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CALORIMETRIC STUDIES OF THE MAGNETIC TRANSITION OF Gd IN Gd–La ALLOYS

G. A. Costa

ISTITUTO DI CHIMICA FISICA, UNIVERSITÀ DI GENOVA, ITALY
GENOVA, ITALY

Heat capacity measurements on h.c.p. solid solutions of lanthanum in gadolinium have been performed in an adiabatic calorimeter over a wide temperature range, and the temperature-dependence of the ferromagnetic transition of Gd by alloying with La has been evaluated.

The hardening effects of this alloying are pointed out.

A linear dependence of the molar volume on the concentration, close to Vegard's law, is found at room temperature; the effects of a second-order transition are outlined.

It is well known that the magnetic ordering in the rare earth metals (R) is due to a long-range indirect interaction responsible for the coupling between $4f$ orbitals, which involves the polarization of the conduction electrons.

The theory is associated with the names of Rudermann, Kittel, Kasuja and Yosida (RKKY). Reviews have been given, for example, by Kittel [1]. Such an interaction is capable of giving rise to a variety of periodic spin structures, as are indeed observed for the heavy R. The neighboring R are quite similar in their physical and chemical properties (excluding those depending directly on the $4f$ electrons) because of the regular filling of the inner $4f$ level. This similarity has an important effect on the intra-R binary alloys. There is a tendency for these to behave as ideal alloys at high temperature: thus, there is no measurable difference in the liquidus and solidus temperature; further, the liquidus/solidus line is practically a straight line connecting the respective melting points of the pure metals. This behavior is closely followed if neighboring elements are alloyed.

Deviations from ideal behavior are to be expected when the atomic numbers of the two lanthanides become more and more different. However, an extended solid solubility is always to be expected.

Up to 16 at.% La enters the h.c.p. cell of Gd [2], resulting in the magnetic dilution of the Gd.

For concentrations between 16 and 42 at.% La, the Gd–La alloy system presents [3, 4] an intermediate phase (δ) that has the same structure as metallic samarium. At concentrations higher than 42 at.% La, the d.h.c.p. structure of La is stable.

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From a magnetic point of view, when the Gd/La ratio is decreased, a transition occurs in the magnetic phase diagram, from ferromagnetic dispositions to antiferromagnetic ones [2, 5].

In this paper, experimental results obtained during the study of the alloying effect on the ferromagnetic transformation of Gd will be reported.

Experimental

The starting materials, 3N La and 2N5 Gd, were obtained from Rare Earths Products Inc. and Koch–Light Co., respectively.

Alloys up to 12 at.% La (each consisting of ~6 g a stoichiometric mixture of the elements) were prepared for direct synthesis in an arc furnace under an argon inert atmosphere. The samples were melted 5 times to obtain a first homogenization. The buttons thus obtained were then wrapped in high-temperature degassed tantalum foil, sealed in vacuum in silica tubes, and annealed for a week at about 800°.

Every sample was examined micrographically and X-ray analyzed, and Vickers microhardness measurements were performed.

The reticular parameters obtained by the powder method of Debye–Sherrer showed, in agreement with the literature values [3], a linear dependence on the composition, following the Vegard law relationship in the considered range. The calorimetric measurements were made in a continuous heating adiabatic [6] computer-controlled [7] calorimeter. The microhardness measurements were carried out with a Leitz Durimet microhardness tester.

Results

In Table 1, experimental values of C_p (for one mole of substance) and other thermodynamic data for $Gd_{1-x}La_x$ alloys are reported.

Figure 1 presents the molar heat capacities of such alloys *vs.* the temperature.

The dilution of the magnetic rare earth is accompanied by a linear lowering of the Curie temperature (Fig. 2) with $dT_c/dC_{Gd} = 410$ K where C_{Gd} is the gadolinium concentration. For this high dependence on the concentration, impurities of the order of 0.1 at.% will also depress the Curie temperature: this can account for the different values for T_c found in the literature [2, 8].

The effect of impurities on the hardness can be seen in Fig. 3, where Vickers microhardness data are reported *vs.* Gd concentration, together with literature data.

Table 1 Experimental values of C_p and thermodynamic data for $Gd_{1-x}La_x$ alloys. (C_p in cal mole^{-1} deg^{-1} and T in K)

	T	C_p	T	C_p	T	C_p
	270.0	11.45	287.8	13.90	299.9	8.74
	275.2	11.92	288.1	13.52	305.3	8.50
	280.1	12.59	288.5	12.83	310.2	8.40
$X=0$	285.1	13.41	288.9	11.98	315.2	8.34
	286.1	13.66	289.3	11.13	320.1	8.30
	287.1	13.88	290.1	10.15	325.1	8.32
	287.4	13.95	295.2	9.07		
	210.1	9.33	250.1	10.80	271.3	11.76
	215.0	9.46	255.1	11.08	272.1	10.36
	220.2	9.63	260.2	11.47	275.1	9.12
	225.0	9.79	265.0	11.92	280.0	8.63
$X=.04$	230.0	9.95	270.0	12.60	285.1	8.36
	235.2	10.10	270.3	12.61	290.0	8.16
	240.0	10.35	270.5	12.65	295.2	8.05
	245.0	10.54	270.8	12.54	300.0	7.98
	100.1	6.96	210.1	9.40	259.4	11.86
	110.3	7.19	220.2	9.66	260.0	11.62
	120.1	7.43	230.2	10.13	261.1	10.19
	130.0	7.62	240.0	10.66	262.1	9.46
	140.3	7.84	245.2	10.93	263.1	9.23
$X=.07$	150.0	8.01	250.0	11.10	265.1	8.94
	160.1	8.22	255.2	11.47	270.2	8.52
	170.3	8.42	256.0	11.58	275.0	8.29
	180.2	8.64	257.1	11.67	280.1	7.90
	190.2	8.86	258.3	11.80	290.1	7.76
	200.1	9.10	259.2	11.85	300.0	7.75
	100.3	6.78	180.1	8.12	238.0	11.26
	110.3	6.98	190.3	8.39	239.2	11.13
	120.4	7.14	200.3	8.73	240.1	9.71
	130.3	7.32	210.0	9.03	245.3	8.61
	140.0	7.48	220.2	9.30	250.3	8.10
$X=.12$	150.0	7.59	230.1	10.58	260.3	7.75
	155.1	7.66	235.2	11.16	270.2	7.53
	160.2	7.72	236.0	11.21	280.2	7.42
	170.3	7.85	237.3	11.28	290.3	7.36

	$X=0$	$X=.04$	$X=.07$	$X=.12$
$C_p$max	13.95	12.63	11.86	11.28
T_C	287.5	270.0	259.2	237.3
$\Delta C_p/T_C$	.020	.017	.016	.017

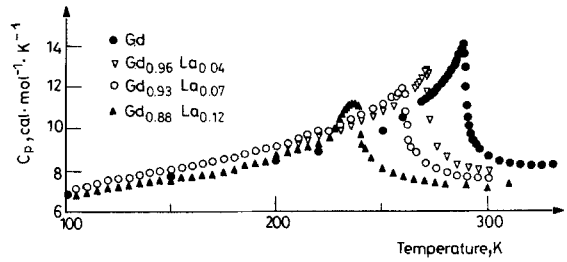

Fig. 1 Trends of C_p as a function of the temperature for some $Gd_{1-x}La_x$ alloys

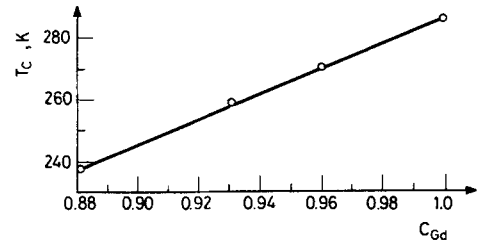

Fig. 2 Dilution effects of La in Gd–La alloys on the Curie temperature

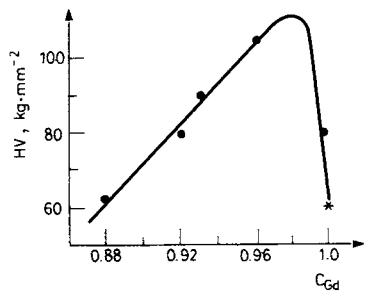

Fig. 3 Behaviour of the microhardness of Gd on alloying with La (*from ref. [16])

The T_c for pure Gd can also be lowered by applying pressure, as shown in Fig. 4, where the data of McWhon are used [8]; from these, $dT_c/dP = -16.3$ K/GPa. Thus, alloying and the application of pressure lead to a similar effect on T_c, even though the physical processes are different. In fact, while the external pressure affects the physical properties of pure Gd by shortening the Gd–Gd distances, the alloying with lanthanum determines a modification of T_c for Gd, because of the dilution of the Gd atoms. It must be pointed out that the atomic volumes follow Vegard's law (Fig. 5), which makes it reasonable to treat Gd–La alloys according to a rigid-sphere model, excluding the possibility of the existence of "chemical pressure" or strain due to the introduction of partner atoms.

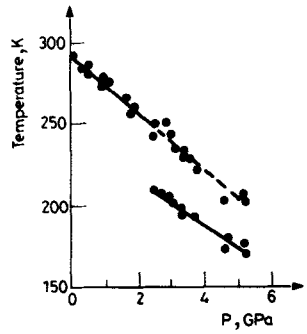

Fig. 4 Pressure dependence of T_c [8]

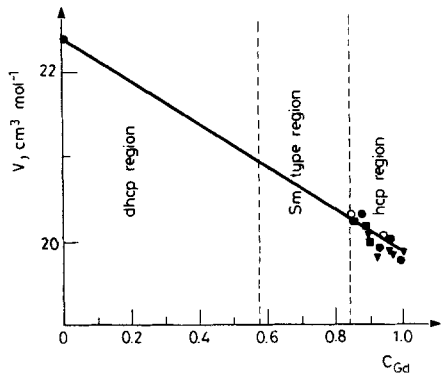

Fig. 5 Molar volumes at room temperature of $Gd_{1-x}La_x$ alloys. The solid line connecting end points represents the Vegard's law relationship.
(● this work, ■ Lundin [17], ▼ Beznosov [18], ○ Thoburn [2])

This is confirmed by the fact that the same effect of the depression of T_c can be obtained by introducing both atoms with larger dimensions (lanthanum) and smaller ones (lutetium) into the Gd lattice [9].

The temperatures of many transformations in pure metals and in intermetallic compounds [10] can be appropriately shifted by the formation of solid solutions or by applying pressure. A very impressive case is presented by SmS [11] that, differently from the other rare earth monosulfides (yellow–gold–colored), is black (it is a semiconducting compound). Under pressure it becomes a conductor and yellow–gold in color. By substitutional alloying with Gd (~16 at.% Gd) [12], it is possible to observe the same result in $Sm_{1-x}Gd_xS$ at room temperature and standard pressure: the transition temperature conductor-semiconductor can be shifted toward lower temperature.

Obviously, this can result only when the phase at higher temperature is denser than that at lower temperature [13].

The transformation of the SmS phase, collapsed by the alloying effect, is of first order, however, while the magnetic transformation studied in the alloys $Gd_{1-x}La_x$ has proved to be of second order (Fig. 1) [14].

dT_c/dP can be calculated from thermodynamics using Ehrenfast's equation for constant concentration:

$$\frac{dT_c}{dP} = T_c V \frac{\Delta\alpha}{\Delta C_p} = \frac{\Delta\beta}{\Delta\alpha} \tag{1}$$

where $\Delta\alpha$, $\Delta\beta$ and ΔC_p are the anomalies in the thermal expansion, compressibility and heat capacity at constant pressure at the transition temperature.

This relation was used by Costa *et al.* [6] and reasonable agreement was found between the experimental and calculated values.

When different concentrations are involved, two other equations become suitable. The first is:

$$\Delta \frac{\partial S}{\partial C_{Gd}} = -\frac{\partial T_c}{\partial C_{Gd}} \frac{\Delta C_p}{T_c} \tag{2}$$

If $\Delta C_p/T_c$ is considered practically constant for the observed alloys, this gives for the entropic jump: $\Delta \dfrac{\partial S}{\partial C_{Gd}} \cong 8$ cal/mol deg.

The second equation is:

$$\frac{\partial T_c}{\partial P} \cdot \Delta \frac{\partial S}{\partial C_{Gd}} = \Delta \frac{\partial V}{\partial C_{Gd}} \tag{3}$$

This suggests that a discontinuity is to be expected in the derivative of the molar volume *vs.* the Gd concentration at a temperature lower than T_c, even in the region of solid solubility of the considered alloys.

Conclusion

The presence of extended solid solubility in the Gd–La phase diagram made it possible to study the second-order magnetic phase transition of Gd.

A number of features of these alloys were pointed out.

A linear dependence of the T_c of Gd on the concentration was found in the h.c.p. region of the phase diagram.

Similarly, a linear dependence of the molar volume with respect to the concentration of Gd was found at room temperature. However, due to the presence

of a second-order phase transition, a deviation from this behavior must be expected in lattice parameters measured at lower temperatures for alloys of different composition.

As the Gd–La alloys form an intermediate phase, the calorimetric study will be continued in the region of the δ phase, and low-temperature structural measurements will be performed to ascertain the effect of the structural transformation on the magnetic transition [15].

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Zusammenfassung — Mit einem adiabatischen Kalorimeter ausgeführte, sich über einen weiten Temperaturbereich erstreckende Wärmekapazitätsmessungen an festen h. c. p. Lösungen von Lanthan in Gadolinium und die Temperaturabhängigkeit der ferromagnetischen Umwandlung von Gd beim Legieren mit La werden einer Betrachtung unterzogen. Die Härteeffekte des Legierens werden erörtert. Bei Raumtemperatur wurde eine lineare Abhängigkeit des molaren Volumens von der dem Vegard'schen Gesetz nahekommenden Konzentration festgestellt; die Effekte einer Umwandlung zweiter Ordnung werden erörtert.

Резюме — В адиабатическом калориметре в широком температурном интервале были проведены измерения теплоемкостей твердых растворов лантана в гадолиние с гексагональной плотноупакованной структурой и была определена температурная зависимость ферромагнитного перехода гадолиния в сплаве его с лантаном. Отмечены эффекты отверждения, наблюдаемые при сплавлении двух элементов. Установленная при комнатной температуре линейная зависимость молярных объемов от концентрации, близка к закону Вегарда, что указывает на переход второго рода.