

# Inelastic Neutron scattering in $\text{CeSi}_{2-x}\text{Ga}_x$ ferromagnetic Kondo lattice compounds

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Inelastic neutron scattering investigation on ferromagnetic Kondo lattice compounds belonging to  $\text{CeSi}_{2-x}\text{Ga}_x$ ,  $x = 0.7, 1.0$  and  $1.3$ , system is reported. The thermal evolution of the quasielastic response shows that the Kondo interactions dominate over the RKKY interactions with increase in Ga concentration from 0.7 to 1.3. This is related to the increase in k-f hybridization with increasing Ga concentration. The high energy response indicates the ground state to be split by crystal field in all three compounds. Using the experimental results we have calculated the crystal field parameters in all three compounds studied here.

## I. INTRODUCTION

Cerium in its intermetallic compounds and alloys exhibits various types of anomalous ground states that are closely linked with the hybridization strength between the conduction electrons and the Ce 4f electrons. The two processes viz, interatomic RKKY interaction and the single site Kondo interaction compete with each other in cerium Kondo lattice compounds. Dominance of one over other leads to either magnetically ordered or a non magnetic ground state. Many cerium systems [1–4] have been studied to understand the competition and various types of ground states these materials exhibit. Cerium silicides with either hole doping ( $\text{CeSi}_x$ , [5],  $\text{Ce}(\text{SiAl})_2$  [6],  $\text{Ce}(\text{SiGa})_2$  [7–9]) or isoelectronic substitution ( $\text{Ce}(\text{SiGe})_2$  [10]) have been of lot of interest in recent years. All these systems show an evolution from nonmagnetic to a magnetically ordered ground state. In  $\text{CeSi}_{2-x}\text{Ga}_x$ , the system evolves from nonmagnetic - ferromagnetic - antiferromagnetic ground state associated with a structural transition from tetragonal - hexagonal structure near the ferro - antiferromagnetic transition [7–9].

In addition to the competition between the Kondo and RKKY interactions, in nearly all cerium Kondo systems, crystalline electric field (CEF) plays an important role in deciding 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 and hence is also required in any rigorous theoretical model [11]. In addition, Levy and Zhang [12] have also proposed that the hybridization interaction between the localized f electron states and the band states plays an important role in the strength of the CF potential.

The most direct method of determining CEF in a metallic compound is inelastic neutron scattering for which the scattering cross-section is proportional to dynamic susceptibility. In  $\text{CeSi}_2$  [13] the CEF splits the  $j = 5/2$  ground state into three doublets with the excited doublets lying at 297K and 555K from the lowest doublet. Khogi et al [14] have shown that in  $\text{CeSi}_x$  system the line widths and the excitation energies of the CEF doublets scale almost linearly with x and the large linewidths at higher values of x is due to increasing k-f

hybridization with x. In CeGa<sub>2</sub> [15] the study of CEF parameters have led to understanding of large easy plane anisotropy and also the absence of any discontinuity in resistivity curve at magnetic ordering temperature.

In this paper we report our inelastic neutron scattering studies on three compounds belonging to CeSi<sub>2-x</sub>Ga<sub>x</sub> with x = 0.7, 1.0 and 1.3. All these three compositions crystallize in  $\alpha$ -ThSi<sub>2</sub> type structure with nearly equal lattice constant values [7]. Magnetic and transport properties have shown that a strong competition exists between the intersite RKKY and the single site Kondo interactions. For x = 0.7 specific heat measurements show a sharp anomaly indicating stable ferromagnetic order. This peak then broadens out at x = 1.0 and 1.3 which is indicative of the dominance of Kondo interaction over the RKKY interactions. We have studied the crystal field excitations in these compounds as well as the thermal evolution of the quasielastic line width in the temperature range 10 - 100 K.

## II. EXPERIMENT AND RESULTS

The polycrystalline CeSi<sub>2-x</sub>Ga<sub>x</sub>, x = 0.7, 1.0, 1.3 and LaSiGa have been prepared by arc melting the pure elements in argon atmosphere using the same procedure as in Ref.7. Neutron diffraction patterns are in good agreement with the tetragonal  $\alpha$  - ThSi<sub>2</sub>-type structure and lattice constant values agreed with those reported in the literature.

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 Cu (111) plane as monochromator and Si (111) plane as analyzer. The collimations used are open, 60', 60', and open between reactor and monochromator, monochromator and sample, sample and analyzer and analyzer and detector respectively. The spectrometer was operated at fixed final energy,  $E_f = 25$  meV with incident energy varying from 65 meV to 20 meV at constant scattering angle,  $\phi$ . The spectra of each sample were recorded at two different scattering angles,  $\phi = 20^\circ$  and  $95^\circ$  ( $Q = 1 \text{ \AA}^{-1}$  and  $5 \text{ \AA}^{-1}$ ) and at different temperatures from 10 K to

100 K using a closed cycle refrigerator.

The phonon contribution for all the three samples was estimated from LaSiGa data using the scaling method proposed by A. P. Murani [16]. The magnetic response then obtained may be related to the dynamic susceptibility  $\chi''(Q, \omega)$ .

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

where  $A = 1/(2\pi)(\gamma r_e/\mu_B)^2$  which describes the coupling between the neutron and electron spin. The Kramers-Kronig relation provides a relationship between  $\chi''(Q, \omega)$  and static susceptibility which can be written as

$$\chi''(Q, \omega) = \pi\hbar\omega\chi(Q)P(Q, \omega) \quad (2)$$

The static susceptibility  $\chi(Q)$  is related to the bulk susceptibility  $\chi_{bulk}$  via a magnetic form factor  $f(Q)$ ,  $\chi(Q) = f(Q)^2\chi_{bulk}$ .  $P(Q, \omega)$  is a spectral function which fulfills the relation  $\int_{-\infty}^{\infty} P(Q, \omega)d\omega = 1$ . A lorentzian form is usually assumed to describe the relaxation processes. For a pure quasielastic response the Lorentzians centered at  $\hbar\omega = 0$  and in presence of crystal field splittings  $P(Q, \omega)$  is described by a series of lorentzians centered at  $\hbar\omega = 0$  (quasielastic) and  $\pm\hbar\omega_i$  (crystal field excitations) as

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

where  $A_0$ ,  $A_i$  are the amplitudes and  $\Gamma_0$ ,  $\Gamma_i$  the half widths of the quasielastic and inelastic structures respectively.

The normalized spectra measured at 12 K on TAS after phonon correction and correction for empty cell scattering are shown in Fig. 1 for the three  $\text{CeSi}_{2-x}\text{Ga}_x$  compounds with  $x = 0.7, 1.0$  and  $1.3$ . The quasielastic peak and 0 meV energy transfer and the inelastic peaks indicates the presence of magnetic scattering in these samples. The solid line in the figure is least square fit line to the data using the equation (3). The least square fit parameters obtained by fitting the spectra at all temperatures for all the three compounds are given in Table I. From the table it is clear that in all the three samples there is quasielastic broadening

as well as inelastic peaks due to CEF splitting of the ground state. In the case of  $\text{CeSi}_{1.3}\text{Ga}_{0.7}$  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 in three doublets as expected for tetragonal point symmetry. Single inelastic peak has been observed previously [17,18] in case of tetragonal symmetry which has been explained by doublet quasiquartet splitting of the ground state. The other reason could also be that the excited doublets are lying very close to each other and due to our moderate energy resolution it is not possible to separate them.

### III. DISCUSSION

The residual quasielastic line width, in Kondo and heavy fermion systems, gives the fluctuation rate and it is often taken as the measure of Kondo temperature or spin fluctuation temperature. The thermal evolution of the quasielastic linewidth can either be fitted to  $T^{1/2}$  law or to a linear T dependence in accordance with Korringa law [19,20]. In figure 2 we have plotted the temperature dependence of the quasielastic line width in all the three compounds. In case of  $\text{CeSi}_{1.3}\text{Ga}_{0.7}$ , both linear as well as  $\sqrt{T}$  lines fit equally well to the data. The data point corresponding to line width at 12K is excluded as it is just within the resolution.  $T_K$  in all the three compounds is estimated from  $\Gamma = \Gamma_0 + k_B T^{1/2}$  with  $\Gamma_0 = k_B T_K$ . For x = 0.7 sample, Kondo temperature is found to be  $T_K = 10$  K which is in quite good agreement with that deduced from other techniques. For x = 1.0 also both the equations fit the data equally well while for x = 1.3 the  $\sqrt{T}$  fit is better. This can be related to the increasing hybridization with increasing Ga concentration. The values of  $T_K$  obtained for x = 1.0 and 1.3 samples are 17 K and 25 K respectively. These values are not in agreement with the values of  $T_K^l$  deduced from resistivity data by assuming the values of excitation energies as that of  $\text{CeSi}_{1.7}$  [8]. It may be noted here that calculating  $T_K^l$  using the actual values of excitation energies gives a far better agreement with the  $T_K$  values deduced from quasielastic line widths.

We have also tried to study the crossover phenomena in  $\text{CeSi}_{2-x}\text{Ga}_x$  by taking into account the present experimental results. In a most divergent approximation of Coqblin-Schrieffer model,  $T_K$  for a Ce system in crystal field is expressed as

$$T_K = D \left( \frac{D}{T_K + \Delta_1} \right) \left( \frac{D}{T_K + \Delta_2} \right) \exp \left[ -\frac{1}{2|\rho J|} \right] \quad (4)$$

where  $D$  is the half width of the conduction band,  $\rho$  is the density of states of the conduction electrons at  $E_F$  and  $J$  is the exchange interaction constant. Using the  $T_K$  values deduced from the quasielastic line widths and assuming  $D \sim 10000$  K we estimate the coupling constant  $|\rho J|$ . The temperature associated with RKKY interactions is expressed as  $T_{RKKY} \sim D|\rho J|^2$ . The results of this analysis are summarized in Table II. These results indicate that there exists a cross over from RKKY dominated region to a region dominated by Kondo interactions at around  $x = 0.7$ . This crossover is caused by increase of k-f coupling constant (increase in k-f hybridization) with  $x$  over its critical value where the intrasite Kondo screening dominates the ferromagnetic ordering due to intersite RKKY interactions. This picture is consistent with the one deduced from the bulk property measurements [8].

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 cerium in tetragonal symmetry can be written as

$$H_{CEF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 \quad (5)$$

where  $O_l^m$  are the Stevens operators and  $B_l^m$  are the phenomenological CF parameters. The values of  $O_l^m$ 's can be obtained from Hutchings [21]. Diagonalization of the CEF Hamiltonian gives us the eigen values and eigen functions and with simple algebra  $B_l^m$  can be written as

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

$$B_4^0 = \frac{\Delta_1}{210} \left[ \eta^2 - \frac{1}{4} \right] + \frac{\Delta_2}{420} \quad (7)$$

$$B_4^4 = \frac{\Delta_1 \eta}{12} \sqrt{\frac{1}{5}(1 - \eta^2)} \quad (8)$$

where  $\Delta_1$  and  $\Delta_2$  are CF excitation energies and  $\eta$  is a coefficient of the doublet wave function

$$|g.s. \rangle = \eta |\pm 5/2 \rangle + \sqrt{1 - \eta^2} |\pm 3/2 \rangle \quad (9)$$

Fixing  $\Delta_1$  and  $\Delta_2$  to experimental values, the CF potential then depends upon the single parameter  $\eta$ . This can be determined by fitting simultaneously the single crystal susceptibility data and the neutron scattering data. Unfortunately single crystal susceptibility data for  $\text{CeSi}_{2-x}\text{Ga}_x$  is not yet reported hence 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 4kG and 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  $c$ - axis and the  $a$ - axis respectively. The estimated  $\eta$  and molecular field constant in paramagnetic phase, for  $x = 0.7, 1.0$  and  $1.3$  were  $0.6223$  and  $\dots, 0.6428$  and  $\dots$  and  $0.5892$  and  $\dots$  respectively. The CF parameters which gave best fits are listed in Table III. It is to be noted here that the second order crystal field parameter  $B_2^0$  at 12K is almost constant for all the three compounds, whereas the fourth order parameters,  $B_4^0$  and  $B_4^4$ , increase with increasing  $x$ . In fact, their behaviour closely resembles the behaviour of excitation energies if one compares the values of excitation energies and CF parameters from Table II and Table III respectively. It may also be noted from Table I that the line width of crystal field excitations (inelastic peak), in these compounds, is quite large. Such a behaviour has been observed in the isostructural  $\text{CeSi}_x$  compounds [14]. Even for the ferromagnetic,  $\text{CeSi}_{1.7}$  the broad inelastic peaks correspond with the anomalous damping of the spin wave excitations in this compound [22]. A similar behaviour is seen here in case of  $\text{CeSi}_{1.3}\text{Ga}_{0.7}$  compound. However no single crystal data on this compound is hiterto reported in literature to check this possibility. The increase of the linewidth of  $\text{CeSi}_{2-x}\text{Ga}_x$  between  $x = 1.0$  and  $1.3$  where the ferromagnetism becomes unstable and the Kondo behaviour develops can be concluded to be due to the increase in the strength of the 4f electron - conduction electron hybridization.

## IV. CONCLUSIONS

The temperature dependence of the quasielastic line widths in  $\text{CeSi}_{2-x}\text{Ga}_x$ , ( $x = 0.7, 1.0$  and  $1.3$ ) has been studied. In the concentration range studied here, there exists a crossover from RKKY dominated region to one dominated by single site Kondo interactions. The ground state in all these compounds is CF split and we have determined the f electron ground state wavefunctions and the phenomenological CEF parameters for all the three compounds.

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TABLE I.

T (K)	$A_0$ (Arb. Units)	$\Gamma_0$ meV	$A_1$ (Arb. Units)	$\Gamma_1$ meV	$\omega_1$ meV	$A_2$ (Arb. Units)	$\Gamma_2$ meV	$\omega_2$ meV
$x = 0.7$								
12	3.6	2.76	.99	9.23	13.36			
25	3.3	3.47	.82	10.76	13.45			
50	3.0	4.09	.69	12.44	13.34			
100	2.7	5.28	.59	13.42	13.27			
$x = 1.0$								
12	4.4	3.1	.90	4.2	15.43	.25	5.3	26.46
25	4.05	3.8	.75	5.4	15.24	.19	6.4	26.52
50	3.6	4.5	.52	6.9	15.32	.13	8.8	26.31
100	2.6	5.3	.42	8.2	15.20	.08	10.4	26.28
$x = 1.3$								
12	3.16	3.6	.81	5.2	9.91	.20	6.2	20.43
25	2.8	4.4	.55	7.4	9.86	.12	8.2	20.43
50	2.4	5.1	.42	9.05	9.84	.08	10.8	20.32
100	1.8	6.1	.32	10.5	9.75	.05	12.4	20.26

TABLE II. Excitation energy  $\Delta$ , Kondo temperature  $T_K$ , c-f coupling constant  $|\rho J|$  and  $T_{RKKY}$  for  $\text{CeSi}_{2-x}\text{Ga}_x$

$x$	$\Delta_1(K)$	$\Delta_2$	$T_K(K)$	$ \rho J $	$T_{RKKY}(K)$
0.7	155	155	10	0.0331	10.95
1.0	179	307	17	0.0363	13.18
1.3	115	237	29	0.0365	13.52

TABLE III. Crystal field parameters of  $\text{CeSi}_{2-x}\text{Ga}_x$

$x$	$B_2^0$	$B_4^0$	$B_4^4$
0.7	-1.06	0.0405	0.243
1.0	-1.72	0.0750	0.283
1.3	-1.32	0.0533	0.176

## Captions to Figures

Fig. 1. Magnetic spectral response of  $\text{CeSi}_{2-x}\text{Ga}_x$  ( $x = 0.7, 1.0$  and  $1.3$ ) at  $T = 12$  K and  $\phi = 20^\circ$ .

Fig. 2. Thermal evolution of the quasielastic linewidth in  $\text{CeSi}_{2-x}\text{Ga}_x$  ( $x = 0.7, 1.0$  and  $1.3$ )



