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Observation of a continuous phase transformation in $LaNi_5$–D

E.MacA. Gray[a,*], E.H Kisi[b], R.I. Smith[c]

[a]*School of Science, Griffith University, Brisbane 4111, Australia*
[b]*Department of Mechanical Engineering, University of Newcastle, Callaghan 2308, Australia*
[c]*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK*

Abstract

We have used high-resolution neutron powder diffraction to study the phase diagram of $LaNi_5D_x$ at temperatures up to 100°C. Diffraction patterns were recorded during consecutive absorption–desorption cycles at 100, 65 and 30°C. In a sequence of four patterns taken during desorption at 100°C, we observed the β phase transforming continuously to the γ phase: the first pattern was 100% β phase; the fourth one was 100% γ phase; the second and third patterns were also single phase, but had lattice parameters intermediate between those of the β and γ phases. The succeeding $\gamma \rightarrow \alpha$ transformation remained discontinuous, that is, co-existing γ and α phases were observed via two diffraction patterns with distinct lattice parameters. The following absorption–desorption cycle was conducted at 65°C. Again, the $\beta \rightarrow \gamma$ transformation was continuous. In the final cycle, conducted at 30°C, the $\beta \rightarrow \gamma$ transformation was discontinuous. Hence, there appears to be a thermodynamic critical point of the $\beta + \gamma$ phase 'equilibrium' in this sample, between 65 and 30°C. This is the first such observation in the $LaNi_5$–H/D system. The pressure–composition isotherms resemble those of a $Mm(NiCoMnAl)_5$ battery alloy in that a considerable fraction of the D capacity appears to lie within the concentration range of the 'hydride phase'.

Keywords: Metal hydrogen; Neutron diffraction; Phase transformation

1. Introduction

Although a phase diagram of surprising richness has been proposed for the $LaNi_5$–H system [1], the existence of only one phase additional to the solid solution (α: $LaNi_5H_x$, $x<0.5$ approx.) and concentrated hydride (β: $LaNi_5H_x$, $x>6$ approx.) phases has been confirmed by diffraction. This is the γ phase ($LaNi_5H_3$ approx.), originally referred to as the β phase by its discoverers [2]. Its structure has been investigated by powder diffraction [2–6] and the signature in the pressure–composition phase diagram, a splitting of the desorption and, ultimately, absorption isotherms, has been observed in other experiments [7–10]. The structure is at least similar to that of the α phase (*P6/mmm*), although the anisotropically broadened diffraction profile made authoritative structure determination difficult [6]. It appears that the temperature or rapidity of appearance, or both, of the γ phase is affected by the level of impurity in the gas stream [8].

The present report concerns a particular aspect of a more comprehensive investigation of the properties of the γ phase, especially its structure, relationship to the α and β phases and reliance on impurities, which will be published in due course [11]. This investigation was carried out under circumstances thought to promise more authoritative results and conclusions than the body of somewhat contradictory work so far accumulated in the literature. In particular, we used a powder diffractometer with very high resolution, viz. HRPD at ISIS in back-scattering mode; a simple solution to modelling the anisotropically-broadened diffraction profiles was available [12]; complete absorption–desorption isotherms were conducted in situ, using an active pressure controller to limit the spatial inhomogeneity of phase proportions that we believe has detracted from previous studies, as demonstrated in [13]; the thermal history of the sample and its exposure to impurities were controlled.

2. Experimental details

A single sample was used for the entire study on which we report in part here, 36 g of $LaNi_{4.92}$ (NUCOR Research Chemicals alloy #1241). The sample holder was constructed of die-extruded aluminium alloy (6061 T6) to a working specification of 5 MPa gas pressure at 125°C. The

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*Corresponding author.

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orientation of the Al crystallites in the manufacturing process means that $(111)_{\mathrm{Al}}$ is very small and so interferes little with the diffraction pattern of the sample. Temperature control was by Peltier-effect heat pumps at the top and bottom of the cell, which was shrouded in quartz wool to ensure a uniform temperature distribution in the sample without contributing significantly to the diffraction background. HRPD at ISIS was operated in backscattering mode to give the highest possible resolution of the anisotropic peak broadening, which ranges from moderate (owing to roughly isotropic Lorentzian domain-size broadening) in (00*l*) directions to extreme in the (*hk*0) directions, owing, we believe, to the presence of a very high density of dislocations [14]. In this experiment, 51 diffraction patterns were recorded during consecutive absorption–desorption cycles at 100, 65 and 30°C, over a period of four days, using deuterium (to avoid the incoherent scattering of hydrogen) of purity 99.999%. The lattice parameters of the observed phases were measured using the ISIS CCSL-based Rietveld refinement code, modified to account for the anisotropic peak broadening.

The sample had previously executed 75 absorption–desorption cycles at temperatures around 100°C. Hence the occurrence of the γ phase in both the absorption and desorption isotherms was well established. The deuterium content was set in situ with a manometric hydrogenator able to operate in both isochoral and isobaric modes by virtue of a needle valve positioned using a computer control algorithm and a second pressure transducer monitoring the sample cell. The purpose of the isobaric capability is to minimise the spatial inhomogeneity in the phase proportions caused by the interaction of heat transfer and hysteresis in thick samples when the gas pressure falls during absorption or rises during desorption [13,15]. Each absorption–desorption cycle was executed stepwise by preparing an aliquot of gas in the reference volume and admitting it to the sample cell, determining the change in the deuterium-to-metal atomic ratio (D/M) by the change in system pressure. The step was isochoral or isobaric according to whether gas flowed to or from the sample cell under the constraint of constant system volume or constant pressure over the sample. Steps preceding a diffraction measurement were executed in quasi-isobaric fashion, limiting the pressure rise or fall in the sample chamber to 50 kPa (compared to hundreds of kPa in the reference volume), a compromise between sample homogeneity, slow isobaric kinetics and available neutron beam time.

3. Results

In Fig. 1 the absorption–desorption isotherm recorded during cycle 76 is shown. The values of D/M are relative to an arbitrary zero set by the amount of trapped (i.e., unrecoverable without heating and pumping) deuterium. The isotherms have been considerably shortened by cycling. As detailed elsewhere [16], gravimetric measurements with an absolute zero of H content demonstrate that the total H capacity in fact diminishes very little, and that the pure α-phase region may be displaced to a high value of H/M, up to 0.3 in our experience, the lower values of H/M belonging to the trapping region.

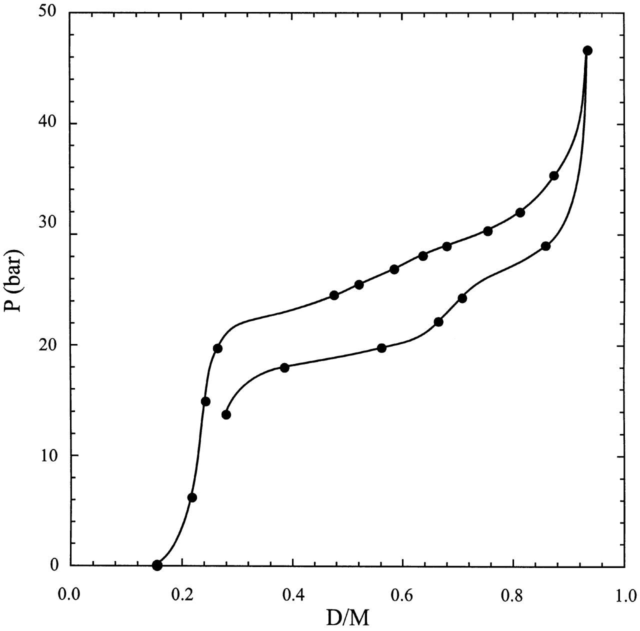

Fig. 1. Pressure composition isotherms for $LaNi_5$–D_x recorded during the neutron diffraction experiment. This report refers to the desorption isotherm. Note the shape of the desorption isotherm above D/M=0.5, which little resembles a two-phase plateau.

Fig. 2 shows a sequence of diffraction patterns taken during desorption at 100°C in cycle 76. The time sequence runs from bottom to top. The values of D/M shown at the right-hand side were determined by correcting the manometric values from Fig. 1 using the model of trapping just described. The assumptions were that (i) the value of D/M in the pure β phase is 0.93 as measured manometrically and (ii) the γ–α phase boundary occurs at D/M=0.08. These values are of course arbitrary to a degree, but serve to give a less distorted picture than the raw value of D/M ignoring the trapped D. This kind of correction is in keeping with the use of a diffraction technique, to which the trapped D appears to be effectively invisible.

The first pattern is unequivocally 100% β phase, the fourth one unequivocally 100% γ phase. The third pattern resembles that of the γ phase, but with larger lattice parameters. The second pattern is also single phase, but has lattice parameters intermediate between β and γ and definitely belonging to neither phase. Either we have traversed one or more extremely narrow two-phase regions and discovered a new phase of this system, or a continuous phase transformation has taken place from the β to the γ phase. There being no evidence to support the first proposition, we strongly favour the second. The $\gamma \rightarrow \alpha$ transformation (upper patterns in Fig. 2) remains dis-

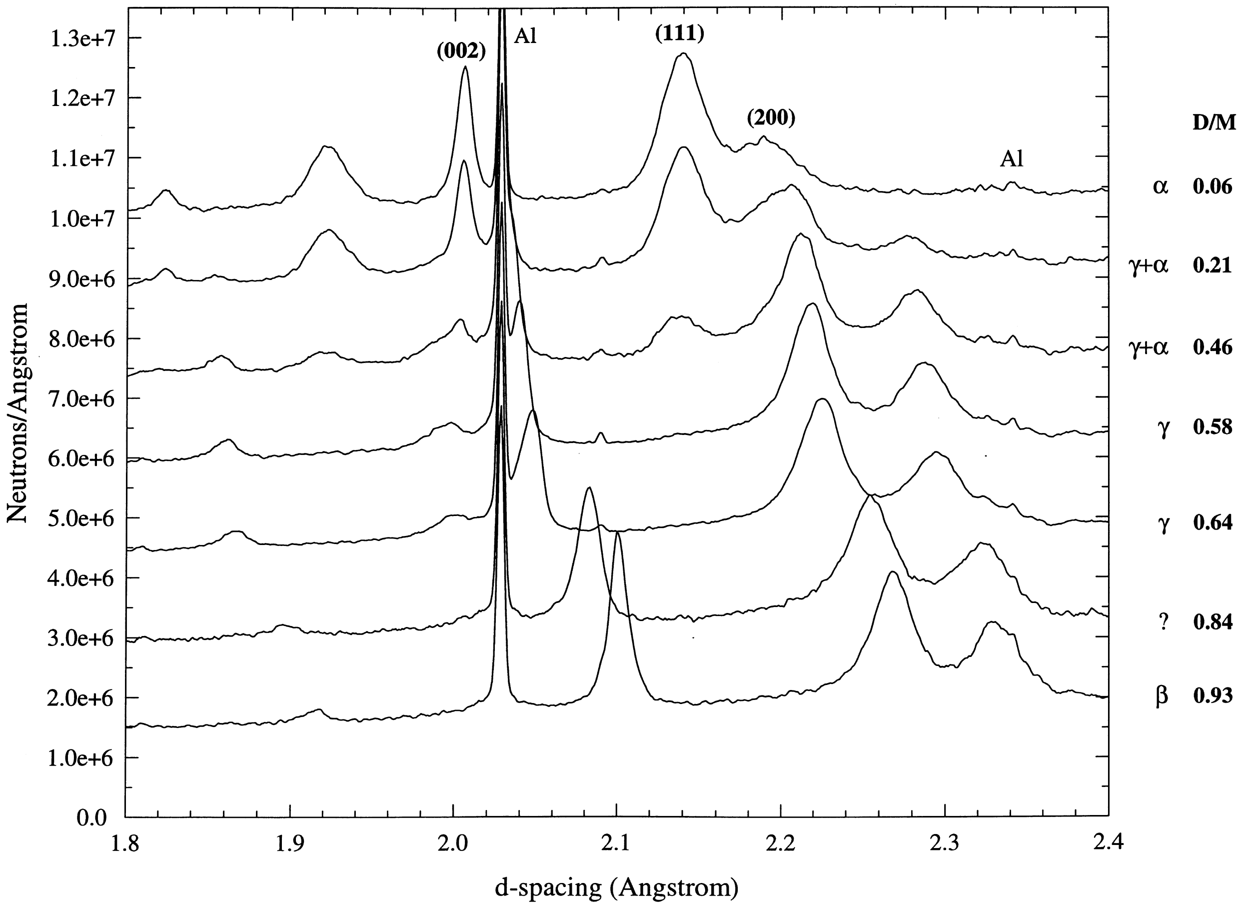

Fig. 2. High-resolution neutron diffraction patterns recorded while the 100°C desorption isotherm of Fig. 1 was executed. The time sequence reads from bottom to top, i.e., beginning with pure β phase and ending with pure α phase. The D/M scale to the right is approximately corrected for the existence of a wide region of trapping, on the assumption that the trapped D atoms are in 'non-crystallographic' sites and therefore do not contribute to the diffraction pattern except in the isotropic background. Note the continuous evolution of the β phase into the γ phase.

continuous, that is, appropriate proportions of co-existing γ and α phases were observed via two diffraction patterns with distinct lattice parameters, in sharp contrast to the first half of the isotherm.

Fig. 3 summarises the behaviour of the lattice parameters during desorption 76 at 100°C. Also shown for comparison are the lattice parameters of the pure α, β and γ phases, measured using the same sample earlier in its life, before the continuous transformation developed. The D/M scale is the same as in Fig. 2, i.e., approximately corrected for the existence of the trapping region. The lattice parameters behave just as expected. That is, during the course of the continuous phase transformation, they change smoothly from those expected for the β phase to those expected of the γ phase, as observed in the usual discontinuous transformation. In contrast, the lattice parameters of both the γ and α phases change relatively little in the two-phase region below D/M=0.5.

The next cycle (77) was conducted at 65°C. Again, the β→γ transformation was continuous. In the final cycle (78), conducted at 30°C, the β→γ transformation was discontinuous, as shown in Fig. 4. Once again, the D/M scale has been corrected for trapping by taking the measured value of 1.07 in the pure β phase to be correct and assuming that the γ–α phase boundary occurs at 0.08.

4. Discussion

In an unbroken sequence of measurements on the same sample on the same diffractometer, we have found the β phase, the γ phase, the β and γ phases in coexistence, and an intermediate phase which in a sense interpolates between the β and γ phases. Given that the continuous transformation at 100°C becomes discontinuous at 30°C on the time scale of our experiment (many hours to complete a desorption isotherm), the simplest inference is that a thermodynamic critical point of the β+γ phase 'equilibrium' occurs in this sample, between 65 and 30°C. This is the first such observation in the $LaNi_5$–H/D system.

Supporting evidence comes from measurements of the peak breadths. Fig. 2 demonstrates that the ratio of breadths for the (002) and (200) peaks is different between the β and γ phases, the γ-phase pattern being more

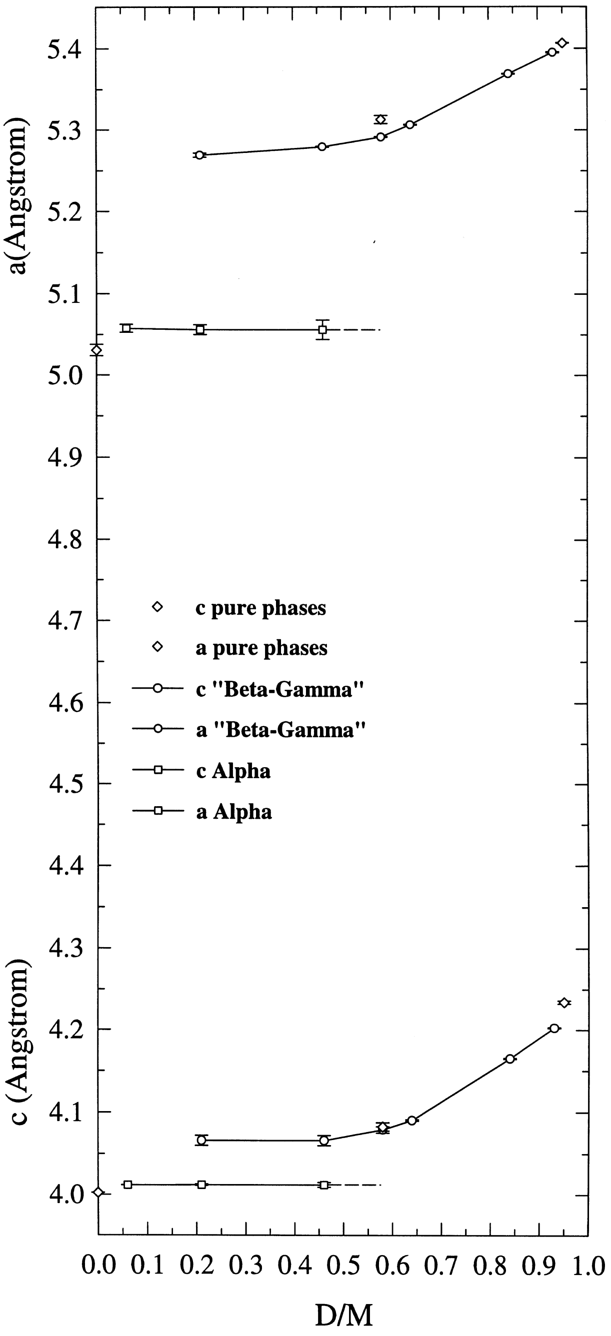

Fig. 3. Lattice parameters of the α and 'β–γ' phases derived from the diffraction patterns in Fig. 2. Notice the continuous change of *a* and *c* from values close to those for pure β to values close to those for pure γ, as previously measured in the same sample prior to the development of the continuous transformation. As expected, the lattice parameters of the γ and α phases change relatively little in the γ+α two-phase region.

isotropic. Measurements of the FWHMs of these peaks showed a smooth evolution of the above breadth ratio from β-like to γ-like as the transformation proceeded at 100°C.

The appearance and disappearance of the γ phase (i.e., $LaNi_5H_{\approx 3}$) depends on several factors, including measurement temperature, thermal history, exposure to gas impurities and the microstructure of the host metal [8–10]. After the appearance of the γ phase (pure-phase points in Fig. 3), then cycling continued at 100°C with 99.999% D_2 until cycle 76. It therefore seems that the continued application of the same conditions that lead to γ formation in the first place eventually affected the β–γ phase diagram in the way observed here. That this sample has probably been cycled more than any other on which a comprehensive in-situ diffraction experiment was performed appears to account for the absence of previous observations of the continuous transformation.

It is interesting to compare the behaviour of this sample with that of the $Mm–(NiCoMnAl)_5$ alloys used to fabricate Ni–metal–H batteries. It has been observed that, in the battery alloys, a significant proportion of the total H capacity is contained in the single-phase concentrated hydride (e.g. [17]), which we would naturally refer to as the β phase, whose isotherm spans a wide range of H/M for a modest increase in pressure. This is very much the behaviour of our sample, except that there is no doubt that the γ phase exists and that transformations occur between it and the β phase. We speculate that an in-situ diffraction study of the battery alloy throughout the entire H composition range will reveal the existence of a phase best described as γ.

We are unable to say whether the occurrence of the continuous transformation depends absolutely on the exposure of the sample to impurities or whether the regime under which our sample was cycled serves only to hasten its onset. Experiments at considerably higher temperatures are expected to clarify this matter.

5. Conclusions

Owing to the combined effects of absorption–desorption cycling at 100°C and exposure to impurities in the deuterium gas, $LaNi_5–D_x$ was found to exhibit the γ and β phases in coexistence at low temperatures. At 65°C and 100°C, the β→γ transformation in desorption was continuous. That is, the lattice parameters and the peak breadths characteristic of the β phase were smoothly transformed into those characteristic of the γ phase, in the absence of any other detected phase. This transformation traversed about half the D capacity of the sample, in which it resembles the behaviour of a Ni–metal–H battery alloy. There appears to be a thermodynamic critical temperature for the β+γ system in our sample in desorption between 30 and 65°C.

Acknowledgements

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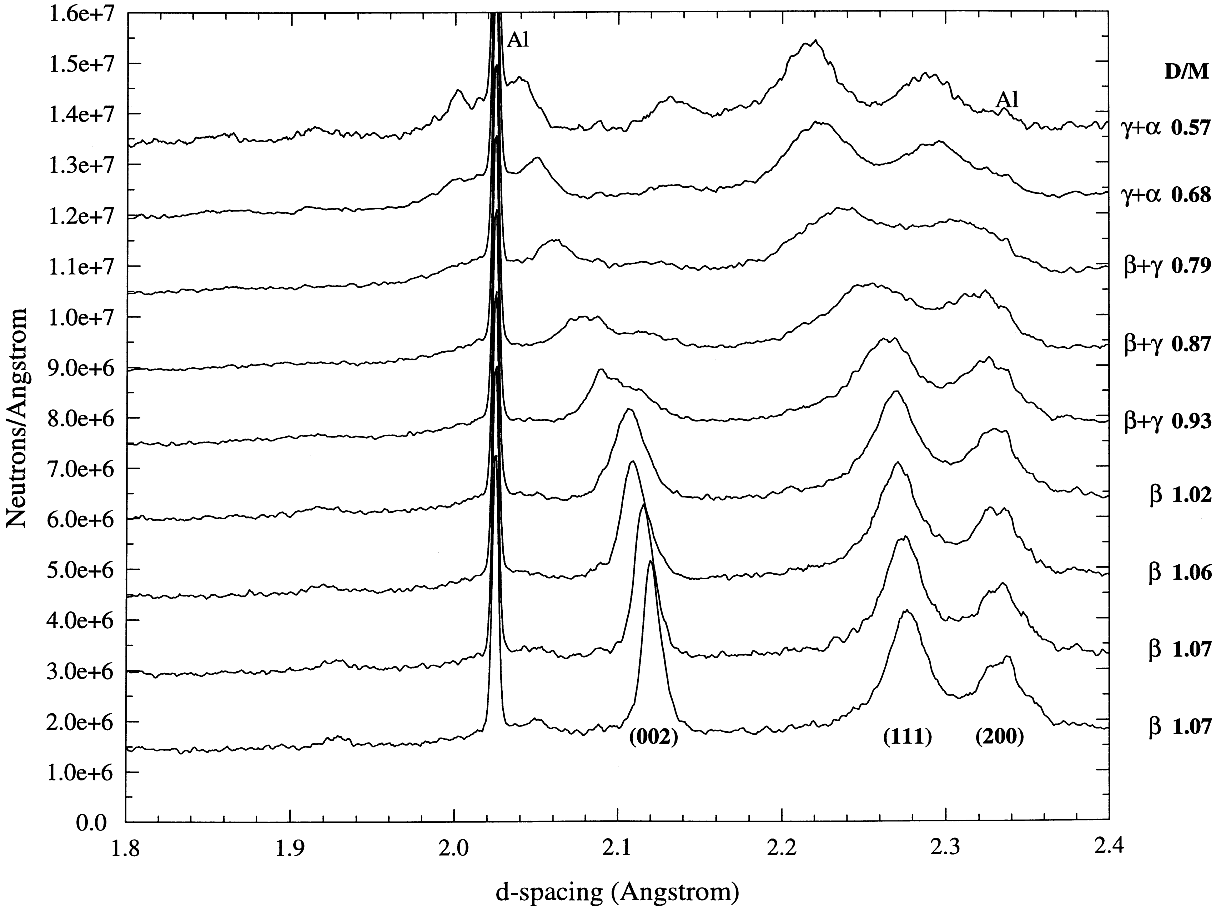

Fig. 4. Diffraction patterns recorded while desorbing at 30°C. The time sequence reads from bottom to top, i.e., beginning with pure β phase. The D/M scale to the right is approximately corrected for trapping, as explained in the text. Note the splitting of the (002) beginning at D/M=0.93.

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