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# Ferromagnetism in the RhGd and PtGd systems<sup>a)</sup>

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Rhodium and platinum have been studied with up to 33% additions of gadolinium. The magnetic properties of the constituents in the layers of a eutectic structure are different from the bulk properties of the constituents. The compound GdPt<sub>3</sub> orders ferromagnetically at 13.9 K.

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#### INTRODUCTION

Recently Matthias et al. (1) demonstrated bulk superconductivity in the eutectic formed between pure Ir and YIr2. The eutectic has a superconducting transition temperature that is much higher than that of either constituent. This enhancement is correlated with a dramatic drop in the Debye temperature at the eutectic composition which is thought to be caused by the longrange strain occurring from the lattice mismatch at the interfaces between the layers of the constituents (2). This led to a study of the magnetic properties of the corresponding system with the yttrium replaced by gadolinium, to a survey of dilute additions of most rare earth elements to iridium, and a survey of dilute additions of gadolinium to ruthenium, osmium, rhodium, and platinum (3). We report here on further work on the RhGd and PtGd systems. The IrGd is somewhat more complicated than reported in ref. (3) and, guite naturally, resembles the RhGd which remains puzzling. The PtGd system is now fully described.

This work was undertaken to elucidate the magnetic behavior of these systems from their dilute limit, through the eutectic composition, to the first compound. That has turned out to be difficult, although in a qualitative sense the results are clear. What is equally important is that once again the need for metallugical examination of samples is clear, and specifically the difficulties encountered with preparing dilute magnets is apparent.

### EXPERIMENTAL

The samples were prepared in an argon-atmosphere arc furnace. Samples with less than 2000 ppm Gd (all % and ppm are atomic) were prepared in more than one dilution step. Weight losses upon melting were neg-Hence, all compositions reported are calculigible. lated and respresent an upper limit to the gadolinium concentration. Annealed samples were wrapped in tantalum foil and held at 1000°C for 8-14 days. Most of the samples were checked by Debye-Scherrer x-ray analysis and several were subjected to metallographic examination. Magnetic measurements down to 1.4 K were made in a vibrating sample magnetometer with the field produced by a superconducting solenoid having a maximum field of 54 kOe. In this work on dilute magnets most of them were run in the nominal zero field of the magnet because of the ease of separating the many magnetic transitions that occur (see ref. 3). This field is moderately reproducible and is usually 50-100 Oe.

#### RESULTS AND DISCUSSION

### I. PtGd

The most dilute compound that we found in PtGd alloys was GdPt<sub>5</sub> with the CaCu<sub>5</sub> structure. Although we found no report of it in the literature, its existence is not surprising. A magnetization cooling curve of GdPt<sub>5</sub> is shown in Fig. 1, and the sample can be seen to order ferromagnetically at  $T_c = 13.9$  K. This curve is not affected by annealing the sample. The saturation

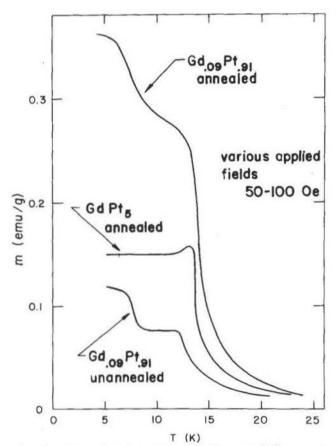


Fig. 1. Magnetization of some <u>PtGd</u> compositions as a function of cooling in a constant magnetic field.

moment is 7.1+0.1  $\mu_B$  for a Gd atom which is in reasonable agreement with the theoretical value of gJ = 7.0. The approach to saturation is dependent on the alignment of the field direction with the cooling direction of the sample in the arc furnace. The m(H) curve rises initially about three times faster when the field is perpendicular to the solidification direction than when parallel. The samples saturate at ~20 kOe, and the anisotropy is gone at that field.

The x-ray examination showed that the sample was pure GdPt5 before annealing, while after, some pure Pt was present. Metallographic examination showed a few percent of a second phase that was unaffected by the anneal. It could be seen in the metallography that a martensitic transformation was induced near the edge where the samples were cut mechanically. The preparation of powder for the x-rays can be expected to induce this transformation. Hence the powders were annealed at 600°C for one hour.

At the composition Gd  $_{09}$ Pt  $_{91}$  a sample is formed that is completely a lamellar eutectic structure of GdPt5 and Pt layers with a layer thickness of  $\gtrsim 5000$  Å. The Pt layers will of course contain dissolved Gd up to its solubility limit. A cooling magnetization curve of an unannealed sample is shown in Fig. 1. Two transitions are observed at  $T_c = 12.8$  K and 7.5 K. The higher  $T_{\rm C}$  must be associated with the GdPt5 lamellae and the lower with the very dilute PtGd lamellae. The reduced Tr in GdPt5 could be a strain effect of the nature of the coherent strains discussed in ref. 2 or could be simply an inhomogeneously broadened transition because the sample can be viewed as Pt with a Gd concentration modulation. The ordering in the dilute phase could occur from some conduction electron polarization that arises in the neighboring layers or may be true dilute magnetic impurity ordering where the non-equilibrium, high concentration of Gd atoms is present. It seems unlikely that Gd clusters are forming in the Pt layers because the existence of the layered structure is, in fact, the thermodynamic response to the solubility problem. After annealing, the GdPt5 Tc moves up to the value for the pure compound and the dilute  $T_c$  is severely broadened. This suggests simply that the Gd atoms are moving out of the dilute layers into better positions in the GdPt5 structure or equivalently that the lattice strain is being relieved.

As the Gd concentration is reduced, this same eutectic structure with its two magnetic transitions persists down to at least 1000 ppm Gd. Metallographic examination of a 2000 ppm sample shows that the Gd is in fact not all dissolved. This is in disagreement with the recent work of Hardiman et al. (4) who report no magnetic ordering of the Gd in Pt over concentration levels that overlap our levels. On the other hand they do have to deal with a troublesome "cluster" line in their electron paramagnetic resonance studies.

At concentration levels below ~1% Gd, the dilute transition is usually not seen in cooling curves but shows up in the warming curves of field cooled samples. It is then quite broad, resembling the transition in the annealed sample curve in Fig. 1. This dilute transition is obviously weakened as the amount of eutectic present decreases to what is likely the limit of one layer of GdPt5 between grains of Pt. However, even at 1000 ppm Gd the 12.8 K transition is clear. We conclude that the true solubility of Gd is below 1000 ppm and that the Gd that does dissolve does not order magnetically. We report no magnetic parameters on the eutectic magnetic phases because it is difficult to do this on an inherently two-phase system. The m(H) curves at Gd levels below ~3000 ppm show no sign of saturation at 54 kOe, but even at that field they suggest a moment greater than 7  $\mu_B$ . This could be caused by problems of eddy-current signals that appear in our magnetometer as the samples become very dilute.

#### II. RhGd

The RhGd is more complicated than the PtGd system. The Gd-Rh phase diagram is known (5). However, we were not able to find any trace of the reported GdRh<sub>3</sub> compound. We were able to retain some GdRh<sub>5</sub> in the CaCu<sub>5</sub> structure by quenching the samples. However, there was a second unidentified phase. After annealing, the GdRh<sub>5</sub> disappeared and Rh and an unidentified phase appeared which was consistent with the metallographic examination.

Because of the difficulty of correlating various phases with up to three magnetic transitions in some samples, we simply present  $T_c$ 's versus nominal composition in Table I. We have made a tentative identification of the  $T_c$ 's in Table I with various phases which is 76,56 K - GdRh<sub>2</sub>, 49 K - GdRh<sub>2</sub> or unidentified phase present in eutectic layers, 33 K - dilute Gd in Rh in eutectic layers, 20 K - GdRh<sub>5</sub>, ~10 K - ordering of dilute Gd in Rh grains. These identifications are only suggestions. It is clear that this is a more complicated system than PtGd and it seems likely that no more insight can be gained by the difficult task of more sorting out of phases. It is however obvious that eutectics are magnetically different from their comstituent phases. Also, there may be ordering at ~10 K of

Table I. Magnetic transition and x-ray results for various  $Rh_{1-x}Gd_x$  compositions. The asterisks (\*) represent the transition present, while the T's represent very small traces of transitions.

	- (						
	76	56	49	$\frac{C_{c}(K)}{33}$	20	~10	X-ray
GdRh2	*						MgCu <sub>2</sub>
GdRh2 <sup>a)</sup>		*					
GdRh3			*	Т			MgCu2+Rh
GdRh3 <sup>a)</sup>			*	*			
GdRh5			*		*		CaCu5+?
GdRh5 <sup>a</sup> )			*	*			Rh+?
Rh.87Gd.	13 <sup>b)</sup>		T	T	*		CaCu5+Rh
Rh.87Gd.	13 <sup>a)b</sup>	)	*	*			
Rh.990Gd	.010			*	*	*	
Rh.9945G	d.005	5		*	*		
Rh.9969G	d.003	1				*	
Rh.9982G	d.001	8				*	
Rh.9982G	d.001	8a)	Т			*	

a) annealed

b) eutectic composition

dissolved Gd in Rh at levels of around 3000 ppm. Interestingly, the properties of the dilute samples are independent of field direction. Some extra solubility is obtained at even 1800 ppm by quenching, since annealing brings up another magnetic transition. Further studies are underway on the dilute limit.

#### CONCLUSIONS

The layered and strained structures present in samples at eutectic compositions modifies the magnetic properties of the constituent phases and may represent a new type of magnetic material. As always, the characterization of the samples is crucial.

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