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Structural and thermal properties in Gd–Y magnetic alloys [1]

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Abstract

This work accurately follows the behavior of the ferromagnetic transition of Gd when alloyed with Y, and seeks to link structural and magnetic properties.

We have measured the lattice parameters, heat capacities and resistivities of recrystallized single-phase solid solutions Gd_xY_{1-x}. The trend of the Curie temperature T_C has been found to have a linear dependence on the molar fraction of the diluting element.

The thermodynamic and structural implications of the appearance of a magnetic transition in a solid solution are discussed.

INTRODUCTION

The rare earths elements (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 infra-R binary alloys [1]. There is a tendency for these to behave as ideal alloys at high temperatures. There is no measurable difference in the liquidus and solidus temperatures due to a close similarity between the thermodynamic properties of the two components of the mixture; furthermore, the liquidus/solidus line is practically a straightline connecting the respective melting points of the pure metals. This behavior is followed closely 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. This is the case, for example, for the Gd–La system, which presents an intermediate Sm-type phase [2]. The Gd–Y alloy system has been examined by Spedding et al. [3]. The room-temperature structure of these alloys is hcp. Both room-temperature and high-temperature forms show complete solid solubility. Lundin and

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Yamamoto [4] studied the thermodynamic activities of Gd–Y alloys at 1600°C by the Knudsen effusion technique. Their activity data fit a straight line and Raoult's law is obeyed in the liquid state. Thus the liquid solutions at 1600°C are thermodynamically ideal. The only difference between these two elements lies in their electronic structure which does not, however, affect the ideality of the Gd–Y solution.

Almost all the rare earths are magnetic and their properties are connected with their unfilled 4f shells. Lanthanum, lutetium, scandium and yttrium are non-magnetic; gadolinium is the only rare earth that orders ferromagnetically, at about 290 K; and the remaining lanthanides show complex magnetic ordering at lower temperatures which is due to a long-range indirect interaction responsible for the coupling between 4f orbitals. The related theory is associated with the names of Ruderman Kittel, Kasuja and Yosida (RKKY); reviews have been published, for example by Kittel [5].

Because there is complete solid solubility of Y in Gd [6], it is possible to study the magnetic dilution of Gd. Magnetic dilution is also possible with Sc [7] and Lu [8], and also with La [9] but to a lesser extent because La enters the hcp cell of Gd to only 16 at.%. Heat capacity measurements of the hcp solid solutions of yttrium in gadolinium are particularly suitable for accurately following the temperature dependence of the ferromagnetic transition of Gd by alloying with Y. Other properties of this alloying are also indicated, such as the dependence of the lattice parameters and the resistivity behavior on the temperature.

EXPERIMENTAL

The gadolinium and yttrium used were 3N purity (Koch Light Laboratories Ltd., UK). Stoichiometric portions of the metals were pressed into pellets and melted several times under purified argon atmosphere (to ensure a first homogenization) in a cold-boat induction furnace. No appreciable weight loss was observed.

The resulting 2-cm-diameter buttons had a high degree of crystal orientation. Grain growth and further homogenization were accomplished by annealing the button wrapped in tantalum foil in a vacuum for 24 hours, at temperatures up to about 1250°C, to avoid the formation of the eutectic Gd–Ta. Grain growth was always observed and the dimensions of the grains ranged from 3 to 8 mm; the grain boundaries were clearly visible due to the thermal etching.

The button was cut by a diamond saw to obtain samples for the heat capacity (about 9 mm × 11 mm × 3 mm) and resistivity (about 1 mm × 1 mm × 12 mm) measurements; the calorimetric samples were thus composed of 3 or 4 grains. The samples were then stress-relief annealed for 24 h at 470°C.

The alloys were examined metallographically and by X-ray powder diffraction.

The samples were reduced to a powder with a small diamond file and the product thus obtained was sieved in a 50 μm sieve; they were then sealed in an outgassed tantalum crucible and annealed in a vacuum at 470°C for a week.

The crystal structure of the alloys was investigated by the X-ray powder method using the Cu Kα radiation. The intensity calculations for the powder patterns were performed using the Lazy Pulverix program [10].

Low-temperature measurements of reticular parameters were carried out using a Huber low-temperature computer-controlled Guinier camera. The measurements were performed, adding silicon to the powders in order to refine the reticular parameters, with an internal standard of which the thermal expansion at low temperatures is well-known [11].

The absolute accuracy of the recticular parameters ranges from 0.05% to 0.01%, depending on the quality of the diffractogram; the temperature control is within 1 K.

The microhardness of the alloys was determined by the Vickers method using a Leitz Durimet hardness tester.

Resistivity tests were performed by the conventional four-wire technique with current reversal, in which the wires were spot welded on the samples.

The calorimetric measurements were performed in a continuous-heating adiabatic computer-controlled calorimeter [12]. The measurements are reproducible to 0.1%; the absolute accuracy strongly depends on the thermal conductivity of the samples, especially at high temperatures, and is estimated to be about 3% at around 200 K for Gd–Y alloys.

DISCUSSION

Figure 1 shows the molar heat capacities of some Gd–Y alloys versus temperature. The jump due to the magnetic ordering is clear; its intensity and temperature depend on the concentration of the magnetic rare earth. The temperature T_C, at which the jump occurs can be carefully determined if C_p/T versus T data are plotted. Moreover, the value of the jump can be readily extrapolated from the plot, giving for these alloys a roughly constant value of $\Delta C_p/T_C \cong 0.07$ J mol^{-1} K^{-2}.

The dependence of T_C on the molar fraction of gadolinium x is reported in Fig. 2. The dependence is linear with $\partial T_C/\partial x = 245$ K. Notice that this high dependence of the concentration can account for the different values of T_C found in the literature [13, 14]; impurities as low as 1 at.% can depress the Curie temperature to a measurable extent.

We have not observed two-phase behavior, indicative of the simultaneous presence of ferromagnetic and antiferromagnetic ordering as reported by Thoburn et al. [15]. Bagguley et al. [16] indicated the limit of

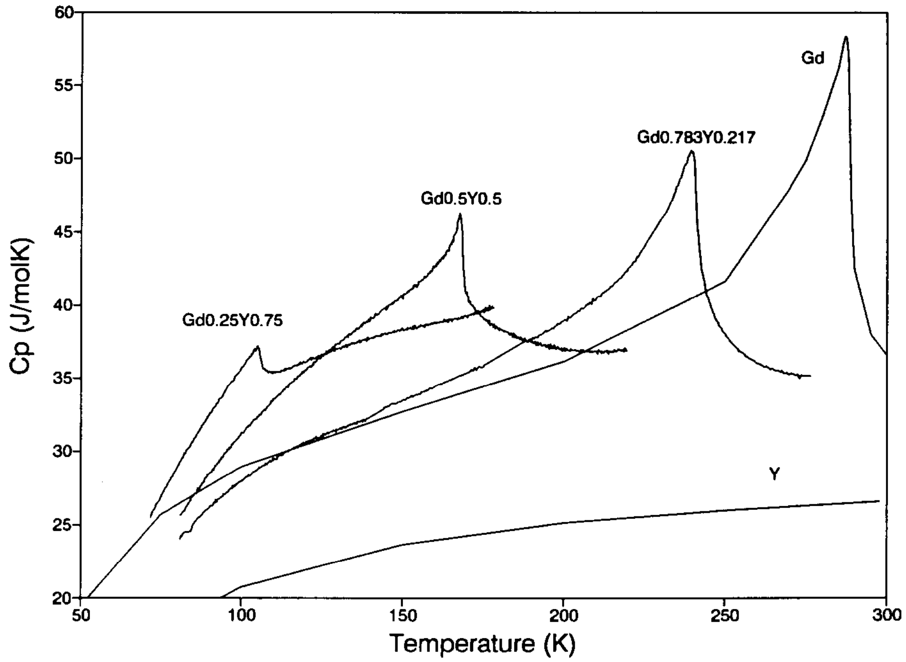

Fig. 1. Trends in C_p as a function of temperature for some Gd–Y alloys.

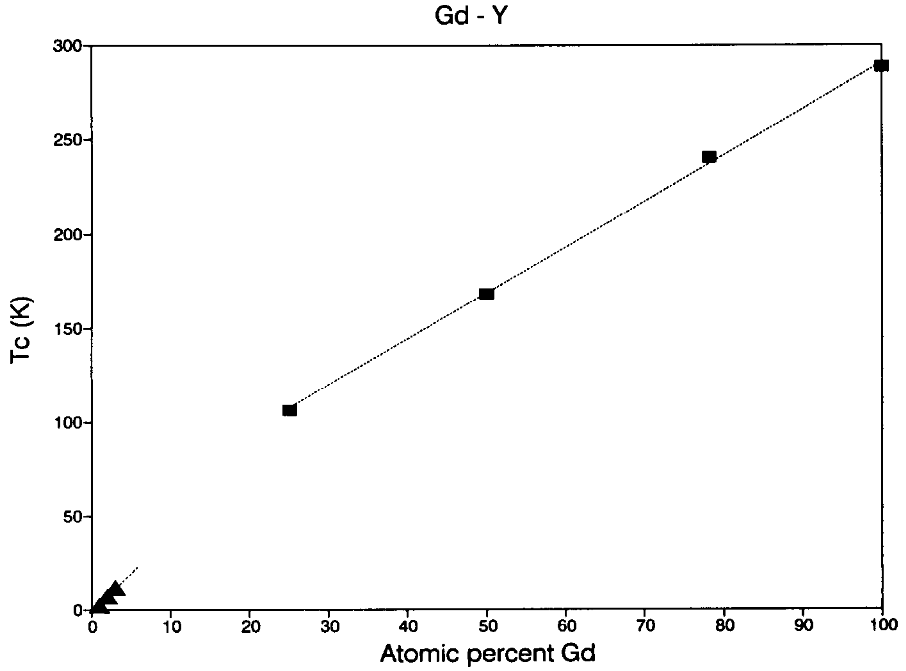

Fig. 2. The lowering of T_C for Gd–Y alloys: ■, this work; ▲, from ref. 17.

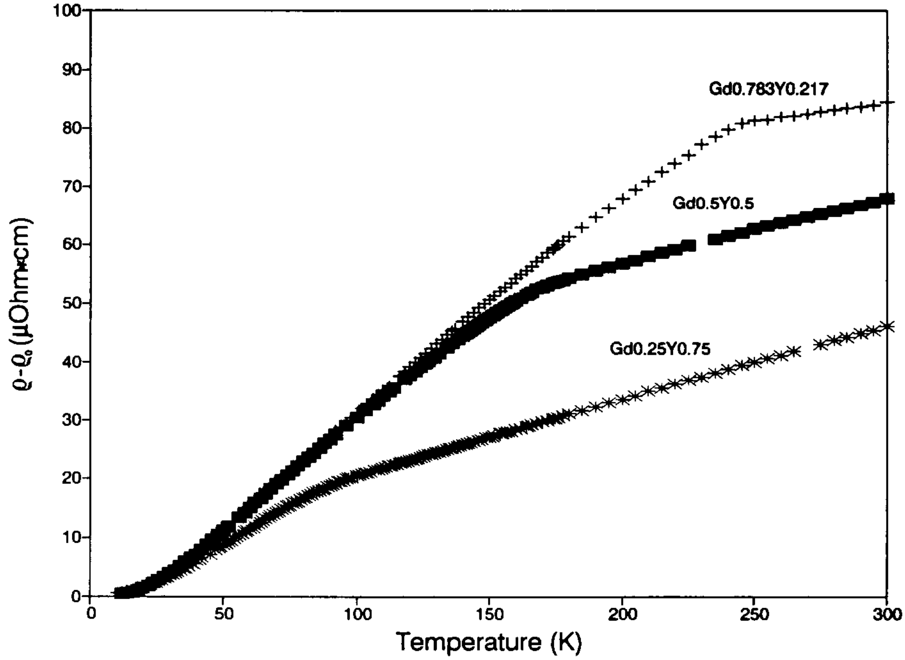

Fig. 3. Comparison of the temperature dependence of the resistivity for different alloys in the Gd–Y system.

ferromagnetism as lying at roughly 60 at.% gadolinium. To date we are not able to confirm the existence of this limit; thus the T_C on Fig. 2 must more correctly be considered as the limit to the paramagnetic state. We note that at low gadolinium concentration (1–3 at.%), the existence of an antiferromagnetic state is confirmed by Pureur et al. [17] (Fig. 2, triangles) and that the limit of the paramagnetic state neatly deviates from the behavior extrapolated at higher gadolinium levels.

The ordering temperatures given in Fig. 2 were also confirmed from the discontinuity of the derivative of the resistivity versus the temperature for each of the alloys. Resistivity data for three Gd–Y alloys are reported in Fig. 3. The behavior of the resistivity is characteristic of a typical metallic ferromagnet: above the ordering temperature it varies linearly, due to phonon contribution. At the ordering temperature, a change of slope can be seen. There is a gradual change characteristic of a ferromagnet. At low temperatures, the "residual" resistivity (not reported) versus the composition follows approximately the parabolic behavior predicted for disordered alloys.

The temperature of many transformations in pure metals, alloys and intermetallic compounds can be appropriately shifted by the formation of solid solutions or by applying pressure. McWhon and Stevens [18] observed that the T_C for pure Gd can be lowered by applying pressure, with

$dT_C/dP = -17.2 \text{ K GPa}^{-1}$. They also found a transition, under pressure, to the Sm-type structure, a common structure in intra-rare-earth phase diagrams. We have not found evidence of any structural change in the alloys we examined by X-ray diffraction at low temperatures.

When the transformation is second order, the temperature or the compositional dependence of T_C can be correlated by using Ehrenfast's equations, which generally provide a reasonable agreement [19]. Thus, alloying and applying pressure have the same effect on T_C, even if the physical processes are different: in fact, while the external pressure has the effect of shortening the Gd–Gd atomic distances, the alloying determines the modification of T_C because of the dilution of the Gd atoms.

Figure 4 shows the lattice parameters of several Gd–Y alloys together with their literature values [20, 21]. It should be noted that the lattice parameters follow Vegard's law, which makes it reasonable to treat the Gd–Y alloys according to a rigid sphere model, excluding the possibility of the existence of a "chemical pressure" or strain due to the introduction of partner atoms. This is confirmed by the fact that a similar depression of T_C can be obtained by introducing both atoms with larger (La) [9] or smaller (Sc, Lu) [7, 8] dimensions, or of about the same dimension (Y), into the Gd lattice.

In fact, even if the lattice parameters are slightly different, the atomic

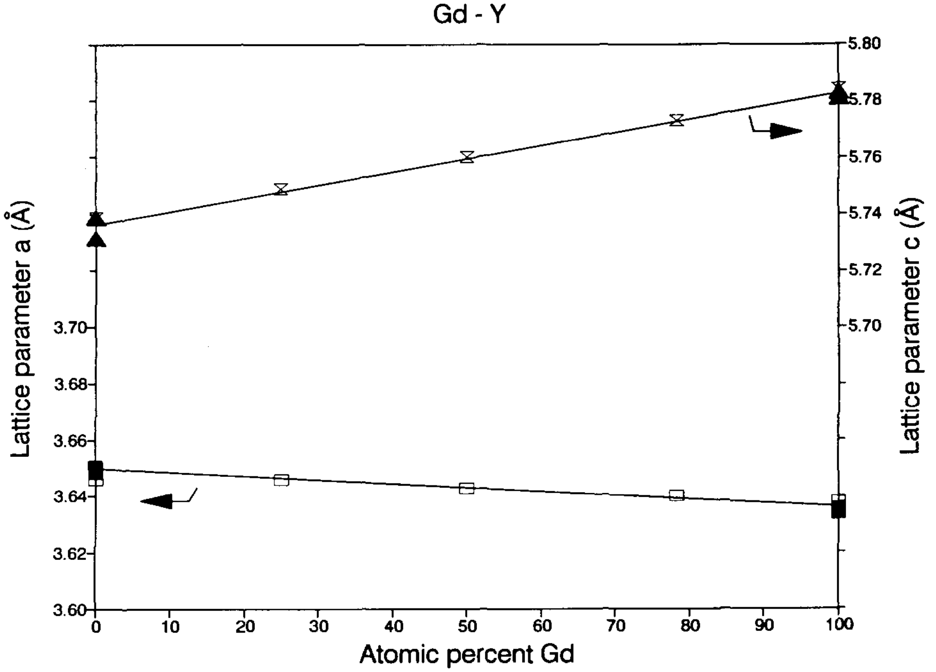

Fig. 4. Lattice parameters of Gd–Y alloys (open symbols) compared with the literature end members [19, 20] (solid symbols).

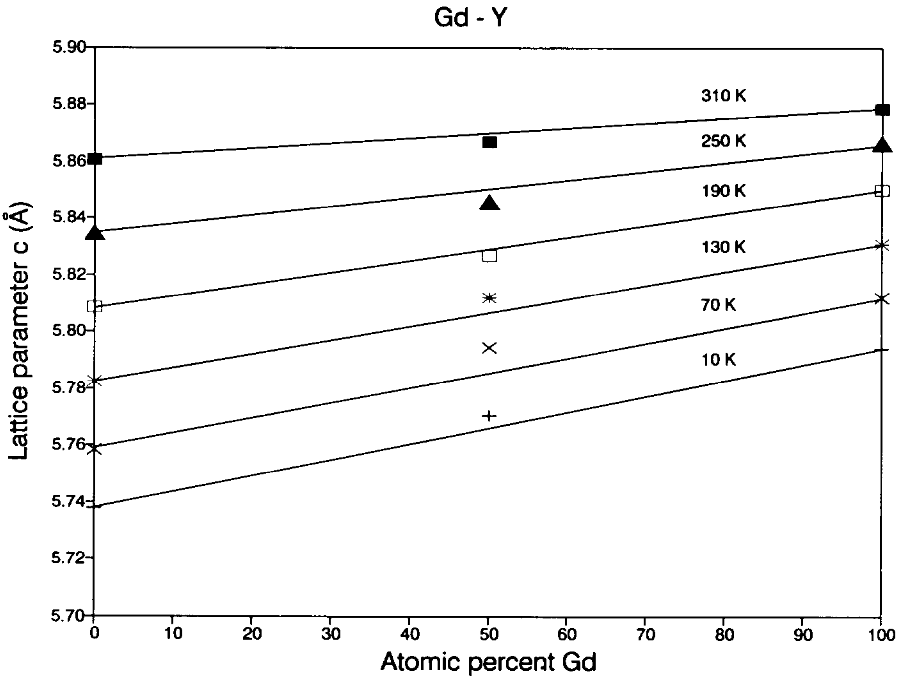

Fig. 5. Compositional dependence of the lattice parameter *c* at different temperatures. The lattice parameters are scaled to each other by adding 0.02 Å, starting from the data at 10 K.

volumes at room temperature of Gd and Y are practically the same ($\Delta V/V \cong 0.05\%$).

We have performed several structural measurements with respect to temperature for Gd, $Gd_{0.5}Y_{0.5}$ and Y. A thermal behavior was obtained from the lattice parameters and smoothed by best fit, taking into account the accepted values of the end members. Thus it was possible to obtain the trends of the lattice parameters at different constant temperatures as functions of the alloy composition. The *a* lattice parameter behaves linearly with composition at all temperatures, while the *c* lattice parameter seems to deviate from linearity at temperatures below T_C (Fig. 5).

The temperature dependence of the lattice parameters of the magnetic alloys is fairly complex due to the magnetic transition. The thermal behavior of the lattice volume of yttrium was determined very accurately and could be fitted by the simple cubic relation

$$V(\text{Å}^3) = 5.054 \times 10^{-4}T + 66.080 + 3.102 \times 10^{-6}T^2 - 1.835 \times 10^{-9}T^3$$

from which the coefficient of volume thermal expansion 3α can be deduced from the thermodynamic relation $3\alpha = 1/V(\partial V/\partial T)_p$. The value of $28 \times 10^{-6}\,K^{-1}$ can be favorably compared with the literature value [20] of $31.8 \times 10^{-6}\,K^{-1}$. The Grüneisen parameters $\gamma = 3\alpha K_T/C_V$, where K_T is the isothermal bulk modulus and C_V is the specific heat at constant volume, can be calculated by using our results for 3α and V and the literature data for C_V [22] and K_T [23].

CONCLUSIONS

The presence of extended solid solubility in the Gd–Y phase diagram made it possible to study the magnetic phase transition of Gd. A number of physical characteristics of these alloys were identified.

The dilution of the magnetic rare earth Gd is accompanied by a linear lowering of the temperature of magnetic ordering. Similarly, a linear dependence of the molar volume with respect to the concentration of Gd at room temperature was found.

The magnetic transformation studied in the alloys Gd_xY_{1-x} was found to be second order (Fig. 1).

The dT_C/dP values can be calculated from the thermodynamics using Ehrenfast's equation for constant concentration

$$dT_C/dP = T_C V(\Delta\alpha/\Delta C_p) = \Delta\beta/\Delta\alpha$$

connecting the thermal expansion, heat capacity and pressure measurements. The parameters $\Delta\alpha$, $\Delta\beta$ and ΔC_p are the anomalies in the thermal expansion, compressibility and heat capacity at constant pressure at the transition temperature, respectively.

When different concentrations are involved, two other equations are applicable. The first is

$$\Delta(\partial S/\partial x) = -(\partial T_C/\partial x)(\Delta C_p/T_C)$$

If $\Delta C_p/T_C$ is considered practically constant for the observed alloys, for the entropic jump this gives $\Delta(\partial S/\partial x) \cong 17\ \mathrm{J\ mol^{-1}K^{-1}}$.

The second equation is

$$(\partial T_C/\partial P)\Delta(\partial S/\partial x) = \Delta(\partial V/\partial x)$$

This suggests that a discontinuity is to be expected in the derivative of the molar volume versus Gd concentration dependence at temperatures lower than T_C; in other words, the presence of a second-order phase transition leads to a deviation from the expected linear behavior in lattice parameters below T_C. This is confirmed in Fig. 5.

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