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Inelastic neutron scattering in $CeSi_{2-x}Ga_x$ ferromagnetic Kondo lattice compounds

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Abstract. An inelastic neutron scattering investigation of the ferromagnetic Kondo lattice compounds belonging to the $CeSi_{2-x}Ga_x$ system that have $x = 0.7$, 1.0, and 1.3 is reported. In these compounds, the ground state is expected to be split by a crystalline electric field. Using the experimental results, we have calculated the crystal-field parameters for all three compounds studied here.

1. Introduction

Cerium, in its compounds, often exhibits competition between the RKKY and the Kondo interactions, which leads to some exotic ground states [1, 2]. In addition to this competition, for nearly all cerium Kondo systems, the crystalline electric field (CEF) plays an important role in determining the ground state of the system. It determines the degeneracy of the f level and the f-electron ground-state wave function involved in the hybridization. This is required in any theoretical analysis that extends beyond simple phenomenology [3]. Also Levy and Zhang [4] have proposed that the CF potential itself is largely due to the hybridization interaction between the localized f-electron states and the conduction band states that are responsible for the heavy-fermion behaviour. The most direct method of determining the CEF splitting of the ground state in such systems is by means of inelastic neutron scattering. Here, the scattering cross-section is proportional to the dynamic magnetic susceptibility. This technique has been widely used to study the spin dynamics as well as the CEF excitations in cerium-based Kondo systems [5–7]. In $CeSi_x$, $1.7 \leqslant x \leqslant 2$ [6], the linewidth and the excitation energies of CEF doublets scale almost linearly with x, and the strong hybridization between the 4f electron and the conduction electrons, which increases with x, is the cause of the large linewidths. For $CeGa_2$ [7], study of the CEF parameters has led to an understanding of the large easy-plane anisotropy. The absence of any discontinuity in the resistivity curve at the magnetic ordering temperature can be explained on the basis of CEF studies.

$CeSi_{2-x}Ga_x$ ($0.7 \leqslant x \leqslant 1.3$) is one cerium system which shows typical anomalies associated with the competition between RKKY and Kondo interactions [8, 9]. These compounds crystallize in tetragonal structures (space group $I4_1/amd$) with nearly equal cell volumes and each has a ferromagnetic ground state at low temperature. For $x = 0.7$,

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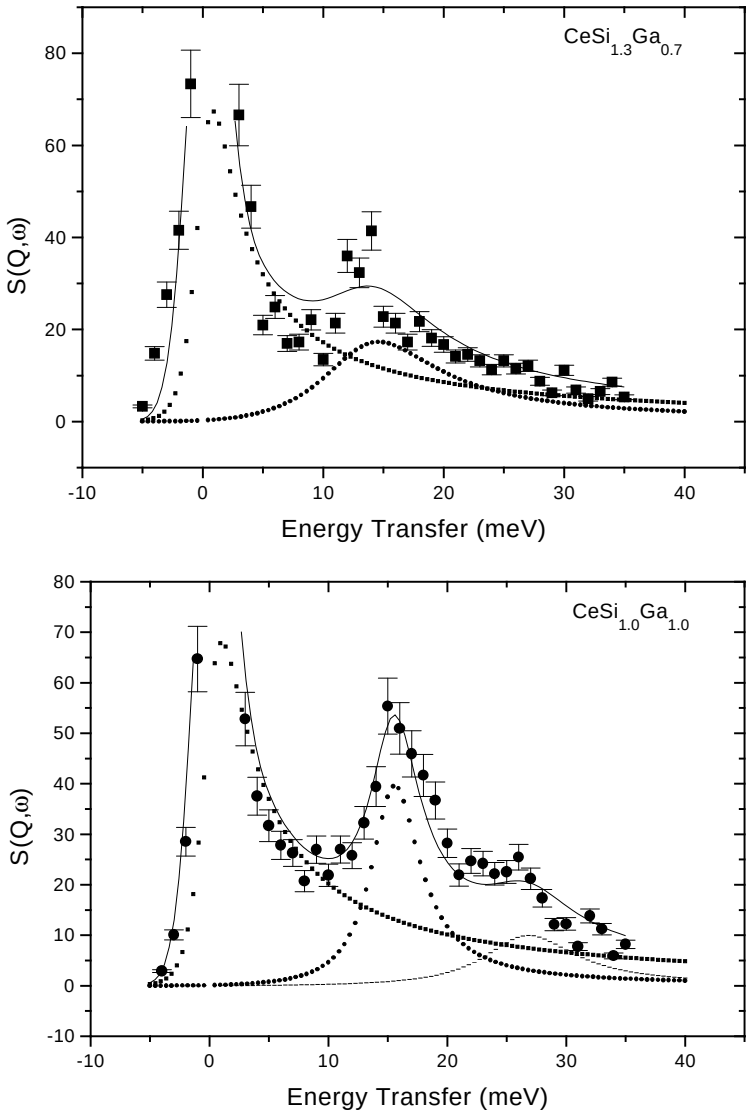

Figure 1. The magnetic spectral response of $CeSi_{2-x}Ga_x$, $x = 0.7$, 1.0, and 1.3, at $T = 12$ K. The symbols represent the experimental data, the solid line represents the least-squares fit to the data, and the dotted and dashed lines represent the individual components of the quasielastic and inelastic peaks respectively.

specific heat measurements show a sharp anomaly at the magnetic ordering temperature (T_C). This peak then broadens out and considerably decreases in intensity for $x = 1.0$ and 1.3, which is indicative of the dominance of the Kondo interaction over the RKKY interactions. This dominance is mainly due to the increasing hybridization between the 4f and conduction electrons (p electrons of Si/Ga in this case). The f–p (or, in general, f–conduction electron) hybridization has been seen to be responsible for exotic properties in many cerium-based systems. For example, the anomalous magnetic properties of cerium monopnictides have been explained on the basis of anisotropic p–f mixing [10]. In the case

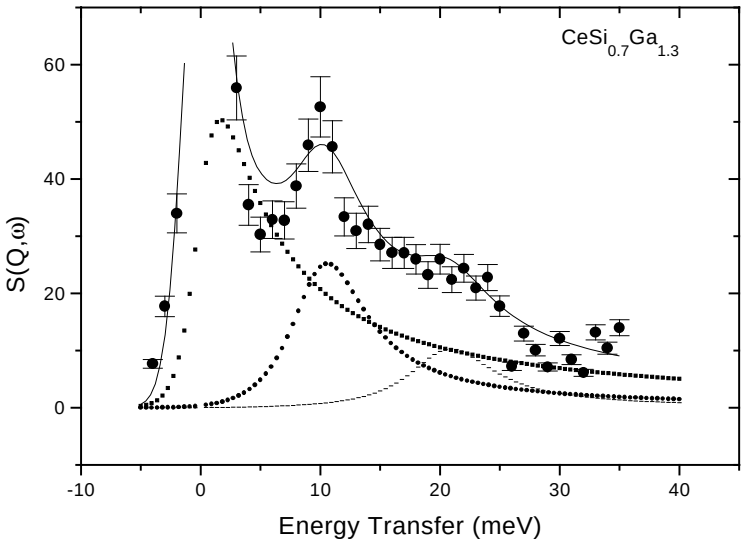

Figure 1. (Continued)

of $CeCu_2Si_2$, it has been shown that the f–p hybridization is responsible for the heavy-fermion behaviour of this compound [11]. In this paper we report on our inelastic neutron scattering studies on three compounds with $x = 0.7$, 1.0, and 1.3.

2. Experiment and results

The polycrystalline $CeSi_{2-x}Ga_x$, $x = 0.7$, 1.0, and 1.3, and LaSiGa were prepared by arc melting the pure elements in an argon atmosphere using the same procedure as in reference [8]. About 20 grams of each sample were used for the experiment. The neutron diffraction patterns are in good in agreement with a tetragonal α-$ThSi_2$-type structure, and the lattice constant values agree with those reported in the literature.

The inelastic neutron scattering experiments were performed at the DHRUVA reactor on the triple-axis spectrometer (TAS) installed on a tangential thermal neutron beam hole T 1007 at Trombay. TAS is a medium-resolution spectrometer which employs a Cu(111) plane as the monochromator and a Si(111) plane as the analyser. The collimations used are open, 60′, 60′, and open between the reactor and monochromator, monochromator and sample, sample and analyser, and analyser and detector respectively. This results in there being $\sim 10^6$ neutrons at the sample position. The spectrometer was operated at fixed final energy, $E_f = 25$ meV, with the incident energy varying from 65 meV to 20 meV at constant scattering angle, ϕ. The spectra of each sample were recorded at two different scattering angles, $\phi = 20^\circ$ and 95° ($Q = 1$ Å^{-1} and 5 Å^{-1}), and at different temperatures from 10 K to 100 K using a closed-cycle refrigerator.

The phonon contributions for all three samples were estimated from LaSiGa data using the scaling method proposed by Murani [12]. The magnetic response so obtained may be related to the dynamic susceptibility $\chi''(Q, \omega)$:

$$S(Q, \omega) = A \left[\frac{1}{1 - \exp(-\hbar\omega / k_B T)} \right] f^2(Q) \chi''(Q, \omega) \tag{1}$$

where

$$A = 1/(2\pi)(\gamma r_e/\mu_B)^2$$

which describes the coupling between the neutron and the electron spin. The Kramers–Kronig relation provides a relationship between $\chi''(Q,\omega)$ and the static susceptibility which can be written as

$$\chi''(Q,\omega) = \pi\hbar\omega\chi(Q)P(Q,\omega). \tag{2}$$

The static susceptibility $\chi(Q)$ is related to the bulk susceptibility χ_{bulk} via a magnetic form factor $f(Q)$: $\chi(Q) = f(Q)^2\chi_{\text{bulk}}$. $P(Q,\omega)$ is a spectral function which fulfils the relation

$$\int_{-\infty}^{\infty} P(Q,\omega)\ \mathrm{d}\omega = 1.$$

A Lorentzian form is usually assumed to describe the relaxation processes. For a pure quasielastic response, the Lorentzians centred at $\hbar\omega = 0$ and in the presence of crystal-field splittings $P(Q,\omega)$ are described by a series of Lorentzians centred at $\hbar\omega = 0$ (quasielastic) and $\pm\hbar\omega_i$ (crystal-field excitations) as follows:

$$\chi(Q)P(Q,\omega) = \frac{A_0(T)\Gamma_0(T)}{\Gamma_0^2(T)+\omega^2} + \sum_1^n \frac{A_i(T)\Gamma_i(T)}{\Gamma_i^2(T)+(\omega\pm\omega_i)^2} \tag{3}$$

where A_0, A_i are the amplitudes and Γ_0, Γ_i the halfwidths of the quasielastic and inelastic structures respectively.

Table 1. Values of the best-fit parameters: amplitudes (A_i), widths (Γ_i), and positions (ω_i) of the Lorentzians for the magnetic response in $CeSi_{2-x}Ga_x$.

T (K)	A_0 (arbitrary units)	Γ_0 (meV)	A_1 (arbitrary units)	Γ_1 (meV)	ω_1 (meV)	A_2 (arbitrary units)	Γ_2 (meV)	ω_2 (meV)
$x = 0.7$								
12	3.6	2.76	0.99	9.23	13.36			
25	3.3	3.47	0.82	10.76	13.45			
50	3.0	4.09	0.69	12.44	13.34			
100	2.7	5.28	0.59	13.42	13.27			
$x = 1.0$								
12	4.4	3.1	0.90	4.2	15.43	0.25	5.3	26.46
25	4.05	3.8	0.75	5.4	15.24	0.19	6.4	26.52
50	3.6	4.5	0.52	6.9	15.32	0.13	8.8	26.31
100	2.6	5.3	0.42	8.2	15.20	0.08	10.4	26.28
$x = 1.3$								
12	3.16	3.6	0.81	5.2	9.91	0.20	6.2	20.43
25	2.8	4.4	0.55	7.4	9.86	0.12	8.2	20.43
50	2.4	5.1	0.42	9.05	9.84	0.08	10.8	20.32
100	1.8	6.1	0.32	10.5	9.75	0.05	12.4	20.26

The normalized spectra measured at 12 K on TAS, after phonon correction and correction for empty-cell scattering, are shown in figures 1(a)–1(c) for the three $CeSi_{2-x}Ga_x$ compounds with $x = 0.7$, 1.0, and 1.3. The quasielastic peak at 0 meV energy transfer and the inelastic peaks indicate the presence of magnetic scattering in these samples. The solid lines in the figures were obtained by least-squares fitting to the data using equation (3). The least-squares fitting parameters obtained by fitting the spectra at all temperatures for all three compounds are given in table 1. From the table it is clear that for all three

samples there is quasielastic broadening and there are inelastic peaks due to CEF splitting of the ground state. In the case of $CeSi_{1.3}Ga_{0.7}$ only one broad inelastic peak can be seen, while for the other two samples the spectra can be fitted to two Lorentzians, which implies that the ground state is split into three doublets as expected for tetragonal point symmetry. A single inelastic peak has been observed previously [11, 13] in the case of tetragonal symmetry, and has been explained by doublet–quasiquartet splitting of the ground state. Another possible reason is that the excited doublets lie very close to each other, as was the case for polycrystalline $CePd_2Si_2$ [16].

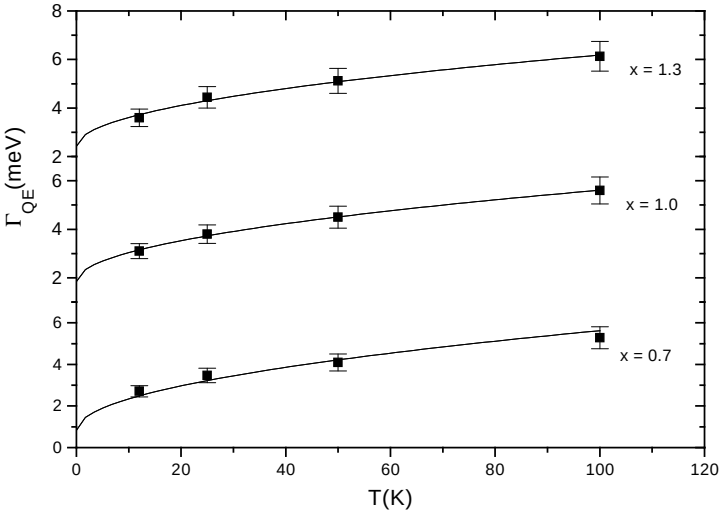

Figure 2. The thermal evolution of the quasielastic linewidth in the case of $CeSi_{2-x}Ga_x$ ($x = 0.7$, 1.0, and 1.3).

3. Discussion

The magnetic spectral response presented in figures 1–3 shows a quasielastic peak at around 0 meV and inelastic peaks. The width of the quasielastic peak increases with temperature. The thermal evolutions of the quasielastic linewidths for all three compounds studied here are presented in figure 2. The Kondo temperature (T_K) was for each compound estimated from the residual linewidth value (Γ_K) obtained by fitting the data to the equation $\Gamma_{QE} = \Gamma_0 + Ak_BT_K$, where A is a constant. The T_K so obtained are listed in table 2. It can be seen that as the Ga concentration increases, T_K also increases, while the ferromagnetic ordering temperature decreases. This suggests that there is an increase in 4f–conduction electron hybridization with increasing Ga concentration. We have, in a detailed analysis reported elsewhere [14], shown that there is in fact a crossover from a state wherein RKKY interactions dominate to a state wherein Kondo interactions dominate as the Ga concentration is increased from 0.7 to 1.0 in this system. A Lorentzian lineshape has been assumed to describe the shape of the quasielastic peak at all temperatures. It may be mentioned here that in some magnetically ordered cerium compounds, deviations from Lorentzian lineshapes have been seen at low temperatures. In the case of compounds like $CeAu_2Si_2$ [15], a deviation is seen far above its magnetic ordering temperature. For such compounds, the quasielastic peak is very narrow, indicating that the Kondo interactions are weak compared

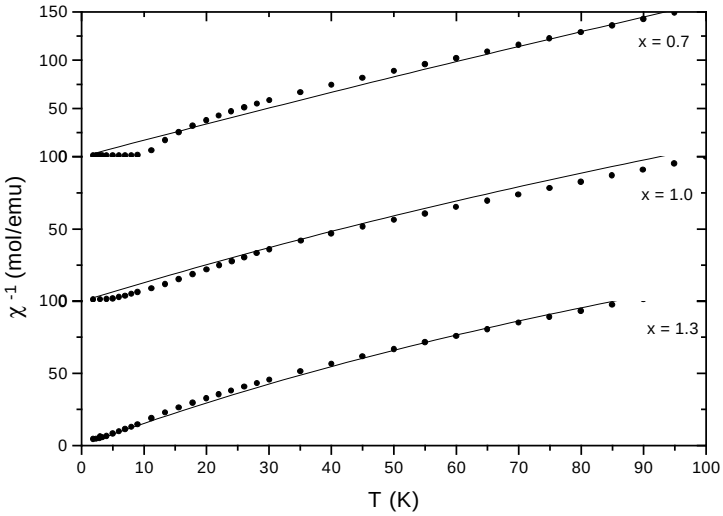

Figure 3. The calculated and the measured susceptibility for $CeSi_{2-x}Ga_x$ ($x = 0.7$, 1.0, and 1.3).

Table 2. The Kondo temperature, the Curie temperature, and the crystal-field parameters of $CeSi_{2-x}Ga_x$.

x	T_K	T_C	B_2^0	B_4^0	B_4^4
0.7	10	10	−1.06	0.0405	0.243
1.0	19	8	−1.72	0.0750	0.283
1.3	27	3	−1.32	0.0533	0.176

to RKKY interactions, whereas in the case of compounds like $CePd_2Si_2$ [15], such deviations are seen only below the ordering temperature. In these compounds, the Kondo and RKKY interactions are of comparable magnitude. In the case of the compounds studied here, no deviations from Lorentzian lineshapes were seen. This could be because of the fact that all of our neutron data were collected above the magnetic ordering temperatures of these compounds, and also because in these compounds the two processes are of comparable strength.

The high-energy response, in all the three samples, can be interpreted in terms of crystal-field excitations broadened by hybridization. The crystal-field Hamiltonian for Ce^{3+} (total angular momentum $J = 5/2$) in a field with tetragonal symmetry can be written as

$$H_{CEF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 \tag{4}$$

where the O_l^m are the Stevens operators and the B_l^m are the phenomenological CF parameters. The values of the O_l^m can be obtained from Hutchings [17]. Diagonalization of the CEF Hamiltonian gives us the eigenvalues and eigenfunctions. The eigenfunctions are

$$\Gamma_{t7}^{(2)} = \eta|\pm 5/2\rangle + \sqrt{1-\eta^2}|\pm 3/2\rangle \tag{5}$$

$$\Gamma_{t7}^{(1)} = \sqrt{1-\eta^2}|\pm 5/2\rangle - \eta|\pm 3/2\rangle \tag{6}$$

$$\Gamma_{t6} = |\pm 1/2\rangle \tag{7}$$

where each one is doubly degenerate, and, by simple algebra, B_l^m can be written as

$$B_2^0 = \frac{\Delta_1}{14}\left[\eta^2 - \frac{5}{6}\right] - \frac{\Delta_2}{21} \tag{8}$$

$$B_4^0 = \frac{\Delta_1}{210}\left[\eta^2 - \frac{1}{4}\right] + \frac{\Delta_2}{420} \tag{9}$$

$$B_4^4 = \frac{\Delta_1\eta}{12}\sqrt{\frac{1}{5}(1-\eta^2)} \tag{10}$$

where Δ_1 and Δ_2 are CF excitation energies. Fixing Δ_1 and Δ_2 at experimentally observed values, the CF potential then depends upon the single parameter η. This can be determined by simultaneously fitting the single-crystal susceptibility data and the neutron scattering data. Since no single-crystal susceptibility data for $CeSi_{2-x}Ga_x$ have yet been reported, we have calculated the susceptibility $\chi = M/H$ for each set of B_2^0, B_4^0, and B_4^4, assuming that H is an external field of 4 kG and that the magnetization M can be averaged according to $M = (M_c + 2M_a)/3$, where M_c and M_a are the magnetizations for fields along the c-axis and the a-axis, respectively. The estimated η and molecular-field constant in the paramagnetic phase, for $x = 0.7$, 1.0, and 1.3, were 0.6223 and 50 mol emu^{-1}, 0.6428 and 40 mol emu^{-1}, and 0.5892 and 48 mol emu^{-1} respectively. The CF parameters which gave the best fits are listed in table 2, and the calculated CF susceptibility along with our experimental susceptibility data for all three compounds are shown in figure 3. The close agreement between the calculated and the measured susceptibilities in the case where $x = 1.3$ almost up to the ordering temperature is most probably due to the narrow CF splitting in this compound. It may also be seen here that the behaviour of the CF parameters closely resembles the behaviour of the excitation energies if one compares their values from table 1 and table 2, respectively. Such a non-linear behaviour of the CF splitting was observed earlier for $CeSb_{1-x}Te_x$ [18]. Here too, the decrease in the CF splitting energies in the case of $CeSi_{1.3}Ga_{0.7}$ with respect to that of $CeSi_2$ [5] can be understood on the basis of a p–f mixing model [10]. Substitution of Ga for Si in the lattice probably decreases the number of p holes, which in turn strengthens the p–f mixing. But the subsequent increase in the CF splitting for $CeSi_{1.0}Ga_{1.0}$ cannot be explained within the framework of this model. The second feature that remains to be understood is the observation of a single inelastic peak in the case of the $x = 0.7$ compound. As discussed earlier, there are several possible explanations for this; single-crystal studies are needed to decide amongst them. It may also be noted from table 1 that the linewidth of the crystal-field excitations (inelastic peak), in these compounds, is quite large. Such a behaviour has been observed in the isostructural $CeSi_x$ compounds [6]. Even for the ferromagnetic $CeSi_{1.7}$, the broad inelastic peaks correspond to the anomalous damping of the spin-wave excitations in this compound [19]. A similar behaviour is seen here in the case of the compound $CeSi_{1.3}Ga_{0.7}$. However, no single-crystal data on this compound have been hitherto reported in the literature, so we cannot check on this possibility. The large width could also be due to the fact that there are two closely spaced doublets which cannot be separated in a polycrystalline sample, and data obtained using a good-quality single crystal are needed to confirm or refute this possibility. Hence, it would be too ambitious to comment on the anomalously large width of the CF peak for $CeSi_{1.3}Ga_{0.7}$. It can be concluded, however, that the increase of the linewidth in going from $x = 1.0$ to $x = 1.3$, whereupon the ferromagnetism becomes unstable and the Kondo behaviour develops, is due to increasing hybridization between the 4f and the conduction electrons.

4. Conclusions

In this paper, we have measured the inelastic neutron spectra of three ferromagnetic Kondo compounds, $CeSi_{1.3}Ga_{0.7}$, $CeSi_{1.0}Ga_{1.0}$, and $CeSi_{0.7}Ga_{1.3}$. In the first case, only one broad inelastic peak—as compared to two for the other two compounds—is seen. This could be due to the damping of spin-wave excitations, or there could actually be two peaks lying too close to each other to be separated for a polycrystalline sample. The increasing linewidths of the CF excitations and the decreasing CF splitting with increasing Ga concentration indicate increasing 4f–conduction electron (p) hybridization in these compounds.

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