Study of magnetic properties in doped intermediate valent Ce_2Rh_2Ga

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Abstract. The magnetic properties of intermediate valent Ce_2Rh_2Ga were investigated by means of substituting lanthanum (La) and yttrium (Y) into the cerium (Ce) sublattice to achieve negative and positive chemical pressure, respectively. In this study we report on the synthesis, characterization, dc-magnetic susceptibility and magnetization of two doped variants namely, $Ce_{1.8}La_{0.2}Rh_2Ga$ and $Ce_{1.8}Y_{0.2}Rh_2Ga$. The doped variants crystallize in the same orthorhombic version of the La_2Ni_3-structure type at room temperature (space group *Cmce*) as the undoped Ce_2Rh_2Ga compound. The dc-magnetic susceptibility of $Ce_{1.8}Y_{0.2}Rh_2Ga$ demonstrates behaviour similar to that of the parent compound with a simultaneous valence and crystal structure transition at T_t = 112.29 K, close to that of Ce_2Rh_2Ga at T_t = 130 K. However, no transition was observed in $Ce_{1.8}La_{0.2}Rh_2Ga$ throughout the accessible temperature range. We discuss our findings in terms of the control that doping exercises over the valence-induced crystal structure instability in Ce_2Rh_2Ga.

1. Introduction

Cerium-based compounds show varying ground states as a result of hybridization between the single 4*f* electron of nominally trivalent Ce and the conduction electrons in a metal. Cerium-based compounds usually have their magnetism dominated by the localized spin- and orbital magnetic moment of the 4*f* electron. In the strongly correlated electron class of materials however, conditions may be favourable for the 4*f* electron band to be in close proximity to the metallic Fermi energy, in which case the 4f electron of Cerium acquires a degree of itineracy, with concomitant instability in the Cerium valence. This phenomenon has become known as intermediate or fluctuating valence, and it leads in many cases to heavy-fermion behaviour in Kondo systems [1]. Given this propensity to valence instabilities however, remarkably few Ce compounds are known for temperature-driven valence transitions. In this work we focus on such rare example, namely the ternary intermetallic compound Ce_2Rh_2Ga.

Ce_2Rh_2Ga was reported to exhibit dimorphism, with the crystal structure outcome attendant on the annealing temperature administered during synthesis [2]. When the sample is melted in an arc furnace and subsequently annealed at a temperature of 900ºC, it forms in the orthorhombic (space group *Cmce*) crystal structure of La_2Ni_3 type (high-temperature variant, henceforth termed as HT-Ce_2Rh_2Ga). This dimorphic variant is at the focus of this manuscript. By contrast, when annealed at the lower temperature of 700ºC the compound adopts a monoclinic structure (space group: *C2/c*) of the nominal Pr_2Co_2Al type [2].

In our initial study [2] on HT-Ce_2Rh_2Ga a robust anomaly was found consistently in the temperature dependencies of the specific heat and magnetic susceptibility at 130 K. Even though this apparent phase transition was shown to be temperature hysteretic, it was presumed to characterize a long-range paramagnetic-to-antiferromagnetic phase transition by virtue of the shape of the anomaly in magnetic susceptibility together with the observation that the phase transition was accompanied by an amount of spin-configurational entropy being released at the transition. However, further studies on this compound have shown the 130 K anomaly to be of a more complex nature than a long-range magnetic phase transition. Firstly, our muon spin-resonance study on HT-Ce_2Rh_2Ga [*A. M. Strydom, ISIS μSR Experimental Report No. 2010475 (unpublished)]* failed to detect any time-dependent oscillations in the muon spin relaxation, which argued against the involvement of any spin ordering in HT-Ce_2Rh_2Ga down to 0.3K. Second, in a resonant X-ray emission spectroscopy experiment [3] persuasive evidence was found for a reconstruction of the Fermi surface and a slight increase of the Ce valence beyond 3+ at 130 K. The average Ce valence v increases by ~0.7% from the higher temperature orthorhombic phase ($v \sim 3.053$) to the T<130 K monoclinic phase ($v \sim 3.075$). Finally, in ^{69,71}Ga nuclear quadrupole resonance studies [4] the possibility of quenching of charge degrees freedom at the 130 K anomaly was also ruled out, and instead the data formulated evidence for a highly unusual two-ion Kondo state that forms at low temperatures in HT-Ce_2Rh_2Ga.

The aim of this work is to report on the first doping studies of HT-Ce_2Rh_2Ga, namely, $Ce_{2-x}T_xRh_2Ga$ (T = Y, La) in which 10% of the cerium sublattice is being replaced. The two doped compounds were conformed to form in the expected orthorhombic (*Cmce*) La_2Ni_3-structure type at room temperature. From our magnetic measurements we derived the behavior of the paramagnetic Weiss temperature and the effective magnetic moment values of the cerium ions in the pair of doped compounds in order to shine a light on the electronic dispensation and the chemical pressure stability of the 130 K simultaneous valence and crystal structure transition.

2. Experimental details

Polycrystalline samples of two $Ce_{2-x}T_xRh_2Ga$ (T = Y, La) compounds were prepared from high purity (weight-%) elements of Ce (99.99), Y (99.99), La (99,9), Rh (99.97), and Ga (99,9999). Owing to a weak oxidative reactivity of metallic Ce and La in air, extra precautions were taken to limit the exposure of these two reactants before melting the samples under Zr-gettered ultra-high purity argon in the arc-furnace enclosure. Stoichiometric ratios of the elements were used. The sample ingots were flipped over and remelted at least three times to promote homogeneity. Weight losses attributable to the arc-melting procedure were confined to within 0.5 weight-%. The as-cast samples were characterized by powder X-ray diffraction at room temperature. A Rigaku SmartLab powder diffractometer was used in the Bragg-Brentano geometry (CuK$_\alpha$ scattering radiation collected in the 2θ diffraction interval between 10° and 90°, 2θ stepsize 0.02°). The resulting X-ray diffraction spectra were analyzed using a FullProf suite of programs for full-profile Rietveld refinement [5]. The dc-magnetic measurements on the polycrystalline samples were carried out using the vibrating sample magnetometer platform of a PPMS Dynacool system from Quantum Design, San Diego, in the sample temperature range of 1.8 – 330 K, and with applied magnetic fields up to 9 T.

3. Results and discussion

Crystallography: The profile analyses of the powder X-ray diffractograms collected for $Ce_{1.8}Y_{0.2}Rh_2Ga$ and $Ce_{1.8}La_{0.2}Rh_2Ga$ confirmed that both compounds crystallize in the desired orthorhombic ordered version of the La_2Ni_3-structure type at room temperature with space group *Cmce*, similar to that of the undoped Ce_2Rh_2Ga compound. The refinement fits yielded values of the lattice parameters and unit cell volumes, and these are summarized in Table 1. Fig. 1 shows the powder X-ray diffraction pattern obtained together with the full-profile least-squares refinement fit to the data for the representative compound $Ce_{1.8}Y_{0.2}Rh_2Ga$.

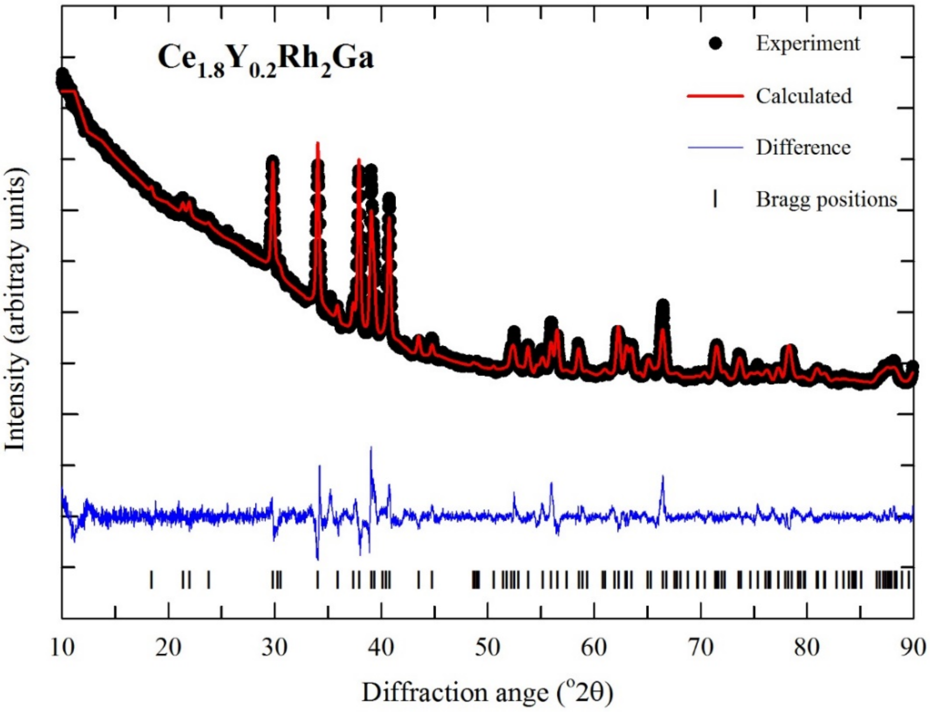

Fig 1: Experimental powder X-ray diffraction spectrum of $Ce_{1.8}Y_{0.2}Rh_2Ga$ at room temperature denoted by circle symbols, Rietveld refinement denoted by a red line, theoretical Bragg positions corresponding to the theoretical *Cmce* space group denoted by vertical bars, and the blue line denoting the difference curve between experimental, and Rietveld calculated intensities.

Table1: Crystallographic lattice parameters and unit-cell volume values obtained from powder X-ray diffraction analyses of the two title compounds [this work], including values for the parent compound [2] for comparison.

Comp.	**Atom**	**Wyckoff sites**	***x***	***y***	***z***	**Occupation (×100%)**
$Ce_{1.8}Y_{0.2}Rh_2Ga$	Ce	*8f*	0	0.34103	0.09336	0.9
	Y	*8f*	0	0.34103	0.09336	0.1
	Rh	*8e*	0.25	0.08920	0.25	1.0
	Ga	*4a*	0	0	0	1.0
$Ce_{1.8}La_{0.2}Rh_2Ga$	Ce	*8f*	0	0.34149	0.08818	0.9
	La	*8f*	0	0.34149	0.08818	0.1
	Rh	*8e*	0.25	0.08228	0.25	1.0
	Ga	*4a*	0	0	0	1.0

Comp.	***a*** (Å)	***b*** (Å)	***c*** (Å)	***V*** **(Å^3)**
Ce_2Rh_2Ga [2]	5.86139(8)	9.63938(7)	7.49652(8)	423.555(8)
$Ce_{1.8}Y_{0.2}Rh_2Ga$	5.85466(3)	9.61734(6)	7.47766(2)	421.040(2)
$Ce_{1.8}La_{0.2}Rh_2Ga$	5.86116(4)	9.66798(3)	7.48185(1)	423.963(5)

Magnetic properties: The temperature dependencies of dc-magnetic susceptibility, $\chi(T)$ of both title compounds were measured in the field-cooled protocol (data collected while cooling the sample in the excitation field from high to low temperatures) in a magnetic field of 0.1 T ($Ce_{1.8}Y_{0.2}Rh_2Ga$) and 0.5 T ($Ce_{1.8}La_{0.2}Rh_2Ga$). Fig. 2(a) and 2(b) show $\chi(T)$ for these compounds, normalized on a per-mole Ce basis.

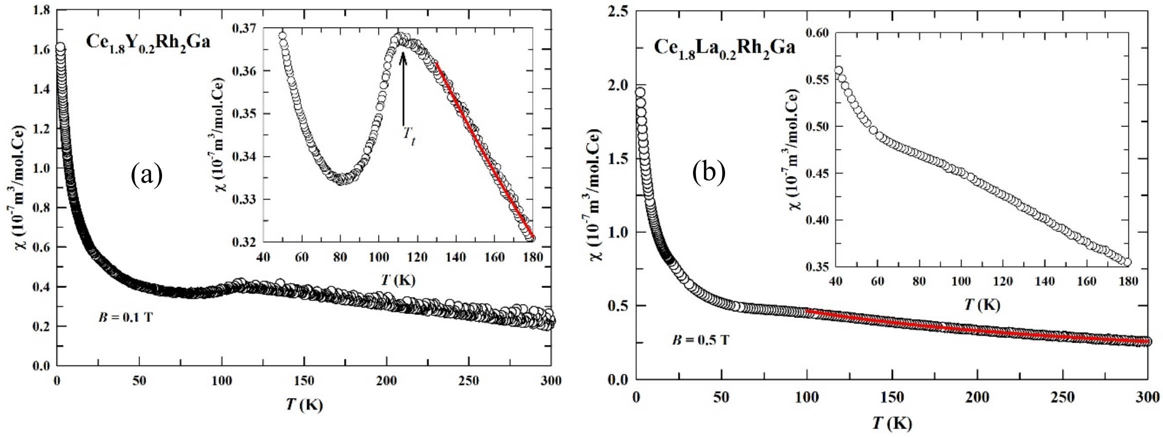

Fig. 2: (a) (main panel) Temperature dependent dc-magnetic susceptibility $\chi(T)$ of $Ce_{1.8}Y_{0.2}Rh_2Ga$ measured from 300 K to 1.8 K in a constant applied magnetic field of B = 0.1 T. For the sake of simplicity, we assume that the magnetic induction B inside the sample is numerically equal to the applied magnetic field intensity $\mu_0 H$. (inset) Magnified view of $\chi(T)$, which displays a cusp-like anomaly at T_t = 112.4 K, while below the minimum at 80 K $\chi(T)$ increases further towards 1.8 K. The red line is obtained through a Curie-Weiss fit as described in the text.
(b) (main panel) dc- magnetic susceptibility $\chi(T)$ of $Ce_{1.8}La_{0.2}Rh_2Ga$ measured from 330 K to 1.8 K in a constant applied magnetic field of B = 0.5 T. The red line is the obtained Curie-Weiss fit. (inset) Magnified view of $\chi(T)$, which displays the absence of a cusp-like anomaly as compared to the data in Fig. 2(a).

The inset of Fig. 2(a) displays a magnified view of the susceptibility with a red line obtained by fitting the data to the Curie Weiss expression [6]

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$$\chi(T) = {N_A \mu^2}_{\text{eff}} \Big/ 3k_B(T-\theta_P)\,, \qquad (1)$$

Where N_A, $\mu^2{}_{\text{eff}}$, , k_B, and θ_P are Avogadro's number, the effective magnetic moment, Boltzmann's constant and the paramagnetic Weiss temperature, respectively. The best fit was achieved in the temperature range of 130 – 180 K and from the fit values of $\mu_{\text{eff}} = 2.26(3)\ \mu_B$/Ce and $\theta_p = -286.98(5)$ K were obtained. The data below 120 K deviates from the Curie Weiss law prediction due to the maximum reached in $\chi(T)$ at 112.4 K. The observed changes of $\chi(T)$ on $Ce_{1.8}Y_{0.2}Rh_2Ga$ were comparable to that of HT-Ce_2Rh_2Ga looking at the $\chi(T)$ values at the maximum peak. By contrast, in $Ce_{1.8}La_{0.2}Rh_2Ga$ no anomaly is found in $\chi(T)$ – see Fig. 2(b). The $\chi(T)$ data of $Ce_{1.8}La_{0.2}Rh_2Ga$ followed equation 1 in the range 330 – 100 K; see red line in the inset to Fig. 2(b). The least-squares fit yielded an effective moment value $\mu_{\text{eff}} = 2.02(5)\ \mu_B$/Ce and a paramagnetic Weiss temperature $\theta_p = -148.61(4)$ K. By contrast to what was reported on the undoped Ce_2Rh_2Ga [2], we note that the effective moment values for both doped compounds are somewhat reduced from that of the full free-ion Ce value of 2.54 μ_B.

The dc-magnetization isotherms of $Ce_{1.8}Y_{0.2}Rh_2Ga$ measured at a number of fixed temperatures between 2 – 140 K are presented in Fig. 3(a). The magnetization at 9 T attains a value of ~0.11 μ_B/Ce at 10 K which is less than the expected saturation value of free-ion Ce which is 2.14 μ_B/Ce. However, the magnetization isotherms of $Ce_{1.8}La_{0.2}Rh_2Ga$ between 2 – 90 K presented in Fig. 3(b) attain a high-field magnetization ~0.15 μ_B/Ce at 2 K in 9 T. These small magnetization values are often observed in correlated electron Ce-based compounds [7-8] and are typically caused by crystal-electric field effects associated with the $L = 3$ orbital angular momentum of the 4*f* electron of a trivalent Ce ion.

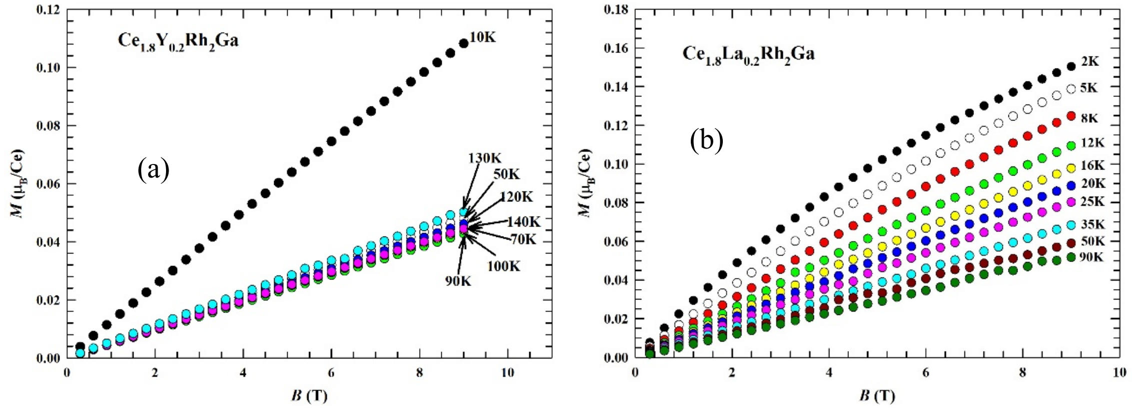

Fig. 3: Isothermal magnetization per Ce of (a) $Ce_{1.8}Y_{0.2}Rh_2Ga$ and (b) $Ce_{1.8}La_{0.2}Rh_2Ga$ at temperatures close to the expected valence transition temperature (~100 K) and at low temperature.

4. Conclusion

This study investigated the magnetic properties in the pair of doped compounds $Ce_{1.8}Y_{0.2}Rh_2Ga$ and $Ce_{1.8}La_{0.2}Rh_2Ga$. We anticipated to observe effects of a simultaneous dilution of the 4*f*-electron density at the Fermi energy and lattice expansion (La) and contraction (Y). Although the crystal structure at room temperature was found to remain invariant upon doping, the two doped compounds revealed unexpected variations in the (undoped) valence transition at 130 K. The combined valence and crystal structure transition is retained in $Ce_{1.8}Y_{0.2}Rh_2Ga$, albeit with a huge increase in the antiferromagnetic Weiss exchange parameter (−287 K) compared to that of the undoped compound (−120 K, [2]). In $Ce_{1.8}La_{0.2}Rh_2Ga$ on the other hand the Weiss temperature is largely unchanged (−148 K) but the transition has practically disappeared from the temperature progression of $\chi(T)$. These findings support the notion that hybridization between the Ce 4*f* electrons and the conduction electrons play a dominant role over that of 4*f* electron density of states at the Fermi energy, and that the combined valence and structure transition at 130 K may be manipulated in a facile manner through varying chemical pressure. Further studies are needed in order to disambiguate the influences of positive versus negative pressure in Ce_2Rh_2Ga and in particular the apparent rapid demise of the phase transition upon application of negative chemical pressure. Further studies are planned to achieved isoelectronic doping and co-doping aimed at keeping the unit cell volume invariant.

Acknowledgments

SPX thanks the UJ-GES for financial support, and AMS thanks the SA-NRF (93549) and the FRC/URC of UJ for financial assistance.

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