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Authors

Petrovic, C
Hundley, MF
Movshovich, R
et al.

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Magnetic and transport properties of RIr_2Ga series ($\text{R}=\text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}-\text{Tm}$)

C. Petrovic^{a,*}, M.F. Hundley^b, R. Movshovich^b, P.G. Pagliuso^b, J.L. Sarrao^b, J.D. Thompson^b,
Z. Fisk^{a,b}

^aNational High Magnetic Field Laboratory (NHMFL), Florida State University, 1800 E. Paul Dirac Drive, Tallahassee, FL 32306, USA

^bLos Alamos National Laboratory, Los Alamos, NM 87545, USA

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Abstract

We report results of magnetic and transport measurements on single crystals of a new rare earth series RIr_2Ga ($\text{R}=\text{La}, \text{Pr}, \text{Nd}, \text{Sm}$, and Gd through Tm). These compounds appear to crystallize in the triple-hexagonal Na_3As structure with space group $P6_3cm$. Magnetic ordering temperatures show deviation from De Gennes scaling. These compounds are an interesting example of a quasi-2D structure in which there are anisotropic magnetic interactions. © 2001 Published by Elsevier Science B.V.

Keywords: Rare earth compounds; Magnetically ordered materials; Anisotropy; Magnetic measurements

1. Introduction

We present the results of magnetic and transport studies on members of a new rare earth ternary series RIr_2Ga that crystallizes in the Na_3As hexagonal structure [1–3]. As is the case in many other rare earth (R) intermetallics, physical properties of the system are governed by the interplay of crystal–field interactions (CF) caused by ligand atoms, by the Ruderman–Kittle–Kasuya–Yosida interaction among the $4f$ moments and, in some cases, by the hybridization of $4f$ and conduction electrons. Most of the compounds in this series exhibit long-range magnetic order ($\text{R}=\text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$ and Tm). SmIr_2Ga also orders antiferromagnetically at low temperatures, but its inverse susceptibility saturates at high temperatures instead of showing Curie–Weiss behavior. PrIr_2Ga , CeIr_2Ga (C. Petrovic et al., unpublished data) and YbIr_2Ga (C. Petrovic et al., unpublished) do not show signs of magnetic order down to 2 K, while attempts to grow the Eu member of this series failed.

2. Crystalline structure and experimental techniques

Single crystals of RIr_2Ga were grown from the Ga-rich flux starting from the initial composition of R, Ir and Ga in the ratios 1:1:20. The constituent elements were placed in alumina crucible and sealed in a quartz ampoule in vacuum. The melt was heated to 1175°C, cooled to 500°C over a period of 84 h, and then spun in centrifuge to remove the Ga flux. The resulting crystals had the morphology of large hexagonal needles up to 1 cm long and a few millimeters in diameter. Smaller crystals were produced for the lighter rare earths (La, Pr, Nd, Sm) than for the heavier (Gd through Tm). It appears that the crystalline structure of the RIr_2Ga series is most likely a new example of a triple hexagonal unit cell ($a'=\sqrt{3}a$, $c'=c$, space group $P6_3cm$), as proposed by Hafner et al. [1,3]. Powder X-ray diffraction spectra taken at room temperature could be indexed using the hexagonal structure of Na_3As with the space group $P6_3cm$ [1,3]. This structure has lower symmetry than the Na_3As structure model originally proposed by Zintl [2] (lattice constants a and c) with the space group $P6_3/mmc$. While the major peaks for all members of the series could be indexed by both structures, in all patterns, peaks with small relative intensity were observed that could only be indexed within the structure with the space group $P6_3cm$, thus ruling out the possibility of $P6_3/mmc$.

*Corresponding author. Tel.: +1-850-644-5996; fax: +1-850-644-5038.

E-mail address: petrovic@magnet.fsu.edu (C. Petrovic).

Na_3As with the $P6_3/mmc$ space group consists of Na–As layers with hexagonal symmetry. Arsenic atoms bind two more Na atoms above and under the layers. The unit cell of the extended Na_3As structure (space group $P6_3cm$) consists of six formula units of Na_3As in the unit cell [3] and is isostructural with Cu_3P , Mg_3Ir and Mg_3Pt . It is constructed by the extension of the ordinary unit cell in hexagonal Na–As planes. Six As atoms and 12 Na atoms distributed in two sets (Na(1) and Na(2)) share the same 6c position with mirror symmetry along the c -axis in the space group. Four Na(3) atoms have positions $4b$ with 3-fold rotation axis, while the remaining two Na(4) atoms are in the $2a$ position of the space group [3] with both mirror plane and 3-fold rotation axis symmetry. A detailed description of the structure can be found in the work by Olofsson [4]. It is a structure in which different types of atomic layers are stacked in the c -direction (Fig. 1): one layer consists of Na atoms which form a net of six-membered rings, the other one of Na and As which are connected into the rings in the two possible ways. A Na–As layer lies between each pair of Na layers. The connection pattern of the Na–As layers alternates along the c -axis. It is conceivable that, in the 6-fold unit cell of RIr_2Ga , 12 Ir atoms occupy two sets of 6c positions between R–Ga layers. The stoichiometry requires that either six R or six Ga atoms occupy the two different sites in the unit cell ($4b$ and $2a$). In the effort to distinguish exact site occupancy, two different X-ray diffraction patterns were generated using Powdercell software for each of the two possibilities without conclusive results.

However, the intensity distribution in the calculated pattern suggests that the rare earth atoms occupy inequivalent lattice sites. The effective magnetic moment obtained for CeIr_2Ga indicates the same (C. Petrovic et al., unpublished). Some deviations from stoichiometry were observed in the case of other isostructural compounds with the extended Na_3As unit cell [2]. At the present level of knowledge, we cannot exclude deviations from stoichiometry in the case of the RIr_2Ga series. These deviations are estimated to be less than 5% based on the effective moments inferred from magnetic susceptibility except for ErIr_2Ga where the deviation is 10%.

The electrical resistivity $\rho(T)$ was measured using a standard four-probe method. Because the as-grown samples are rather large hexagonal rods, there was no ambiguity in determining the crystallographic orientation. Resistivity has been measured in the c -axis direction, along the rod. Magnetization measurements were made in a commercial SQUID magnetometer in the temperature range $2\text{ K} < T < 350\text{ K}$.

3. Results and discussion

Lattice constants for all members of the series taken at the room temperature are shown in Table 1. They were obtained from the peak positions by Cohen's least squares method, with Si as the internal standard. For comparison, lattice constants of Ce and Yb members of the series are also included (C. Petrovic et al., unpublished). The unit

Fig. 1. Crystal structure of RIr_2Ga (assuming R occupies both $2a$ and $4b$ sites). Black dotted spheres: R($2a$), black full spheres: R($4b$), small black spheres: Ir($6c$). Small gray spheres: Ga($6c$).

Table 1

Room-temperature lattice parameters and unit-cell volumes for members of the RIr_2Ga series^a

Lanthanide	a (Å)	c (Å)	V (Å ³)
La	7.639	9.549	482.6
Ce	7.615	9.528	478.0
Pr	7.599	9.539	477.4
Nd	7.584	9.524	474.4
Sm	7.533	9.460	464.9
Gd	7.528	9.484	465.0
Tb	7.529	9.439	463.3
Dy	7.516	9.413	460.5
Ho	7.491	9.410	458.0
Er	7.498	9.400	457.7
Tm	7.488	9.392	456.1
Yb	7.490	9.408	457.0

^a Estimated uncertainty in lattice constants is ± 0.001 Å.

cell volume is shown in Fig. 2. Deviation from the usual lanthanide contraction is seen for CeIr_2Ga , YbIr_2Ga and SmIr_2Ga . For the Ce and Yb members of the series it is a sign of possible mixed valence behavior (C. Petrovic et al., unpublished). It is unlikely that deviating behavior of flux grown single crystals of SmIr_2Ga is due to the loss of Sm during melting and the presence of homogeneity region that would also occur in other members of the series.

Magnetic susceptibility was measured on single crystals for a magnetic field $H=0.1$ kOe applied in basal plane as well along the c -axis direction. Curie–Weiss (CW) fits give rough estimate of the high temperature effective moment μ_{eff} and the Weiss temperature θ . A polycrystalline average θ_p was obtained from the CW fit of the average susceptibility calculated from $\chi_p = (1/3)\chi_{\parallel} + (2/3)\chi_{\perp}$. In addition, values of θ were obtained for fields applied along the hexagonal axis (θ_c) and in the basal plane (θ_a). The results are summarized in Table 2. Susceptibility measurements at low temperature indicate an easy-plane magnetic anisotropy in most members of the series. This anisotropy is seen by comparing data in the hexagonal basal plane (θ_a) and along the c -axis (θ_c) (see Table 2).

Fig. 2. Lattice constants for the RIr_2Ga series as a function of rare earth.

Table 2

Effective magnetic moment in the paramagnetic state μ_{eff} , the Curie temperatures (polycrystalline average θ_p and along the a (θ_a) and c (θ_c) axes), magnetic ordering temperatures T_m and the ratio of the magnetic susceptibilities at the ordering temperature (χ_a/χ_c) _{T_m}

Lanthanide	μ_{eff} (μ_B)	θ_p (K)	θ_a (K)	θ_c (K)	T_m	$\left(\frac{\chi_a}{\chi_c}\right)_{T_m}$
Ce	1.85	−120	−106.0	−148.0		
Pr	3.53	−23	−11.3	−53.8		
Nd	3.80	−53	−39.7	−88.6	5.2	1.15
Sm					7.5	0.86
Gd	8.00	−41.2	−42.4	−39.8	7.3	2.30
Tb	10.10	−40.6	−53.6	−17.7	5.2	1.48
Dy	10.20	−15.7	11.0	−95.1	5.5	2.21
Ho	9.90	−5.2	4.4	−31.9	3.0	8.50
Er	8.6	−1.8	12.0	−18.3	2.5	12.50
Tm	7.1	−10.6	−69.0	41.4	2.0	0.05

Both the polycrystalline and anisotropic Weiss temperatures are negative for the lighter rare earth members, indicating the dominance of antiferromagnetic interactions; while ferromagnetic interactions are indicated for a field applied in the hexagonal plane in some heavier rare earth members. Anisotropic Weiss temperatures show that crystal-electric fields for Pr, Nd, Dy, Ho and Er confine the moments to the basal plane ($\theta_a > \theta_c$), in contrast to Tm. As expected, GdIr_2Ga did not show anisotropy in its magnetic susceptibility for $T > T_c$, since the Hund's-rule ground state for Gd has orbital angular momentum $L=0$. Magnetism in the Tb case is likely to be similar to the Gd, but with an anisotropic exchange interaction. The magnetic susceptibility of SmIr_2Ga cannot be described by a Curie–Weiss law even at high temperatures, where it shows signs of saturation to a temperature-independent value, indicating a non-negligible Van Vleck contribution. The magnetic susceptibility for magnetically ordering members shows evidence for antiferromagnetic transitions in an applied field of 0.1 kOe, except for TbIr_2Ga and GdIr_2Ga which show ferromagnetic-like transitions but with a negative Weiss temperatures.

Magnetization curves as a function of applied field for the TbIr_2Ga and GdIr_2Ga are presented in Fig. 3. The Gd moment in the hexagonal plane saturates in less than 0.1 kOe with a small moment per Gd $\mu \approx 0.1(\mu_B/\text{Gd})$, while the magnetization is linear in field if the field is applied along the c -axis. The small magnitude of the ordered Gd moment indicates that in the ordered state all Gd moments are not pointing in the same direction. Tb moments along both axes show saturation around 0.25 kOe with $\mu \approx 0.25(\mu_B/\text{Tb})$ along the c -axis and $\mu \approx 0.35(\mu_B/\text{Tb})$ in the hexagonal plane. In both compounds, there is a change in the magnetic structure at higher fields. The magnetization anomaly is weak and broad in GdIr_2Ga for field applied along the a -axis, but it is quite sharp for TbIr_2Ga . This anomaly may correspond to canting of moments into the c -direction. The overall ferrimagnetic interaction could be

Fig. 3. Magnetization as a function of field for GdIr_2Ga and TbIr_2Ga for field applied parallel and perpendicular to the c -axis. The inset shows the saturation of magnetic moments at low fields.

caused by either canted spins or anisotropy of magnetic order in the two R–Ga planes.

The resistivity has been measured in the temperature range 2–290 K with the current applied along the c -axis of the crystal. As shown in Fig. 4, resistivities are metallic and relatively featureless. For the magnetically ordered compounds, there is a distinct loss of spin-disorder scattering below the ordering temperature, except in the Tb case where the loss is rather weak. Dy, Ho, Er and Tm exhibit featureless $\rho(T)$ down to 2 K. Residual resistivities for most of the compounds are in the range of a few tenths of $\mu\Omega\text{-cm}$. By analyzing $d\rho/dT$ curves, peaks in the differential resistivity were found for Nd, Gd, Sm and Tb members of the series. These temperatures coincided well with peaks in $d(\chi T)/dT$ in case of Nd and Sm and thus are taken as the ordering temperatures. Dysprosium did not show a

Fig. 4. Electrical resistivity of RIr_2Ga as a function of temperature for $\text{R} = \text{Tb}, \text{Sm}, \text{Gd}$. The inset highlights the loss of spin-disorder scattering at the onset of magnetic order.

Fig. 5. Approximate magnetic ordering temperatures T_m and De Gennes scaling along the series.

well-defined peak in $d\rho/dT$ down to the lowest measured temperature. In the cases of Dy, Ho, Er and Tm, ordering temperatures were estimated based on the position of peaks of $d(\chi T)/dT$ only. Fisher and Langer [5], in considering the role of short-range magnetic fluctuations, have concluded that the magnetic part of the specific heat and the T coefficient of ρ are proportional in magnetic systems. Therefore, ordering temperatures for members of the rare earth series that are heavier than Dy should be taken as approximate.

The magnetic ordering temperatures T_m for the RIr_2Ga series are plotted along with the DeGennes factor $DG = (g_J - 1)^2 J(J+1)$ (normalized to Gd) in Fig. 5. The ordering temperatures show clear deviation from the linearity predicted by DeGennes scaling, suggestive of a rare-earth dependent exchange interaction. Magnetic susceptibility data are also consistent with a description in which the exchange interaction is not constant in the series due to the influence of crystalline-electric field and magneto-crystalline anisotropy. Uncertainty in the determination of T_m could also be a factor in the apparent non-DeGennes scaling. For more precise determination of the influence of crystalline electric fields, ESR measurements would be useful.

4. Conclusion

A new rare earth series of ternary intermetallic compounds has been synthesized. Members of the series that commonly possess an anomalous valence state deviate from the usual lanthanide contraction in the unit-cell volume. Effects of anisotropy and interlayer coupling are likely to be responsible for the long range magnetic order observed in most of the investigated materials. The small ordered moments of GdIr_2Ga and TbIr_2Ga could indicate

rather weak interplanar exchange between the magnetic sublattices. This new rare earth series represents an interesting example of a quasi-2D magnetic lattice with anisotropic interactions.

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