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Possible heavy-fermion behavior and field-induced transitions in new R–Pt–Ga compounds

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Abstract

We have discovered a new family of rare earth compounds that we identify as $R_{2-x}Pt_4Ga_{8+y}$. Single crystals of this family have been grown for R≡La, Ce, Pr, Nd, Sm, Gd, Er, Yb and Y. Many members (cerium, praseodymium, neodymium, samarium and erbium) show large anisotropies in their magnetic susceptibility; further, electrical resistance, magnetic susceptibility and specific heat measurements on the cerium member indicate that it is very possibly a heavy-electron compound with an electronic specific heat $\gamma \approx 1$ J K^{-2} mol^{-1}. Additionally, other members of the family have a magnetic transition at low temperatures. The electrical resistance, magnetic susceptibility and specific heat in fields will be presented for the praseodymium-based compound in which there is a field-induced transition.

1. Introduction

We have discovered a new family of rare earth–platinum–gallium compounds R–Pt–Ga (R≡La, Ce, Pr, Nd, Sm, Gd, Er, Yb and Y) that have been grown as single crystals. These compounds have been studied through electrical resistance, d.c. magnetic susceptibility and, in a few cases, by specific heat and single-crystal X-ray diffraction. From growth considerations, preliminary structural analysis and magnetic susceptibility measurements, which will be discussed in the next sections, the chemical formula for the family seems to be $R_{2-x}Pt_4Ga_{8+y}$. For the cerium-compound, experiments on specific heat at ^{3}He temperatures reveal a possible heavy-fermion state with a large electronic term of order 1 J K^{-2} mol^{-1}. Additional interesting members of this family are the praseodymium and neodymium compounds, which display a large jump in their magnetization near 20 kOe and 30 kOe respectively at 7 K. We present an account of our preliminary results on the series and concentrate on the striking properties of the cerium- and praseodymium-based compounds.

2. Materials and experimental techniques

Hexagonal cross-section single crystals of the $R_{2-x}Pt_4Ga_{8+y}$ family with volumes of up to 0.10 cm^3 have been grown out of excess gallium. Both powder X-ray and neutron diffraction* as well as single-crystal X-ray diffraction

*Neutron diffraction experiments were performed on the general-purpose powder diffractometer at Argonne National Laboratory.

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indicate that the structure is hexagonal with the lattice parameters for the cerium compound being $a = 4.313$ Å and $c = 16.516$ Å. The precise refinement of the single-crystal X-ray and powder neutron data is still in progress and quite difficult owing to apparent disorder on one or more of the sites as will now be discussed.

Table 1 is to date the best solution of the crystal structure, giving an agreement factor R between the calculated and measured diffraction spectra of better than 10%. From the occupancies given in Table 1 we arrive at values of $x \approx 0.66$ and $y \approx 2.0$ for the cerium compound. These values are in good agreement with the results of electron microprobe elemental analysis (for various members of the series $0 < x < 1$ and $1 < y < 2$) and magnetic susceptibility measurements (Table 2). One possibility that we are still examining is that there is some correlation between the vacancies associated with the cerium 2c site and the gallium occupancy of the 6h site. This would lead to acceptable interatomic distances and hopefully allow further reduction in the R factor. Finally, it is worth noting that the sites which our refinements indicate as being occupied lead us to believe that this is an unreported crystallographic system.

TABLE 1

Lattice constants, site parameters and occupancy for $Ce_{2-x}Pt_4Ga_{8+y}$ determined from single-crystal X-ray and neutron powder diffraction (space group 163 ($P\bar{3}12/c$); $a = 4.313$ Å; $c = 16.516$ Å; $R \approx 8\%$)

Atom	Wyckoff notation	x/a	y/a	z/c	Occupancy
Ce	2c	0.333	0.666	0.2500	0.60
Pt	4f	0.666	0.333	0.3919	1
Ga(1)	4f	0.666	0.333	0.5443	1
Ga(2)	4e	0.000	0.000	0.3664	1
Ga(3)	6h	0.534	0.068	0.2500	0.30

TABLE 2

Paramagnetic temperature Φ for field applied parallel (Φ_{par}), and perpendicular (Φ_{perp}) to the c axis, magnetic transition temperature T_m from susceptibility anomalies, deficiency in the rare earth site from susceptibility results (see text) for $H \parallel c$ ($x_\parallel$) and $H \perp c$ ($x_\perp$) and $x = \frac{1}{3}(2x_\parallel + x_\perp)$ for $R_{2-x}Pt_4Ga_{8+y}$

R	Φ_{par} (K)	Φ_{perp} (K)	$x_\parallel/x_\perp$	T_m (K)	x
Ce	−9.5	−56.3	0.35/0.88	–	0.53
Pr	+33.7	−35.0	0.73/0.64	16	0.70
Nd	+5.0	−2.2	0.71/0.75	10	0.73
Sm	–	–	–	8	–
Gd	−2.7	−4.9	0.62/0.55	9	0.60
Er	+13.4	−9.4	0.68/0.68	–	0.68

Although the quantitative nature of the crystal structure may change slightly with further refinement, the qualitative aspects of it seem to be quite robust. The structure can be described as two-dimensional (2D) nets of rare earth atoms perpendicular to the **c** axis that are separated by Pt–Ga slabs. For the cerium member, the R–R separation in the nets is 4.313 Å and the distance between the nets is 7.47 Å. Within these nets there are both rare earth vacancies and partial occupancy of the gallium 6h site. The question of how random these occupancies truly are is the issue that we are pursuing.

The resistivity was measured using a conventional a.c. four-probe method in the temperature range 1.3 K$<T<$300 K. Magnetic susceptibility measurements were performed on a Quantum Design superconducting quantum interference device magnetometer between 2 and 300 K. Heat capacity measurements were carried out using a quasi-adiabatic thermal relaxation technique [1] in the temperature range 0.3–2 K at zero field, and 1.3 K$<T<$20 K in fields up to 50 kOe.

3. Results and discussion

Resistance measurements show that all members have a resistance ratio R(300 K)/R(2 K) of order unity, suggesting the presence of crystallographic disorder. Further evidence for this comes from magnetic susceptibility measurements. At high temperatures, above about 100 K, all compounds except samarium and ytterbium exhibit an inverse susceptibility ($1/\chi$) linear in temperature. Assuming a Curie constant given by Hund's rules, we can calculate the rare earth occupancy from these data. The results are summarized in Table 2, where the values of x are given for the series assuming the composition $R_{2-x}Pt_4Ga_{10}$. We see that the rare earth stoichiometry range is reasonably constant, ranging from 1.27 for neodymium to 1.47 for cerium, consistent with the poor resistance ratios. Also given in Table 2 are the paramagnetic temperatures Θ determined from the field perpendicular and parallel to the hexagonal c axis. Note that Θ is negative for the perpendicular direction and positive or much less negative for H parallel to the c axis. These and the crystallographic anisotropy suggest that the dominant interaction within the planar network of R atoms is antiferromagnetic and that the planes may be coupled ferromagnetically. The extent to which disorder on the R sites affects these observations remains an open question.

Figure 1 shows the low-temperature specific heat (0.32 K$<T<$2.0 K) of $Ce_{2-x}Pt_4Ga_{8+y}$. The rapid rises in C/T with decreasing temperatures could indicate heavy-electron behavior but equally well could be the approach to a magnetic transition. Indeed, support for the latter is shown in Fig. 1(b) where we see a weak maximum in C centered near 1 K and then a sharp drop in C below 0.5 K. If this does represent a magnetic transition, entropy associated with it is very small, certainly much less than R ln 2. The argument could be made that, if the change in slope in C *vs.* T near 1.5 K represents the onset of a transition, then C/T just above 1.5 K is already large,

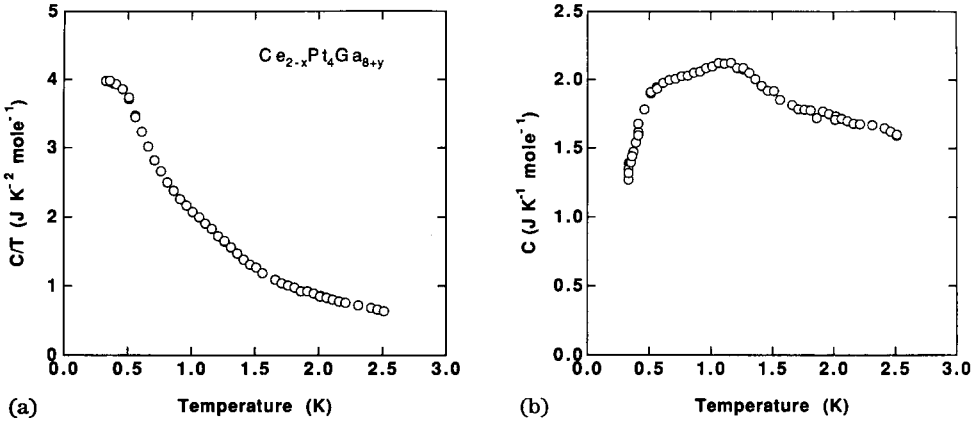

Fig. 1. (a) C/T as a function of temperature for $Ce_{2-x}Pt_4Ga_{8+y}$. (b) C *vs.* T on $Ce_{2-x}Pt_4Ga_{8-y}$.

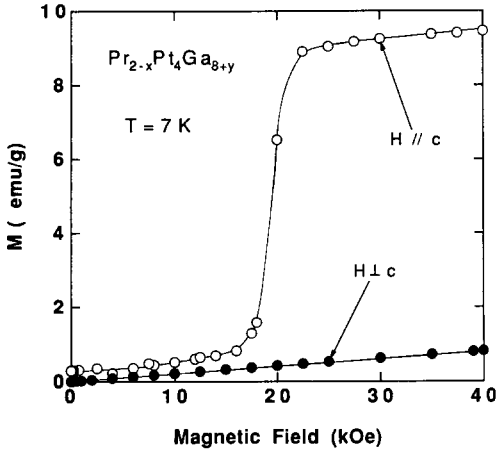

Fig. 2. Isothermal magnetization *vs.* field for $H \parallel c$ and $H \perp c$ at 7 K for $Pr_{2-x}Pt_4Ga_{8+y}$.

approximately 1 J K^{-2} mol^{-1}, and that the transition develops out of a heavy-fermion state. Similar behavior has recently been found in YbBiPt [2], in which C/T above a weak anomaly in C is huge, about 8 J K^{-2} mol^{-1}. On the contrary, if there is no magnetic transition in $Ce_{2-x}Pt_4Ga_{8+y}$, the low-temperature state has a very large $C/T \approx 4$ J K^{-2} mol^{-1}. In fact this value of C/T is very close to that expected if the specific heat maximum near 1 K is attributed to the Kondo effect in a ground-state doublet.

We turn now to $Pr_{2-x}Pt_4Ga_{8+y}$. Magnetization M measurements made upon cooling in a 10 Oe field parallel to the c axis indicate a weak ferromagnetic-like transition at $T_m = 16$ K, and a saturated moment at 5 K of $M_s \approx 0.07$ μ_B per praseodymium atom, assuming the value of x given in Table 2. No evidence for ferromagnetism is found for H perpendicular to the c axis; rather, M *vs.* H is linear and reversible at 7 K, as shown in Fig. 2. Also shown in Fig. 2 is the isothermal magnetization at 7 K for $H \parallel c$ where a

sharp field-induced transition appears at $H^* = 19$ kOe with a change in magnetization given by $\Delta M = 2.1\ \mu_B$ per praseodymium atom. The transition itself and the magnetization above H^* are reversible within experimental error. Interestingly, the slopes dM/dH are nearly equal above and below H^*. Nearly identical behavior was observed in a praseodymium compound annealed for 5 days at 600 °C. Annealing increased the resistance ratio from 1.55 to 3.

To investigate the magnetic behavior in greater detail, specific heat measurements were made in zero and applied fields parallel to the c-axis. Figure 3 gives representative results where we see that the mean-field-like anomaly at 16 K in zero field moves to lower temperatures with increasing H and becomes progressively less pronounced, finally becoming imperceptibly small for $H = 19$ kOe. From these specific heat data, a transition temperature T^* can be defined as a function of field H. From isothermal magnetization data, such as those in Fig. 2, a transition field H^* can be determined as a function of temperature. Together these data result in the phase diagram shown as an inset in Fig. 3(b). Within the resolution of these data, it appears that H^* decreases discontinuously from 10 kOe to zero near 16 K. If it is not discontinuous, the slope dH^*/dT^* is very large and negative. This phase diagram resembles closely that found for La_2CuO_4 [3], which at low fields undergoes a paramagnetic-to-antiferromagnetic transition and at temperatures below T_N ($= 253$ K) transforms to a weak ferromagnetic state with increasing field. The pseudo-two-dimensional structure of $Pr_{2-x}Pt_4Ga_{8+y}$ could argue for a metamagnetic transition, as found in La_2CuO_4 for fields applied perpendicular to the planar magnetic ions.

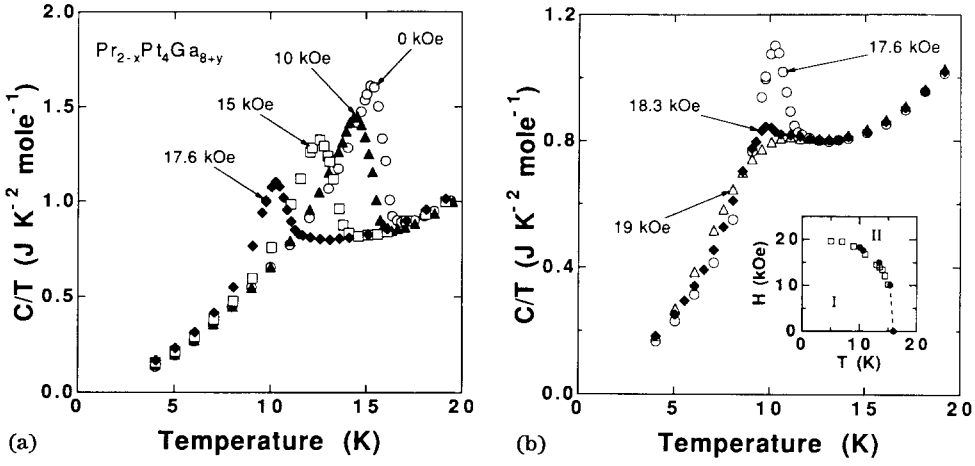

Fig. 3. (a) C/T *vs.* temperature for $Pr_{2-x}Pt_4Ga_{8+y}$ in magnetic fields as indicated. The magnetic field was applied along the c axis. For $H = 0$, C/T rises approximately as $1/T^3$ to a value of $C/T \approx 21.8$ J K^{-2} mol^{-1} at 300 mK. We believe that this feature arises from a nuclear Schottky anomaly centered at 200 mK. (b) C/T *vs.* T for $Pr_{2-x}Pt_4Ga_{8+y}$ in magnetic fields as indicated ($H \parallel c$). The inset shows the phase diagram determined from the specific heat in fields (●) and the jump ΔM in the magnetization (□) as a function of temperature (see text).

Although the origin of magnetic behavior in $Pr_{2-x}Pt_4Ga_{8+y}$ is not understood, it is not unique. Magnetization studies of $Nd_{2-x}Pt_4Ga_{8+y}$ reveal similar behavior below a magnetic transition temperature of about 10 K, only in this case the value of H^* at 5 K is 30 kOe and the change in magnetization at H^* is 1.4 μ_B per neodymium atom. A phase diagram such as that shown in Fig. 3(b) also results for $Nd_{2-x}Pt_4Ga_{8+y}$. Finally, $Sm_{2-x}Pt_4Ga_{8+y}$ undergoes a transition to a weak-ferromagnetic-like state below $T_m = 8$ K, with hysteresis present in $M(H)$ curves for H parallel to the c axis. However, there is no field-induced transition below our maximum attainable field of 50 kOe.

In conclusion, the $R_{2-x}Pt_4Ga_{8+y}$ family represent a new rare earth system with extremely interesting, but as yet not understood, properties. The extent to which these properties are driven by the rare earth deficiency certainly must be pursued further, as well as the precise nature of the defect structure. Although we have indicated that the magnetic behavior of $Pr_{2-x}Pt_4Ga_{8+y}$ is similar to that found in La_2CuO_4, we also note that the apparent structure of $R_{2-x}Pt_4Ga_{8+y}$ compounds could lead to magnetic frustration and subsequent field-induced jumps in the magnetization, with a corresponding spin rearrangement. Such a situation has been considered recently to explain the magnetization behavior of RMn_2 [4]. Finally, it would be very interesting to study the effect of a magnetic field on the low temperature magnetization and specific heat of $Ce_{2-x}Pt_4Ga_{8+y}$, which may be a heavy-fermion system. If the cerium compound also exhibits metamagnetism, it may be analogous to other heavy-fermion systems, $CeRu_2Si_2$ (see for instance ref. 5 and references cited therein) and UPt_3 [6, 7], which also undergo metamagnetic transition and show a huge magnetostrictive response.

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