce, which was thought to be due to the *promotion of the 4f electron on each site*

to the *s,p,d-conduction band* [5], was revealed as inadequate by Dan Gustafson [6],
....”

“By positron-annihilation experiments he demonstrated that the number of 4f electrons changes little at the transition and suggested instead that they *metamorphose into delocalised conduction electrons, while maintaining their f character.*”

“This insight that f electrons could form energy bands and contribute to the Fermi surface was controversial for many years, but is now generally accepted.”
“These highly correlated itinerant f states are of great interest, but *neutrons have so far made relatively little contribution to revealing their essential nature.*”

2. Aims of this review

The principal aim of this review is to present neutron scattering data on α -Ce and a few α -Ce-like systems that clearly demonstrate that the 4f state in this metal and similar systems remains essentially and substantially localized rather than form a narrow 4f band as suggested by Mackintosh [4] and which, apparently, is still a commonly held view. We find that the localized state is, nevertheless, strongly energy-broadened due to hybridization with the outer-shell electrons (of neighbouring ions in the lattice) that commonly form the conduction band. This is quite distinct from the formation of a narrow 4f band as a result of which the magnetic moments, both spin and orbital moment, would be substantially quenched (reduced), particularly the orbital moment, in relative terms, with dramatic consequences for the magnetic form factor as found, for example, in the early actinides where the 5f electrons are believed to form narrow 5f bands and show significantly modified magnetic form factors compared with those for a localized 5f ion [7]. We begin this review with an example of a system that is influenced relatively weakly by hybridization effects and where the evolution in the physical properties can be observed readily as hybridization is progressively increased. We present below evidence of single-ion behaviour from: (a) the magnetic form factor determined from the neutron scattering data on α -Ce, (b) the spectral form of the magnetic scattering which is consistent with the predicted (calculated) form for a single-ion in the Anderson model and (c) fits to the neutron spectra which yield parameters that are in good accord with Fermi liquid relations obtained for the single-ion Anderson model.

3. Neutron scattering data on some Ce-systems

The particular magnetic susceptibility and thermodynamic behaviour of α -Ce and similar systems, for example the constant low temperature susceptibility and the large magnitude of the linear specific heat, has been attributed to the hybridization of the f-electrons with the outer-shell electrons of neighbouring ions forming the lattice, in general the conduction electrons. As mentioned above, we show in the following, with the help of a number of different examples from our neutron scattering work, that this hybridization does not involve a 4f band, as often believed, but rather the localized 4f state which, as a result of the hybridization, is energy-broadened while maintaining a substantially localized character.

It is important to recognize that the hybridization also occurs, although somewhat moderately, in the γ -phase of Ce too. In fact, the strength of the hybridization and hence its effect on the physical properties of various systems vary from moderately weak, as in γ -Ce, to being extremely strong as in α -Ce and α -Ce-like systems, particularly CeFe₂ and CeRu₂. The effect of the relatively weak hybridization in γ -Ce-like systems (often referred to as heavy fermions) manifests as a broadening of the crystal field states. Thus in γ -Ce, at temperatures above the γ - α transition, the neutron inelastic scattering data show a moderately broad quasielastic distribution ($\Gamma \sim 5$ meV) associated with the crystal field ground state and a similarly broad inelastic peak corresponding to the excitation from the ground state to the higher-lying cubic crystal field state. Since the same mechanism, viz. hybridization of the localized 4f state with the conduction electrons (or other outer electrons), is operative in the heavy fermion systems as well as α -Ce-like systems, both types of systems are essentially physically similar, except for the stronger charge fluctuations in the latter. The degree of hybridization with conduction electrons represented by the parameter Δ ($=\pi V^2 \rho(E_F)$), where V is the strength of the interaction and $\rho(E_F)$, the density of conduction electron states at the Fermi level) translates into a characteristic temperature T_K , which is expressed as $D \exp(-\pi|\varepsilon_f|/N\Delta)$, where D is the conduction electron bandwidth, ε_f the position of the 4f level relative to the Fermi level and N the degeneracy of the 4f state [8].

The effect of the progressive increase in the hybridization on the physical properties of Ce-based systems is best illustrated with reference to the data on pseudobinary compounds CeIn_{3-x}Sn_x ($0 < x < 3$). The compound CeIn₃ is a heavy fermion system ($T_K \sim 2$ meV) that orders antiferromagnetically at low temperatures (~ 10 K), whereas CeSn₃ is an α -Ce-like (valence fluctuation) system ($T_K \sim 35$ meV) that remains paramagnetic down to low temperatures. Figure 1 shows the magnetic response from CeIn₃ at 20 K [9]. A broad, well-defined crystal field excitation and a central quasielastic distribution are observed in this compound. The quasielastic region measured with better energy resolution (using a lower incident energy) is shown in figure 1b.

Replacement of half of the In by Sn to form the compound CeIn_{1.5}Sn_{1.5} yields a magnetic spectral response that is a single broad hump centred on ~ 9 – 10 meV, where neither the quasielastic nor the inelastic crystal field excitation (expected for a normal cubic compound of Ce) can be resolved. At the Sn-rich end the compound CeSn₃ shows a similar broad hump that is centred on $\omega_0 \sim 35$ meV which corresponds to its characteristic energy T_K .

The bulk of the data we present here are taken on polycrystalline samples. However, our measurements on a single crystal sample of composition CeIn₁Sn₂ [10] show weak modulations of intensity (~ 10 – 20%) as a function of Q , resembling antiferromagnetic correlations. These modulations, in fact, reflect the weakly anisotropic hybridization with the conduction electrons. Interestingly, the characteristic energies obtained from the spectral response at the zone boundary and zone centre are roughly similar, but may be expected to vary by at most 10–20%, for cubic systems. Hence data on polycrystalline samples provide a reasonably good description of the magnetic response from these systems.

The magnetic response from α -Ce is, indeed, very similar to that from CeSn₃ (and CeIn_{1.5}Sn_{1.5}). That is, it is a broad Lorentzian hump centred on a much

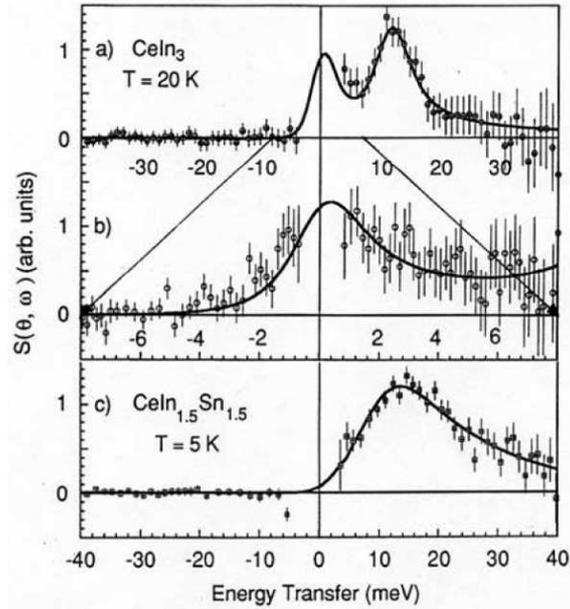


Figure 1. (a) The magnetic spectral response $S(\Theta, \omega)$ at 20 K from CeIn_3 [9]. The central quasielastic region measured with a higher energy resolution is shown in (b). The magnetic scattering from $\text{CeIn}_{1.5}\text{Sn}_{1.5}$ at 5 K is shown in (c). It is fitted to a single broad Lorentzian distribution centred on ~ 10 meV (solid curve, figure 1c).

higher characteristic energy $\omega_0 (=T_K) \sim 170$ meV [11]. Thus, we find that with increasing hybridization we obtain progressively higher characteristic energies ω_0 where the magnetic spectra are interpreted in terms of Lorentzians centred on ω_0 . As discussed in more detail below, a Lorentzian form for the spectral response is a very good approximation to the more complex-looking spectral form calculated by Kuramoto and Müller–Hartmann [12] for the single-ion Anderson model. We mention also that fits to the time-of-flight spectra, taken at constant scattering angles 2Θ , necessarily involve an additional variation of intensity with energy transfer ω (hence Q), corrections for which are made assuming the intensity varies as a function of Q as the Ce^{3+} single-ion form factor $F^2(Q)$. Thus Lorentzian fits to the form-factor corrected data provide reasonably good evidence for the single-ion character of the spectral response. However, as this is not considered sufficient in the context of the continuing debate on the exact nature of the 4f state in α -Ce, we have addressed the question via a direct determination of the magnetic form-factor. For this we measured the spectral response from a Ce–10%Sc alloy on the MARI spectrometer at ISIS which has a wide continuous coverage of scattering angles [13]. An energy-integration of the measured difference spectrum $S(Q, \omega)$ within an energy band of ± 30 meV centred on 170 meV is shown as a function of Q in figure 2. The continuous curve through the data represents the Ce^{3+} single-ion magnetic form factor. In the same figure we have shown the magnetic form factor of Hjelm

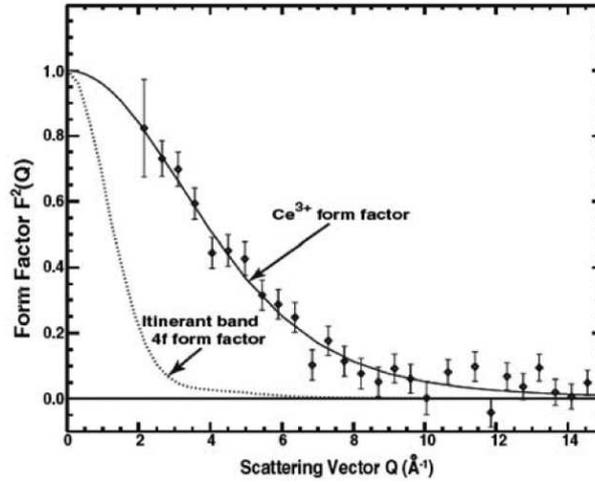


Figure 2. The magnetic form factor of α -Ce (filled circles) determined from the constant- ω integration within an energy bandwidth of ± 30 meV around 170 meV [13]. The continuous curve through the data shows the Ce^{3+} magnetic form factor. The dotted line shows the calculated form factor for an itinerant 4f electron band for α -Ce [14].

et al [14] calculated within the itinerant 4f band model for Ce. Clearly, this is very different from the observed form that closely follows the Ce^{3+} form factor.

From the difference spectrum between the γ -phase and α -phase of Ce measured in our earlier experiment [12] with an incident energy of 2 eV we obtained by integration a 4f occupancy factor $\langle n_f \rangle \sim 0.8 \pm 0.1$ for α -Ce, assuming full 4f occupancy, i.e. $\langle n_f \rangle = 1$, in γ -Ce. Thus, it would appear that a fraction of about 0.2 electrons is missing in the α -phase. This is, perhaps, not surprising due to the strong hybridization with conduction electrons in α -Ce, and the consequent charge fluctuations. Hence, this result indicates that the 4f state in α -Ce remains substantially localized to at least ~ 80 – 90% level.

In the analysis of the neutron spectra as a function of ω , the data corrected for the variation of intensity as a function of Q (which varies with ω for constant scattering angles) using the Ce^{3+} form factor are fitted to the Lorentzian spectral form

$$f(\omega) = (\Gamma/2\pi)/[\Gamma^2 + (|\omega| - \omega_0)^2]$$

with ω_0 representing the centroid of the Lorentzian distribution and Γ its half-width. We recall that the scattering function for a single ion could be expressed as

$$S(Q, \omega) = C\{\omega/[1 - \exp(-\omega/T)]\}f(\omega)F^2(Q),$$

where $[1 - \exp(-\omega/T)]^{-1}$ is the detail balance factor and $F^2(Q)$ the single-ion form factor.

The spectral function $f(\omega)$ for a single ion in the Anderson model calculated by Kuramoto and Müller-Hartmann has the more complex looking form [11]:

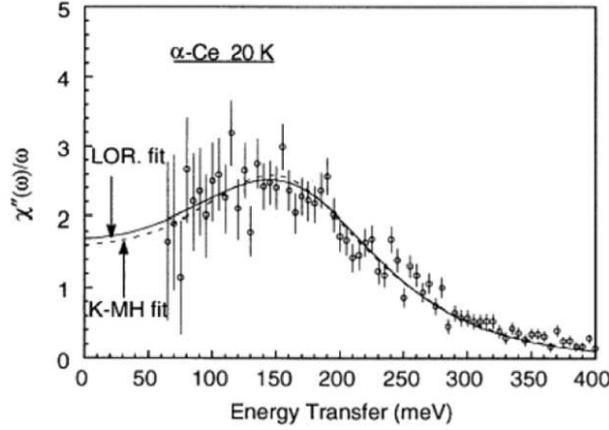


Figure 3. Magnetic spectral response from α -Ce at 20 K plotted as $\chi''(\omega)/\omega$. The solid curve represents the Lorentzian fit to the data while the dashed curve is the best fit to the Kuramoto and Müller-Harmann spectral function [12].

$$f(\omega) = \alpha/[u^2(u^2 + 4\alpha^2)]\{\alpha \ln[(1 - u^2)^2 + 4u^2\alpha^2] + |u|[\pi/2 - \tan^{-1}(1 - u^2)/(2|u|\alpha)]\},$$

where $u = \omega/\omega_0$ and $\alpha = \sin(\pi\langle n_f \rangle/N)$, with ω_0 the characteristic energy, $\langle n_f \rangle$ the 4f occupancy and N the degeneracy of the 4f state.

These two forms of the spectral functions fitted to the observed magnetic response from α -Ce are shown in figure 3, where the data are presented as $\chi''(\omega)/\omega$. This representation amplifies the low energy region where the differences are most pronounced. There are, also, small differences between the two spectral forms at very high energies, not accessed in the measurements presented. That this must be so is evident from the fact that the integral of $S(\omega)$ using the Lorentzian spectral form for $f(\omega)$ diverges logarithmically whereas the Kuramoto and Müller-Hartmann form of $f(\omega)$ yields a finite integral. It is evident that within the measured energy range the difference between the two fitted forms is rather small. Hence a Lorentzian provides a good representation of the single-ion spectral response, but requires an appropriate high-energy cut-off. Also, the characteristic energies ω_0 obtained from the two types of fits are similar in magnitude, to within $\sim 10\%$.

It is interesting that the characteristic energy of ~ 170 meV obtained from our neutron data is well-reproduced by the recent resonant inelastic X-ray scattering (RIXS) measurements on α -Ce (~ 1700 K) [15]. Also the same RIXS measurements suggest a 4f occupancy $\langle n_f \rangle$ of ~ 0.81 , in good agreement with our neutron data $\sim 0.8 \pm 0.1$ [11]. However, since we believe our neutron data underestimate $\langle n_f \rangle$, the agreement between the two techniques can be considered as semi-qualitative.

Additional evidence for the single-ion nature of the spectral response is provided by the characteristic energies $\omega_0(T_K)$ obtained from the spectral fits on a number of systems that are found to be in agreement with the characteristic energies T_K calculated from the single-ion Fermi liquid relations [16] associated with the constant, low temperature Pauli-like susceptibility $\chi_0 (= \mu^2 \langle n_f \rangle / 3T_K)$, where $\langle n_f \rangle$ is the occupancy of the 4f state, μ^2 is the square of the moment of the localized

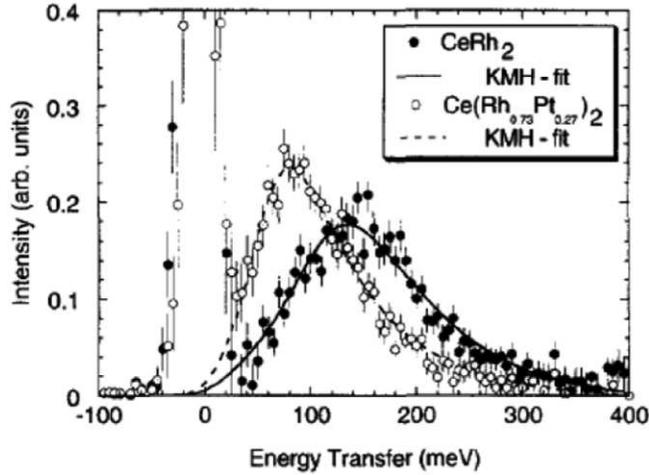


Figure 4. Magnetic spectral response from CeRh_2 and $\text{Ce}(\text{Rh}_{0.73}\text{Pt}_{0.27})_2$ [17]. The solid and the dashed lines represent fits to the Kuramoto and Müller-Hartmann spectral function [12].

state $= g_J^2 J(J+1) \mu_B^2$) and γ the coefficient of the linear term in the specific heat ($\gamma = \pi^2 k_B^2 \langle n_f \rangle / 3T_K$). Neutron data on a number of systems spanning a wide range of characteristic energies have been found to obey these relations. As an example we reproduce in figure 4, the neutron spectra on the compound CeRh_2 and $\text{Ce}(\text{Rh}_{0.73}\text{Pt}_{0.27})_2$ which have characteristic energies $\omega_0 \sim 115$ meV and ~ 65 meV, respectively [16]. They are in reasonably good agreement with those calculated, assuming $\langle n_f \rangle \sim 1$, from the susceptibility χ_0 (~ 100 meV and 53 meV, respectively) and specific heat coefficient γ (~ 120 meV and 72 meV, respectively).

Although the characteristic energies of ~ 115 meV (~ 1300 K) for CeRh_2 and ~ 170 meV (~ 2000 K) for α -Ce are fairly high, they are still relatively modest compared to some of the highest characteristic energies observed in the very strongly hybridized Ce compounds, e.g. CeFe_2 and CeRu_2 (~ 500 – 570 meV, i.e. ~ 6000 K). These compounds, one of which, CeFe_2 , is ferromagnetic (due to ordering within the Fe sublattice) and the other, CeRu_2 , is a Type II superconductor, show saturated valences of around 3.3 in the L_{III} absorption spectra [18], compared with ~ 3.1 – 3.2 found for α -Ce and CeRh_2 . In figure 5 we show the data for CeFe_2 , at several constant scattering angles [19], where the curves are fits to the Lorentzian spectral function including the variation of intensity as a function of Q via the single-ion Ce^{3+} magnetic form factor. The inset shows the integrated intensity, incorporating the form factor correction, plotted as a function of the elastic wave vector Q . The solid line through the data points represents the Ce^{3+} magnetic form factor, which extrapolates to a cross-section that corresponds to a magnetic moment of $\sim 1.9 \mu_B$, consistent with a 4f occupancy of ~ 0.7 , i.e. the valence of ~ 3.3 obtained from the X-ray L_{III} absorption measurements [18].

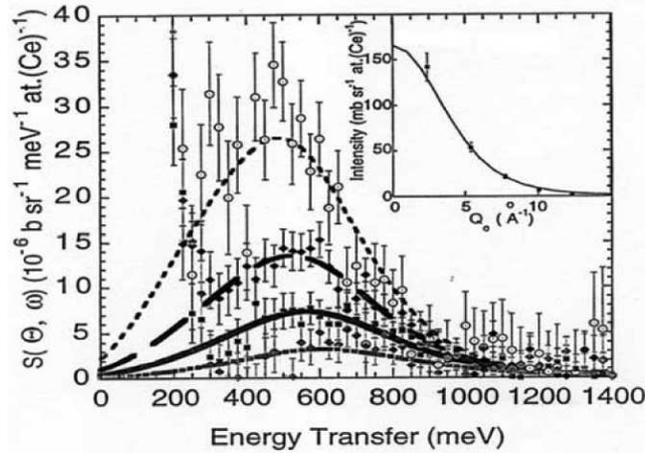


Figure 5. The magnetic response $S(\Theta, \omega)$ from CeFe_2 for several fixed scattering angles. Curves through the data points represent fits to the Lorentzian spectral function with the fixed value of the characteristic energy $\omega_0 = 570 \pm 40$ meV [19]. The integrated intensity, incorporating the form factor correction, is shown as a function of the elastic wave vector Q in the inset. The curve drawn through these data points represents the Ce^{3+} form factor, which extrapolates to $Q = 0$ to yield a scattering cross-section that corresponds to a moment of $\sim 1.9 \mu_B$, consistent with a 4f occupancy of ~ 0.7 .

4. Conclusion

The data on a few Ce-based systems presented above provide a consistent picture of a substantially localized 4f state of Ce in these strongly hybridized systems. We have obtained the magnetic form factor $F^2(Q)$ of α -Ce from our inelastic neutron scattering data and shown that it follows the single-ion Ce^{3+} form rather than the itinerant electron 4f form factor. Also, the integrated spectral weight of the magnetic response represents $\geq 80\%$ of the ground state ($J = 5/2$) moment of the Ce^{3+} ion. We have shown also that the magnetic response of α -Ce-like systems studied to date follows the single-ion spectral form and the characteristic energies obtained from fits to the data follow Fermi liquid relations calculated for the Anderson single-ion model.

References

- [1] P W Bridgman, *Proc. Am. Acad. Arts Sci.* **62**, 207 (1927)
- [2] M R MacPherson, G R Everett, D Wohlleben and M B Maple, *Phys. Rev. Lett.* **20**, 26 (1971)
- [3] D C Koskimaki and K A Gschneidner Jr., *Phys. Rev.* **B11**, 4463 (1975)
- [4] A R Mackintosh, *Neutron News* **6(4)**, 22 (1995)
- [5] see A W Lawson and T-Y Tang, *Phys. Rev.* **76**, 301 (1949)
- [6] D R Gustafson, J D McNutt and L O Roelling, *Phys. Rev.* **183**, 435 (1969)

Neutron scattering from α -Ce at epithermal neutron energies

- [7] M Wulff, G H Lander, B Lebech and A Delapalme, *Phys. Rev.* **B39**, 4719 (1989)
- [8] D L Cox, N E Bickers and J W Wilkins, *J. Appl. Phys.* **57**, 3166 (1985)
- [9] A P Murani, A D Taylor, R Osborn and Z A Bowden, *Phys. Rev.* **B48**, 10606 (1993)
- [10] A P Murani, R Currat, A Severing and R Raphel, *Physica* **B163**, 717 (1990)
- [11] A P Murani, Z A Bowden, A D Taylor, R Osborn and W G Marshall, *Phys. Rev.* **B48**, 13981 (1993)
- [12] Y Kuramoto and E Müller-Hartmann, *J. Magn. Magn. Mater.* **52**, 122 (1985)
- [13] A P Murani, S J Levett and J W Taylor, *Phys. Rev. Lett.* **95**, 256403-1 (2005)
- [14] A Hjelm, J Trygg, O Eriksson, B Johansson and J Wills, *Phys. Rev.* **50**, 4332 (1994)
- [15] J-P Rueff, J-P Itie, M Taguchi, C F Hague, J-M Mariot, R Delaunay, J-P Kappler and N Jaouen, *Phys. Rev. Lett.* **96**, 237403 (2006)
- [16] T V Ramakrishna and K Sur, *Phys. Rev.* **B44**, 8304 (1991)
- [17] A P Murani and R S Eccleston, *Physica* **B230–232**, 126 (1997)
- [18] R A Neifeld, M Croft, T Mihalisin, C U Serge, M Madigan, M S Torikachvili, M B Maple and L E DeLong, *Phys. Rev.* **B32**, 6928 (1985)
- [19] A P Murani, B Ouladdiaf and R S Eccleston, *Physica* **B259–261**, 1167 (1999)