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Crystal Structure of β-$CaNi_5D_{0.77}$ by Rietveld Analysis of Neutron Powder-Diffraction Data

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β-$CaNi_5D_{0.77}$ is orthorhombic (a = 8.6033(13) b = 5.0810(9) c = 7.8557(15) Å, *Pmcm*, Z = 4, D_x = 6.48 g cm^{-3}, V = 343.4 Å^3, FW = 1339.8 amu. Rietveld analysis of a neutron powder-diffraction pattern shows that D atoms occupy the centers of [Ni_4Ca_2] square dipyramids ("octahedra") linked through the Ca atoms at opposite apices and forming chains. About 80% of the deuterium atoms occupy fairly regular sites (D–Ni = 1.53, 1.80, 1.86, 1.86 Å; D–Ca = 2.42, 2.45 Å). The remaining 20% occupy very distorted sites (D–Ni = 1.21, 1.38, 2.07, 2.07 Å; D–Ca = 2.54, 2.60 Å). The average D–D distance in a chain is 4.3 Å. © 1985 Academic Press, Inc.

Introduction

$LaNi_5$ and $CaNi_5$ are both potential hydrogen-storage materials but, whereas the $LaNi_5$–H system has been very extensively studied, the $CaNi_5$–H system has received much less attention. The $CaNi_5$–H system has four phases (α: $CaNi_5H_{\sim0.1}$; β: $CaNi5H_{\sim1}$; γ: $CaNi_5H_{\sim5}$, and δ: $CaNi_5H_{\sim6}$) (Ensslen *et al.* (*1*), Sandrock *et al.* (*2*), Yoshikawa and Matsumoto, (*3*), Cho *et al.* (*4*), Gainsford *et al.* (*5*)). The two phases of the $LaNi_5$–H system are analogous to the α and δ phases of $CaNi_5$–H, and consequently a study of the structures of the β and γ phases is potentially of great interest in identifying possible intermediate stages in the hydriding of $LaNi_5$ which is a paradigm of the widely studied AB_5 compounds. In addition, in view of the continuing controversy on the correct structure and space group of $LaNi_5H_6$ and related compounds (*6*), structural studies of α, β, γ, and δ phases of $CaNi_5$–H could be very useful in helping to resolve these ambiguities. The present paper reports a structure for a β-$CaNi_5D_{\sim1}$ sample in the low pressure region.

Experimental

The material for this study was prepared from a 100-g sample of a 1-kg batch made by Ergenics Ltd. by induction melting of reagent-grade Ca and Ni. To ensure homogeneity, a 15-g fraction of this material was annealed in a stainless steel container under one atmosphere of argon at 1175 K for 1 week. All sample handling was carried out in an argon-filled drybox. The material was

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characterized by X-ray diffraction, DC emission spectroscopy, and chemical analysis (XRF for Ni, wet chemical analysis for Ca) to be 99.7% pure with a composition of 95.1% $CaNi_5$ and 4.9% Ni. The 7.600-g neutron-diffraction sample was prepared from this material and enclosed in a vanadium tube of 7.5-mm outer diameter with 0.25-mm wall thickness. The sample was deuterided by reaction with deuterium gas using the gas titration equipment and techniques described elsewhere (*7*), the final deuterium content at the final deuterium pressure (0.0636 atm) being calculated from the gas titration results. The final composition was [$CaNi_5D_{0.776}$ + $Ni_{0.31}$], the deuterium content being accurate to ±0.5%.

The powder-diffraction profile was measured on the L3 triple-axis spectrometer, operated in a two-axis mode, at the NRU reactor, Chalk River, Ontario. The monochromator was Ge(331) and Sollerslit collimators with horizontal divergences of 0.33 and 0.36° were placed before and after the sample, respectively. The spectrometer was calibrated using germanium powder as a standard and the neutron wavelength was determined to be 1.98904(5) Å. Initial values for the lineshape parameters were also taken from this calibration. The diffraction profile was measured at 298 K between 8 and 108° with the detector moving in 0.1° steps of the scattering angle. The counting time was ≈4 min/point. The homogeneity of the powder specimen was checked by measuring the intensity of a Debye–Scherrer peak as a function of specimen orientation about the cylindrical axis. The peak intensity was measured at intervals of 10° in specimen orientation and these intensities were distributed about their mean with a standard deviation of 1%. The sample was rotated continuously throughout the experiment to minimize any residual errors due to inhomogeneity. The transmission of the sample was measured to be 61%.

Structure Determination

A preliminary inspection had shown that the space group *Im2m*, used by Gainsford *et al.* (*5*) and Calvert *et al.* (*8*) for the metal atoms, could not index all the peaks in the neutron pattern of the deuterated compound, but that all peaks could be indexed by a primitive orthorhombic cell of the same dimensions. The space group *Pm2m* was chosen initially for further refinement.

Integrated intensities were obtained by a Rietveld analysis of the pattern. The metal atom coordinates of Calvert *et al.* (*8*), converted to *Pm2m*, were assumed and held fixed, and an overall isotropic thermal parameter $B = 0.5$ Å^2 was held fixed; the scale factor, unit cell parameters, and profile parameters were refined. There were 86 observed reflections ($I > 2\sigma$) out of a possible 142; 23 of the observed reflections were specific to a primitive cell. The 142 intensities, and their standard deviations were entered manually into the NRCC-PDP8 structure package (Gabe (*9*)) and a Fourier map, phased with the metal atom coordinates of Calvert *et al.* (*8*) indicated two probable sites for D atoms. A series of block-diagonal least-squares cycles was carried out in which, in order to obtain convergence, observed as well as unobserved reflections were refined with unit weights. Difference syntheses were computed at the end of each set of refinements to confirm the D atom sites. Various sets of starting parameters were used to reduce the chances of refining to a false minimum. In this way a consistent set of Ni parameters was obtained. These Ni atom coordinates, six prospective D atom sites, and one set of Ca positions were now used as starting parameters in a normal Rietveld refinement of the full neutron pattern. The sections of the pattern under the 111 and 200 peaks of Ni were omitted but the Ni 220 peak which overlaps both the 620 and 141 peaks of the β phase was retained.

The Rietveld refinements were carried out in several stages. First, the positional parameters of Ca, Ni, and D and the occupancies of the D sites were varied with B fixed at 0.5 Å^2 for Ca and Ni, and at 1.0 Å^2 for D. The refinement converged to give R factors R_1, R_2, R_3 = 5.7, 9.1, 9.2%, respectively, where

$$R_1 = \Sigma_i |I_i(\text{obs}) - I_i(\text{calc})| / \Sigma_i I(\text{obs})$$

$$R_2 = \Sigma_i |y_i(\text{obs}) - y_i(\text{calc})| / \Sigma_i y_i(\text{obs})$$

$$R_3 = [\Sigma_i w_i \{y_i(\text{obs}) - y_i(\text{calc})\}^2 / \Sigma_i w_i \{y_i(\text{obs})\}^2]^{1/2}$$

where I_i(obs), I_i(calc) are the observed, calculated integrated intensities y_i(obs) and y_i(calc) are the intensities observed, calculated at scattering angle $2\theta_i$, and w_i is the weight assigned to the observed intensity.

The occupancies for four of the six D sites were found to be effectively zero, so these sites were omitted from later refinements. In the next refinement stage, only the y coordinates of the Ca atoms and the occupancies of the two D sites were allowed to vary; this gave R_1, R_2, R_3 = 6.9, 9.6, 9.9%, respectively, with the sum of the occupancies of the D sites equal to 0.76. Analysis of this *Pm*2*m* structure revealed the possible presence of a *c* glide plane perpendicular to *b*, suggesting the data might be interpreted in terms of the higher-symmetry space group *Pmcm*. Consequently a refinement with this space group was made starting with the *Pm*2*m* parameters. This refinement led to R_1, R_2, R_3 = 6.86, 9.43, 9.79%. The satisfactory difference plot (Fig. 1) which shows that the data is consistent with the **c** glide plane absences, and the similar structures and residuals obtained with the two space groups show that the higher-symmetry space group *Pmcm* should be preferred. Overlooking an inversion center leads to a singular matrix (see Schomaker and Marsh (*10*)), and is the likely explanation for the convergence problems with the acentric space group *Pm*2*m*, which disappeared when the centric group *Pmcm* was used. The expected residual, from statistics, was 4.31%. However, in view of the fact that the thermal motion parameters were not refined and that the sample is known to contain two phases, we consider the present 6.9% residual to be acceptable. The final atomic parameters are given in Table I, the neutron data and difference plot in Fig. 1, and the relevant interatomic distances in Table II.

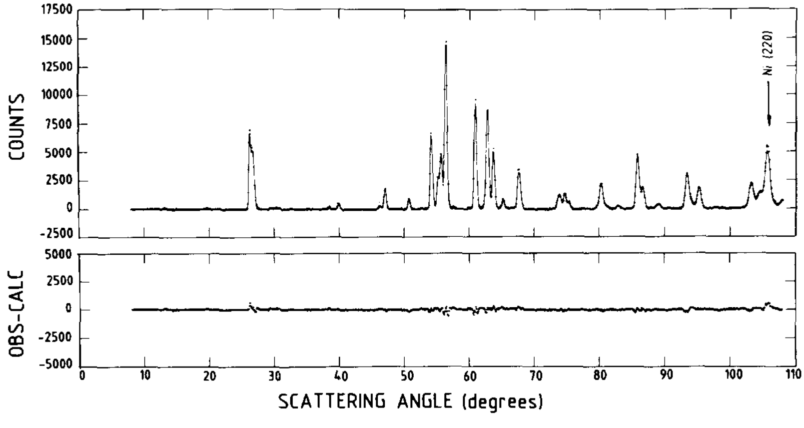

FIG. 1. Comparison of the observed and calculated neutron-diffraction profiles of β-CaNi$_5$D$_{0.77}$. (a) The crosses show the experimental data and the line through them corresponds to the calculated intensity. (b) Plot of the difference y_i(obs) − y_i(calc).

TABLE I

ATOMIC PARAMETERS FOR $CaNi_5D_{0.77}$ IN SPACE GROUP *Pmcm*

	Wyckoff symbol	Site symmetry	Occupancy factor	*X*	*Y*	*Z*	*B* (Å²) (fixed)
Ca_1	2*f*	*m*2*m*	1	$\frac{1}{2}$	0.499(4)	$\frac{1}{4}$	0.5
Ca_2	2*e*	*m*2*m*	1	0	0.052(4)	$\frac{1}{4}$	0.5
Ni_1	4*k*	..*m*	1	0.340(2)	0.039(3)	$\frac{3}{4}$	0.5
Ni_2	4*k*	..*m*	1	0.835(2)	0.547(3)	$\frac{1}{4}$	0.5
Ni_3	2*c*	2/*m*..	1	0	$\frac{1}{2}$	$\frac{1}{2}$	0.5
Ni_4	2*b*	2/*m*..	1	$\frac{1}{2}$	0	0	0.5
Ni_5	8*l*	1	1	0.250(3)	0.253(3)	0.0133(5)	0.5
D_1	4*k*	..*m*	0.640(10)	0.247(4)	0.721(5)	$\frac{3}{4}$	1.0
D_2	4*k*	..*m*	0.116(10)	0.25(3)	0.77(4)	$\frac{1}{4}$	1.0

Note. Coordinates of equivalent positions in *Pmcm*: $+/-(x,y,z;\ -x,y,z;\ x,\ -y,\ \frac{1}{2}+z;\ -x,\ -y,\ \frac{1}{2}+z)$. Cell parameters: $a = 8.6033(13)$, $b = 5.0810(9)$, $c = 7.8557(15)$ Å.

Discussion

The arrangement of metal atoms in β-$CaNi_5D_{0.77}$ can be described as a distortion of the hexagonal $CaCu_5$-type structure of α-$CaNi_5$: the preservation of the C-centering of the orthohexagonal cell combined with the doubling of the period along z due to opposite shifts along y of the hexagons of Ni at $z = \frac{1}{4}$ and $\frac{3}{4}$ (see Fig. 2) permitted the description of the Ca and Ni atomic positions in space group *Im*2*m* by Gainsford *et al.* (*5*). The present neutron diffraction study confirms the structural conclusions by Gainsford *et al.* and shows that the deuterium atoms (which are practically invisible with X-rays) occupy two of the hexagonal 3(*f*) sites, thus leading to the primitive orthorhombic lattice.

TABLE II

SELECTED INTERATOMIC DISTANCES (Å)

D_1–Ca_1	2.45	D_2–Ca_1	2.54
–Ca_2	2.42	–Ca_2	2.60
–Ni_1	1.80	–Ni_1	1.21
–Ni_2	1.53	–Ni_2	1.38
–Ni_5	1.86 (×2)	–Ni_5	2.07 (×2)
Ca–Ca	3.93–3.96		
Ca–Ni	2.89–3.42		
Ni–Ni	2.41–2.84		

The deuterium atoms D_1 and D_2 occupy two $[Ni_4Ca_2]$ square-dipyramidal sites ("octahedral sites"), equivalent in the hexagonal structure but very different here due to the orthorhombic distortion of the network of metal atoms. The occupancies of the two sites are very different, approximately 80% of the available deuterium going in the D_1 site which is not very distorted (D–Ni = 1.53, 1.80, 1.86, 1.86 (3) Å; D–Ca = 2.42, 2.45(4) Å), and the remaining 20% in the D_2 site for which the Ni "square" has a very pronounced diamond shape (D–Ni = 1.21, 1.38, 2.07, 2.07; D–Ca = 2.54, 2.60 Å). It is to be noted that the occupancy factor of the D_2 site is only 0.12(1), and that the sum of the occupancies of the D_1 and D_2 sites is 0.76(2), very close to the value found by chemical analysis. The geometry of the D_2 site observed here is therefore that of an essentially unoccupied site. It is quite possible that the D_1 site is the only occupied site with occupancy equal to the sum of the refined occupancies of D_1 and D_2, and that coherent [010] twinning (which could also be described as coherent domains) gives rise to the present distribution of intensities

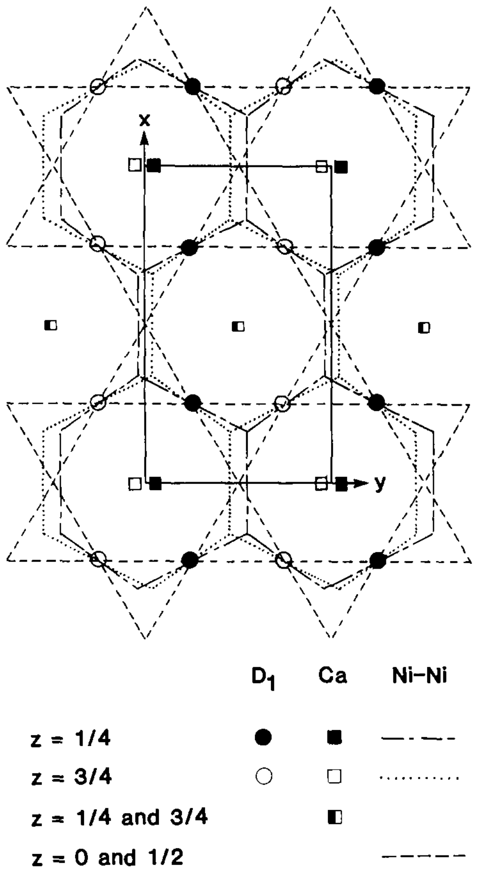

FIG. 2. The (001) projection of β-$CaNi_5D_{0.77}$. Hexagons composed of Ni_1 and Ni_2 share edges to form 6^3 nets (Frank and Kasper (*12*)) in the mirror planes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. The hexagon composed of 4 Ni_1 and 2 Ni_2 is centered by Ca_1, while Ca_2 centers 2 Ni_1 + 4 Ni_2. The Ni_3, Ni_4, and Ni_5 atoms at $z = 0$ form 3636 kagomé nets (Frank and Kasper (*16*)).

which is interpreted here as two occupied sites. The Ca apices at $x = 0$ and $\frac{1}{2}$ are shared, thus giving rise to infinite chains of tilted "octahedra" as illustrated in Fig. 3. The chains of D_1 sites and D_2 sites run parallel to one another and share edges. The D–D distances in both chains are 4.3 Å. The volume increase per D atom is 2.2 Å^3 (equivalent to 2.8%).

Although D atoms are often observed to occupy tetrahedral sites, octahedral coordination has been reported for example in HoD_3 by Mannsmann and Wallace (*11*). More recently, Fisher *et al.* (*12*) report that D atoms occupy the octahedral 3(*f*) sites of *P6*/*mmm* in $LaNi_5D_{0.25}$ and Westlake (*13*) has recently discussed the occupation of octahedral and hexagonal sites in the phases of the Fe–Ti–H system. Yoshikawa *et al.* (*14*) suggested, because the α and β phases (the latter designated as α' by them) of $CaNi_5 + H_2$ expand only in the basal plane and not along the *c* axis, that the hydrogen (or deuterium) atoms probably occupy octahedral sites in the basal planes in both these phases. Based upon the indirect evidence of a thermodynamic model analysis of pressure–composition isotherm data, Yagisawa *et al.* (*15*) have suggested that the β phase (again denoted α' by them) has

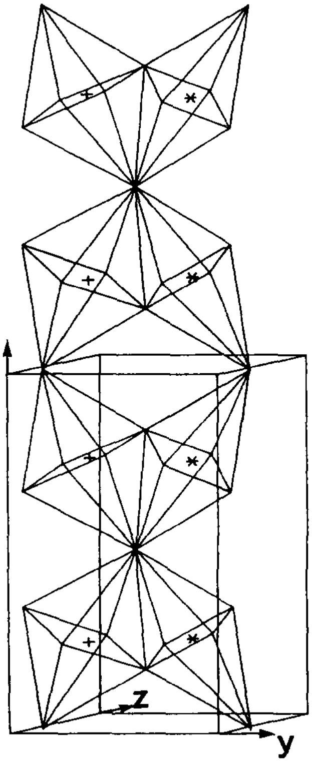

FIG. 3. The chains of Ni_4Ca_2 square dipyramids ("octahedra") which are occupied by the D1 (crosses) and D2 (asterisks) atoms in β-$CaNi_5D_{0.77}$. Symmetry-related chains are omitted for clarity.

three available hydrogen (or deuterium) sites, one of which is a high occupancy site. The present structural determination for the composition $CaNi_5D_{0.776}$, which is near the low pressure limit of the β phase's existence range, shows that at most two sites have significant occupancies (> 0.05). Further discussion of this structure will be deferred until those of the γ and δ phases have been elucidated.

Acknowledgments

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