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Thermoelectric power and resistivity studies in the Kondo-lattice system $CeGa_2$ with Sn or Al substitutions and RGa_2 ($R \equiv$ Ho, Dy, Tb) alloys

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Abstract. Resistivity ρ and thermopower S studies between 1.7 and 300 K have been carried out to examine Kondo and magnetic ordering effects in $Ce(Ga_{1-x}Sn_x)_2$, $Ce(Ga_{0.9}Al_{0.1})_2$ and RGa_2 ($R \equiv$ Ho, Dy, Tb) alloys. Evidence for the presence of the Kondo effect in $CeGa_2$ was deduced from the high-temperature logarithmic variation observed in the ρ data, supporting the conclusions of the earlier neutron studies. In the Sn-doped alloys ($x > 0.1$), the Kondo effect is also found to be present as observed through the evolution of ρ_{min}. Such a ρ_{min} behaviour is not seen in the case of pure $CeGa_2$ alloy. Further, for the Sn-doped alloys, the magnetic ordering temperature is depressed compared with the pure $CeGa_2$ alloy. The development of the low-temperature magnetic order was found in RGa_2 as well as in the Al-doped alloy, whereas both Kondo and magnetic ordering effects were observed in the Sn-doped samples.

In recent years, the magnetic properties of the Kondo-lattice compound $CeGa_2$ have been studied [1] in some detail. This system represents an interesting case where its magnetic properties are governed by two characteristic temperature scales, namely T_K pertaining to the single-ion Kondo effect and T_{RKKY} to the inter-site Ruderman–Kittel–Kasuya–Yosida (RKKY) effect. The theoretical understanding of this problem is also of considerable current interest [2]. When $T_{RKKY} > T_K$, long-range magnetic order of the antiferromagnetic (AF) type is observed whereas, when $T_{RKKY} < T_K$, AF ordering is suppressed. Both these characteristic temperatures depend on the magnetic exchange integral J between the Ce ion and the conduction electrons and are given by $T_K \propto \exp(-1/NJ)$ (where N is the density of states at the Fermi level) and $T_{RKKY} \propto J^2$. As T_K depends exponentially on J, beyond a critical value of J_c, $T_K > T_{RKKY}$ and the long-range ordering would fail to be manifested. The value of the AF ordering temperature $T_N(J)$ thus depends on the relative strength of T_K and T_{RKKY}. In $CeGa_2$, a peak in the susceptibility studies [3, 4] indicated an AF ordering temperature at $T_N = 9.5$ K. Neutron diffraction studies also indicate that $T_N = 9.5$ K, below which a sine-wave modulated structure was observed [1, 5]. The complexity of the low-temperature magnetic ground state is also reflected in the multiple peaks in the specific-heat studies [6]. An interesting aspect is that the AF phase in $CeGa_2$ stabilizes in the presence of a strong single-ion Kondo effect. This effect leads to the observation of a reduced magnetic moment value of 0.7 μ_B, instead of the estimated value of 1.2 μ_B for the crystal-field(CF)-influenced ground state of the Ce ion. However, lattice-constant studies [1] indicated a fixed valency of

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3 for the Ce ions despite the large Kondo compensation.

The ρ measurements are found to be particularly sensitive to effects arising from the above-mentioned two temperature scales. In the presence of Kondo effect, the scattering of conduction electrons at low temperatures, from the Ce ion in its CF ground state, gives rise to a minimum in the magnetic resistivity ρ_m, at T_{min}, followed by a logarithmic variation in ρ_m for $T < T_{min}$. At higher temperatures, where the effect of the excited CF levels becomes important, the ρ_m curve shows a clear maximum followed again by a logarithmic variation in ρ_m at still higher temperatures. The S behaviour exhibits a broad maximum, in many cases, because of the influence of the excited CF levels of the Ce ion. However, no well defined signature exists for the Kondo scattering of the Ce ion in its CF ground state at lower temperatures. In some systems [7] the occurrence of the Kondo effect is evidenced by the development of a minimum in S at negative values whereas, in others [8], no such feature was observed.

When T_{RKKY} plays a dominant role, magnetic ordering is found to develop. The AF ordering in these alloys is also reflected clearly in the ρ measurements. At a temperature T^*, close to the value of T_N (obtained from magnetic measurements), there occurs a change in the slope of the ρ–T curve, giving rise to a maximum in $\partial\rho/\partial T$. In addition, the ρ curves are found to be distinctly different for systems exhibiting simple AF behaviour and those in the presence of Kondo effect. In the simple AF case (at $T > T_N$), the ρ_m behaviour arising from the spin-disorder term is almost temperature independent whereas, in the presence of Kondo effect (with $T_K > T_N$), the ρ_m curve shows marked temperature dependence as explained above. Again, no unique signature from the S measurements has been observed [9] from which the deduction of the value of T_N can be made. In many cases, however, when magnetic ordering effects are observed at low temperatures, an extremum (minimum or maximum) feature is observed at a temperature T_1^*, which may be close to the value of T_N. However, even such studies show that T_1^* cannot strictly be identified with T_N and the occurrence of T_1^* usually reflects the complexity of the S behaviour near T_N (determined from magnetic studies). Thus, these transport measurements become useful in understanding the role of T_K and T_{RKKY}. The earlier studies on $CeGa_2$ were mainly carried out to understand the complex AF behaviour at the lowest temperatures using a variety of magnetic techniques. In the present study, we focus on the role of the Kondo effect at temperatures $T > T_N$, as revealed through the ρ and S measurements, to obtain further information on the nature of the inter-site and single-ion effects present in $CeGa_2$.

To examine in more detail the role of this interplay, we added impurity dopants such as Al and Sn for substitution at the Ga site in $CeGa_2$. The above two dopants were chosen as they are found to form well defined crystallographic phases. Further, as Al and Sn are sp^1 and sp^2 types of non-magnetic metals, respectively, the alloying effects, by substitution of Ga (sp^1 metal), would enable one to trace a smooth variation in the electronic properties over the pure $CeGa_2$ behaviour. The replacement of Ga atoms, on the other hand, by magnetic impurities may lead to rapid changes in the electronic behaviour of the $CeGa_2$ alloys. Also, recent neutron data [5] are available for the Al-doped sample. Our transport study would then serve towards a better understanding of the behaviour of this class of alloys. With this in mind, a Sn-doped series, namely $Ce(Ga_{1-x}Sn_x)_2$ ($x = 0.1, 0.2, 0.3$) alloys, and an Al-doped alloy, namely $Ce(Ga_{0.9}Al_{0.1})_2$, were investigated. Further, we also studied the alloys RGa_2 (R ≡ Tb, Dy, Ho) which are known [3, 4] to exhibit AF order ($T_N < 15$ K) without the competing influence of the Kondo effect. Therefore, these serve as useful candidates for analysing the growth of magnetic order without the influence of the Kondo effect and comparing them with those in the presence of Kondo effect, such as $CeGa_2$.

Table 1. Various characteristic temperatures and lattice parameters for $Ce(Ga_{1-x}Sn_x)_2$, $Ce(Ga_{0.9}Al_{0.1})_2$ and RGa_2 alloys.

Alloy	T_N (K)	T^* (K)	T_{min} (K)	T_1^* (K)	a (Å)	c (Å)
$Ce(Ga_{1-x}Sn_x)_2, x = 0$	9.5 [3]	9.2	—	15	4.285±0.005	4.337±0.005
$Ce(Ga_{1-x}Sn_x)_2, x = 0.1$	—	4.9	—	3	4.317±0.005	4.356±0.005
$Ce(Ga_{1-x}Sn_x)_2, x = 0.2$	—	<1.7	10	<1.7	4.351±0.005	4.366±0.005
$Ce(Ga_{1-x}Sn_x)_2, x = 0.3$	—	<1.7	10	<1.7	4.357±0.005	4.388±0.005
$Ce(Ga_{0.9}Al_{0.1})_2$	11.0 [5]	10.8	—	10	4.297±0.005	4.334±0.005
$TbGa_2$	14.8 [3]	12.7	—	—	4.180±0.005	4.015±0.005
$DyGa_2$	6.4 [3]	6.3	—	—	4.192±0.005	4.063±0.005
$HoGa_2$	8.0 [3]	7.9	—	—	4.185±0.005	4.042±0.005

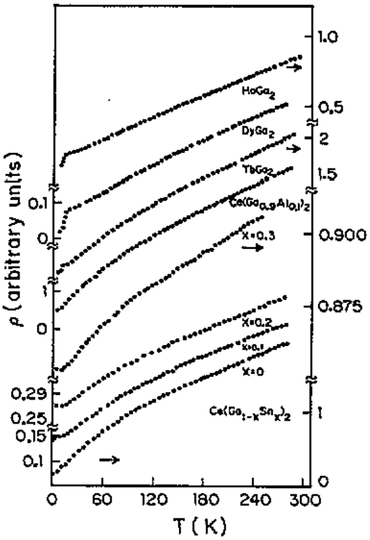

Figure 1. ρ versus T curves for $CeGa_2$, Sn- and Al-doped $CeGa_2$ alloys and RGa_2 ($R \equiv$ Tb, Dy, Ho) compounds.

All the alloys were prepared in an arc furnace in flowing argon and homogenized by repeated melting and annealed at 500 °C for a week to remove microstrains. These systems were found to crystallize in the AlB_2 structure. The lattice parameters a and c were found to increase with both Al and Sn substitutions (table 1). The samples were found to be brittle, and regular geometric shapes were difficult to obtain for most of the samples. Therefore, only in the case of $CeGa_2$ was a rectangular parallelopiped obtained by micropolishing and then annealed to relieve microstrains in the sample. This procedure was necessary to calculate the absolute value of ρ accurately for $CeGa_2$. For all other alloys, the ρ data (figure 1) are expressed in arbitrary units. At

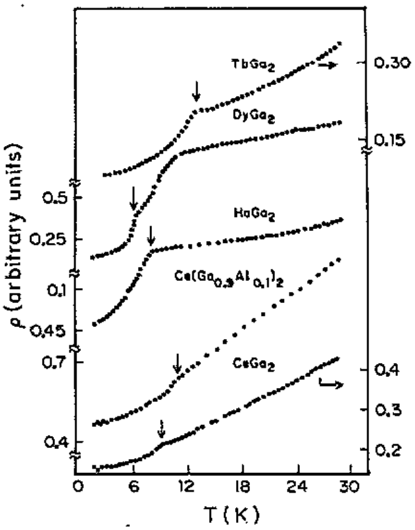

Figure 2. Expanded plots of the low-temperature portion of ρ for CeGa$_2$, Ce(Ga$_{0.9}$Al$_{0.1}$)$_2$ and RGa$_2$(R $\equiv$ Ho, Dy, Tb) compounds. The vertical arrows indicate the temperature where the magnetic transition occurs. The horizontal arrows indicate the appropriate y axes for some of the alloys.

$T^* = 9.2$ K (figure 2), a slight change in slope $\partial\rho/\partial T$ in the ρ curve for CeGa$_2$ is noticed owing to the magnetic transition. We note that T^* from our studies is quite close to T_N obtained from the earlier reported magnetic data. The most striking feature is that, for $T > T^*$, the ρ curve for CeGa$_2$ ($x = 0$) does not show the occurrence of ρ_{min} at low temperatures, even though a pronounced Kondo effect resulting in about 40% moment reduction was inferred from the neutron studies [1]. In order to analyse this aspect further, we studied the higher-temperature Kondo behaviour. We therefore calculated the magnetic resistivity ρ_m by subtracting the ρ contribution of a reference non-magnetic compound LaGa$_2$. We note that this simple subtraction procedure assumes that the phonon contribution to ρ from both LaGa$_2$ and CeGa$_2$ is essentially the same because of the closeness of the ionic masses of La and Ce. Further, deviations from Matthiessen's rule effects are also considered to be small, to the first approximation, to make this method valid. This simplification has been customarily adopted for the estimation of ρ_m for several Ce-based compounds [10]. The ρ_m curve for CeGa$_2$ revealed a maximum at $T_{\mathrm{max}} = 85$ K followed by a logarithmic temperature dependence indicated by the straight-line portion with a negative slope (figure 3). Such a logarithmic behaviour would arise [11] from the Kondo scattering due to the excited CF split levels which are separated from the ground state by an amount $\Delta_1 = 60$ K and $\Delta_2 = 310$ K, both deduced from the same neutron study. A similar logarithmic variation in ρ_m is also expected at lower temperatures owing to the Kondo scattering arising from the Ce ion in the CF ground state. For a strong Kondo system, T_K would be greater than T_N, and therefore ρ_{min} and a lower-temperature logarithmic dependence could be expected to occur for $T \leqslant \Delta_1$. However, we note that no theoretical estimate exists which correlates the degree of moment compensation, arising from the Kondo effect, and the occurrence of ρ_{min}. It seems that CeGa$_2$ could be an unusual case where, even though the higher-temperature Kondo effect is clearly manifested, the system may behave as a low-T_K system at least with respect to the lower-temperature Kondo scattering. It is quite possible that the development of ρ_{min}, at T_{min}, owing to the Kondo effect could become obliterated either because of the proximity of the value of T_{min} to T^* or because of the influence of Δ_1 at low temperatures.

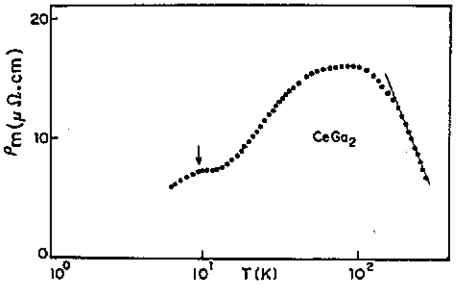

Figure 3. The magnetic resistivity ρ_m of $CeGa_2$ which exhibits $-\ln T$ behaviour (straight line) at high temperatures. ρ_{max} occurs at 85 K. At a lower temperature, the arrow indicates the onset of magnetic order at $T^* = 9.2$ K. The temperature is plotted on a logarithmic scale.

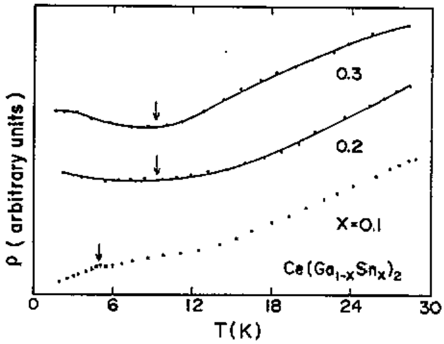

Figure 4. Expanded plots of the low-temperature portion of ρ for $Ce(Ga_{1-x}Sn_x)_2$ ($x = 0.1$, 0.2, 0.3). The arrows indicate $T^* = 4.9$ K, where a kink in the ρ curve occurs (for $x = 0.1$) and the occurrence of T_{min} for the $x = 0.2$ and 0.3 alloys. The full curves are a guide to the eye.

In order to examine further the role of this Kondo behaviour, we have therefore studied the ρ behaviour of $CeGa_2$ with a small amount of Sn substitutions. The interesting feature that emerges is that by the addition of Sn impurities ($x > 0$), T^* moves to lower temperatures compared with $CeGa_2$ and the development of ρ_{min} at T_{min} for $T > T^*$ was clearly observed (figure 4) even without the subtraction of the phonon background. T_{min} was measured (table 1) to be around 10 K in the $x = 0.2$ and 0.3 samples, whereas $T^* = 4.9$ K for $x = 0.1$, as detected from our ρ studies (figure 4). No such feature in $\partial\rho/\partial T$ was observed for the $x > 0.1$ alloys, possibly because T^* becomes less than 1.7 K. The occurrence of this T_{min} suggests that the Sn-doped samples and possibly $CeGa_2$ are characterized by a low value of T_K of magnitude less than 10 K. A contrasting situation is observed for the Al-substituted alloys. For the $Ce(Ga_{0.9}Al_{0.1})_2$ alloy, $T^* = 10.8$ K (figure 2), close to the value for $CeGa_2$, thus indicating that the magnetic ordering temperature is insensitive to Al variation, whereas this is not so with Sn impurities. With Al substitution, no ρ_{min} was observed. The data on the Sn-doped samples are being reported for the first time and the difference between their magnetic behaviour and that of the Al-doped samples needs to be further explored.

We now examine the S behaviour. The $CeGa_2$ alloy shows a relatively sharp positive maximum at $T_1^* = 15$ K (figure 5). S then remains negative with a negative slope ($\partial S/\partial T < 0$) for $T > 25$ K. For all other alloys ($x > 0$) also, the same features are observed, except for $x = 0.3$, where $S > 0$ at higher temperatures (figure 5). We observe that the S behaviour of the non-magnetic reference compound $LaGa_2$ (figure 5) is quite similar in shape, except for the low-temperature behaviour, to that for $CeGa_2$. We find that T_1^* is very sensitive to the addition of Sn, shifting to lower temperatures for $x = 0.1$ and possibly below 1.7 K for $x > 0.1$. We note that, for $CeGa_2$, both T^* and T_1^* differ (table 1) from each other by only a few kelvins. This leads us to conclude that the low-temperature peak at T_1^* is related to magnetic ordering effects. This is also supported by the fact that both T^* and T_1^* drop rapidly to lower temperatures (figure 5) by the addition of Sn impurities. In contrast with this, we find that $T_1^* = 10$ K with Al substitution as seen in $Ce(Ga_{0.9}Al_{0.1})_2$. This shows that Al and Sn substitutions affect the magnetic behaviour of $CeGa_2$ in quite different manners, as also revealed earlier from the ρ studies.

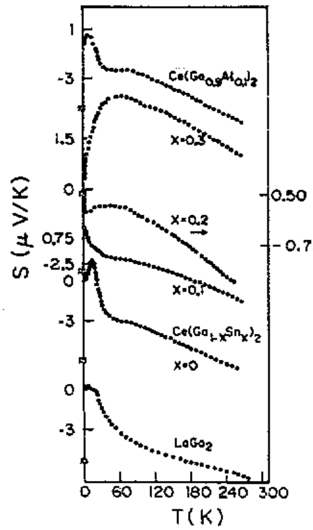

Figure 5. S versus T curves for Sn- and Al-doped $CeGa_2$ alloys and the non-magnetic $LaGa_2$ compound.

We now examine the transport properties of the RGa_2 series (R ≡ Ho, Dy, Tb). These alloys show (figure 2) a pronounced bend in their ρ curves at the AF transition temperatures, in contrast with the $CeGa_2$-based alloys with Sn and Al substitutions. In the absence of the Kondo effect, the critical spin disorder scattering, near T^*, is more pronounced than in the $CeGa_2$ case, and this leads to a much more pronounced bend in the ρ curve for the Ho, Dy and Tb alloys. For $T > T^*$, the spin-disorder scattering would be temperature independent and the ρ curves for RGa_2 exhibit a monotonic

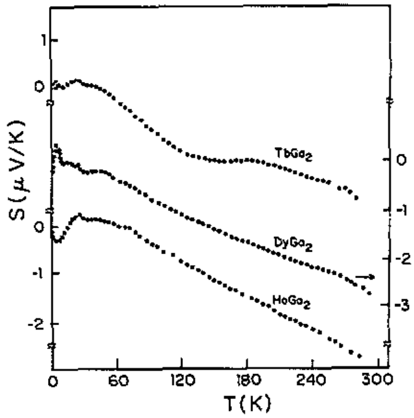

Figure 6. S versus T curves for the RGa_2 ($R \equiv$ Ho, Dy, Tb) alloys.

increase with increasing T whereas, for $CeGa_2$ and its Sn- and Al-substituted alloys, the ρ curves for $T > T^*$ are influenced by the Kondo scattering from the excited CF states. This is faintly reflected (figure 1) in all the $CeGa_2$-based alloys, manifested as the S-shaped curves, at around 50–100 K, and a slight tendency towards saturation at higher temperatures. For $HoGa_2$, the value (table 1) of T^* is 7.9 K, in agreement with the T_N-value obtained [3] from the magnetic studies. However, for $TbGa_2$, the value (table 1) of T^* is about 12.7 K, which is found to be 2 K lower than the T_N-value reported in the same magnetic study. The reason for this difference is not clear at present. For $DyGa_2$, the ρ curve shows a two-step decrease. A broad knee occurs at around 12 K, below which a further sharp drop in ρ occurs at 6.3 K. This low-temperature kink at $T^* = 6.3$ K is identified [3] with the AF transition (where a sharp drop occurs at T_N detected in the susceptibility studies). We note that such a double-kinked feature in ρ (figure 2) could arise from magnetic transitions between differently ordered phases as seen in several types of rare-earth compound [12, 13]. Our measured values of T^* from the ρ studies together with the T_N-values from the magnetic studies are listed in table 1. The S curves (figure 6) for the RGa_2 series, unlike those for $CeGa_2$, show a complex behaviour at low temperatures. Several extremum points are observed for the RGa_2 alloys, reflecting the complexity of the magnetically ordered phases.

The main conclusions that emerge from our studies are as follows. The low-temperature ρ data for the Sn- and Al-doped alloys show complex behaviour in terms of both the Kondo and the magnetic ordering effects. The presence of the Kondo effect is clearly manifested in the Sn-doped samples through the occurrence of ρ_{min}. Such a feature was not observed for pure $CeGa_2$ nor for Al-doped samples. In addition, the magnetic ordering effects are found to be very different for the Al- and Sn-doped systems. While the influence of the T^* variation was found to be quite strong for the Sn-doped samples, such was not the case for the Al-doped samples. The reason for this difference is not understood at present. However, the common feature in all these systems, including the RGa_2 series, is the low-temperature complex features, below 15 K, related to the formation of a magnetically ordered state. The ρ studies on the Sn-doped samples indicate a low value of T_K, possibly below 10 K, for $CeGa_2$. It would be of interest to know whether an independent evaluation of T_K, from quasi-elastic neutron linewidth measurements, would support this estimated value. In view of these conclusions, it is felt that further studies on $CeGa_2$-based compounds would be useful.

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