Determination of the Deuterium Position in DNb_6I_{11}†

Arndt Simon* and Friederike Stollmaier
Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-7000 Stuttgart 80, West Germany
David Gregson and Hartmut Fuess
Institut für Kristallographie, Universität Frankfurt, Senckenberg Anlage 30, 6000 Frankfurt 1, West Germany

Neutron diffraction data from a sample of composition $D_{0.45}Nb_6I_{11}$ were collected on a four-circle diffractometer at 120 K (low-temperature phase, *P*2$_1$*cn*) and 350 K (high-temperature phase, *Pccn*). According to Guinier *X*-ray diagrams, the investigated specimen prepared by heating a Nb_6I_{11} crystal in D_2 consisted of epitaxially intergrown Nb_6I_{11} and DNb_6I_{11}, *i.e.* the deuteriation reaction did not reach the inner part of the crystal. A 'twin' refinement (intensity coupling) was therefore performed. The D atoms occupy central positions in the Nb_6 cage both at high and low temperature. The thermal ellipsoids of the D atoms exclude a time-averaged off-centre position.

The introduction of a non-metal atom into the voids formed by the metal atoms of a cluster compound was first demonstrated with Nb_6I_{11}, HNb_6I_{11}, and DNb_6I_{11}.[1] The neutron powder data of all three compounds could be well accounted for by assuming the H(D) atoms to take central positions in the Nb_6 octahedra. This result seemed somewhat questionable.[2] In fact, a refinement of the structures applying the Rietveld method to a newly measured data set of DNb_6I_{11} suggested an off-centre position for the interstitial deuterium atom.[3] However, this result was not really conclusive as the heavy-atom positions differed considerably from the positions determined by an *X*-ray investigation,[4] some of the Nb–I distances differing by an amount almost as large as the observed displacement of the D atom from the cluster of the Nb_6 cage.

At the same time a series of molecular orbital calculations for HNb_6I_{11} had appeared[5–9] which were all based on the assumption of a central hydrogen position. A reinvestigation of the structure based on neutron single-crystal data, therefore, seemed desirable and was undertaken both for the high- and low-temperature phases[4] of deuteriated Nb_6I_{11}.

Experimental

Preparation.—Single crystals of Nb_6I_{11} of large enough size (3—8 mm^3) were prepared[10] from Nb_3I_8[11] (7.2 g) mixed with Nb powder (4.3 g) and NaI (72.6 g) sealed into a Nb tube of diameter 2.5 cm and length 14 cm. The NaI had been distilled three times at *ca.* 10^{-3} N m^{-2} and was handled in a dry-box prior to the reaction. The Nb tube was enclosed in a quartz ampoule under vacuum and heated to 880 °C at a constant rate over a period of 9 d. Further cooling to room temperature was accomplished with 1 d. Treating the product with distilled water under Ar left crystals of Nb_6I_{11} which after drying *in vacuo* were deuteriated by passing a slow stream of D_2 over the sample at 460 °C. Deuterium of 99.7% purity was used for this reaction.

Neutron Diffraction.—The data collection was performed on the four-circle diffractometer P32 at the Centre d'Etudes Nucléaire (Grenoble). A deuteriated crystal of Nb_6I_{11} (dimensions 0.6 × 3 × 5 mm) was mounted on an aluminium pin and protected from the atmosphere by a surrounding thin-walled quartz glass (suprasil) capillary. A closed-cycle, single-stage He cryostat (Displex C-1003) was used to cool the specimen to 120 K (data set LT) and a stream of hot air provided a temperature of *ca.* 350 K (data set HT). The data were collected in the ω-scan mode (31 steps, each 0.09° in ω) at $\lambda = 1.1874(3)$ Å, measuring $0\bar{4}2$ as a check reflection after every 50 reflections. The experimental conditions are summarized in Table 1.

Table 1. Neutron diffraction data of a sample $D_{0.45}Nb_6I_{11}$ (LT data at 120 K, HT data at 350 K)

	LT	HT
No. reflections for centring	19	20
a/Å*	11.294	11.334
b/Å*	15.387	15.421
c/Å*	13.479	13.579
Range	$2 \leqslant \theta \leqslant 40°$	$2 \leqslant \theta \leqslant 33°$
	$-12 \leqslant h \leqslant 0$	$0 \leqslant h \leqslant 9$
	$-16 \leqslant k \leqslant 0$	$-12 \leqslant k \leqslant 0$
	$-14 \leqslant l \leqslant 0$	$0 \leqslant l \leqslant 12$
No. independent reflections with	1 552	869
$F_o > 2\sigma(F_o)$	1 386	762

* Because of the large standard deviations ($0.012 \leqslant \sigma \leqslant 0.019$ Å) the lattice constants have been determined from Guinier-type *X*-ray diagrams.[17] The following values of the cell dimensions (but with the large errors of the neutron data) have been used for the refinements and calculations of interatomic distances: (LT) $a = 11.289(5)$, $b = 15.385(6)$, $c = 13.429(5)$ Å; (HT) $a = 11.359(4)$, $b = 15.411(6)$, $c = 13.553(6)$ Å.

The data reduction was done according to the method of Lehmann and Larsen.[12] For the refinements the SHELX version of 1978[13] was used, taking scattering cross-sections (× 10^{-12} cm) of 0.6674 for D, 0.7054 for Nb, and 0.528 for I.[14] The positional and thermal parameters of Nb and I were refined using the values of Imoto and Simon[4] as starting parameters. In the final stage the least-squares program UPALS was used.[15] The bond lengths were calculated using BONDLA, part of the *X*-RAY 76 system.[16]

Results and Discussion

After the refinement of the heavy-atom positions using the data set HT (centrosymmetric structure) a $(F_o - F_c)$ map showed a strong peak in the centre of the Nb_6 unit and the D atom was placed into this position. The refinement of all atomic positions using anisotopic thermal parameters made a partial occupation of the D position obvious which converged approximately to 0.45. With different but fixed occupancy factors independent

---

† Supplementary material (including the results of the refinement of the disorder model) can be ordered from Fachinformationszentrum Energie, Physik, Mathematik D-7514 Eggenstein-Leopoldshafen 2, quoting the reference no. CSD-51919.

Table 2. Structure refinement[a] for $D_{0.45}Nb_6I_{11}$

		Twin model	Disorder model
$R(F)$	LT	0.079	0.083
	HT	0.065	0.073
$R'(F)$	LT	0.024	0.026
	HT	0.024	0.029
G.o.f.	LT	1.14	1.24
	HT	1.23	1.47
N.p.p. LT			
	slope	0.94	0.89
	intercept	−0.05	−0.14
N.p.p. HT			
	slope	0.88	0.79
	intercept	−0.12	−0.27
Weights		$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
No. with $\lvert\Delta(F)\rvert/\sigma(F_o) > 3$	LT	17	27
	HT	17	39
No. with $\lvert\Delta(F)\rvert/\sigma(F_o) > 4$	LT	5	12
	HT	3	15
Largest $\lvert\Delta(F)\rvert/\sigma(F_o)$	LT	5.18	7.15
	HT	7.12	8.38
Parameter p	LT	0.450(8)	0.442(8)
	HT	0.447(8)	0.219(4)[b]

[a] No. of variables: 163 (LT) and 85 (HT). N.p.p. = normal probability plot. G.o.f. = goodness of fit. The parameter p is a twin fraction in the twin refinement and a site occupation factor in the disorder refinement. [b] The value of p for the HT disorder refinement has to be multiplied by 2 to account for the special position.

Table 3. Fractional co-ordinates for $D_{0.45}Nb_6I_{11}$ from twin refinement

Atom	X/a	Y/b	Z/c
HT (350 K; *Pccn*)			
D	0	0	0
Nb(1)	0.100 8(2)	0.104 1(1)	−0.025 5(1)
Nb(2)	0.135 5(1)	−0.051 6(1)	0.080 6(1)
Nb(3)	−0.070 0(1)	0.051 3(1)	0.125 0(1)
I(1)	0.158 9(2)	0.113 2(2)	0.179 3(2)
I(2)	0.024 2(2)	0.109 1(2)	−0.227 9(2)
I(3)	−0.094 1(2)	0.213 4(1)	0.023 0(2)
I(4)	0.303 1(2)	−0.003 2(2)	−0.064 6(2)
I(5)	−0.166 0(2)	0.125 7(2)	0.306 1(2)
I(6)	0.25	0.25	−0.076 6(4)
LT (120 K; $P2_1cn$)			
D	−0.005(1)	−0.000 1(6)	0.249 8(8)
Nb(1)	0.089 0(4)	0.109 4(2)	0.223 1(3)
Nb(1a)	−0.110 9(3)	−0.100 2(2)	0.277 8(3)
Nb(2)	0.136 8(4)	−0.051 8(2)	0.326 7(3)
Nb(2a)	−0.131 3(4)	0.056 2(2)	0.164 6(2)
Nb(3)	−0.072 4(4)	0.048 8(2)	0.379 6(2)
Nb(3a)	0.074 1(4)	−0.056 4(2)	0.131 2(2)
I(1)	0.159 6(4)	0.113 8(3)	0.427 1(4)
I(1a)	−0.157 2(4)	−0.112 1(3)	0.069 3(3)
I(2)	0.033 9(5)	0.097 8(3)	0.014 1(4)
I(2a)	−0.020 2(5)	−0.112 6(3)	0.477 6(3)
I(3)	−0.106 4(5)	0.212 7(3)	0.282 2(4)
I(3a)	0.078 7(6)	−0.217 4(3)	0.236 6(3)
I(4)	0.301 0(5)	0.012 0(3)	0.183 9(3)
I(4a)	−0.307 5(5)	0.015 1(3)	0.307 9(3)
I(5)	−0.156 7(5)	0.119 8(3)	0.567 0(3)
I(5a)	0.186 1(5)	−0.141 0(3)	−0.039 4(3)
I(6)	0.216 8(5)	0.267 2(2)	0.173 2(3)

refinements led to the same value corresponding to the minimum of the residual *R* both for the LT and HT data sets.

The unexpected result of a partial occupation of the clusters contrasted with earlier work[1,4] on microcrystalline Nb_6I_{11} indicating the hydrogen absorption to be complete within minutes and yielding a product HNb_6I_{11} or DNb_6I_{11}, respectively, under comparable experimental conditions.

To investigate the nature of the deuterium deficiency in the $D_{0.45}Nb_6I_{11}$ specimen, the sample used for the neutron diffraction experiments was powdered and investigated by means of the modified Guinier technique.[17] The high-resolution *X*-ray diagram clearly indicated that the sample consisted of both Nb_6I_{11} and DNb_6I_{11}. This was especially visible with the 042 reflection which was split into two closely spaced lines of equal intensity ($\Delta\theta = 0.1°$ at room temperature). The splitting is too small to be seen in the neutron diffraction experiment ($\Delta\theta = 0.07°$ at 120 K and 0.12° at 350 K, using the lattice constants of ref. 4).

According to the *X*-ray investigation the hydrogenation reaction is too slow to have reached the central part of the investigated 'monocrystal'. The centre still consists of pure Nb_6I_{11}. The refined crystal structure of $D_{0.45}Nb_6I_{11}$ (termed the 'disorder model' hereafter) corresponds to a superposition of the structures of Nb_6I_{11} and DNb_6I_{11} with approximately equal weight. The given interpretation of the nature of the deuterium deficiency is in agreement with both the observed lattice constants as well as the refined atomic positions in the disorder model which approximately correspond to the average of values found for Nb_6I_{11} and DNb_6I_{11}.[4] As the Nb and I atomic co-ordinates in both compounds are nearly identical no irregularities of the anisotropic thermal parameters due to split positions are observed.

The disorder refinements treat the sample as a homogeneous single crystal with the deuterium site partially occupied, *i.e.* a static disorder. This implies a phase coherence between the occupied and unoccupied sites and the calculated structure factor is given by equation (1), where p is the site occupation

$$F_{hkl} = pF'_{hkl} + (1 - p)F''_{hkl} \qquad (1)$$

factor for deuterium and F' and F'' are the calculated structure factors with and without a contribution from the deuterium atom.

Due to the heterogeneous nature of the $D_{0.45}Nb_6I_{11}$ sample the neutron diffraction data had been measured from effectively two macroscopic epitaxially intergrown crystals of different compositions. A refinement which takes account of the intensity coupling between the two regions of the sample, rather than a phase coherence, would be a better description of the diffraction pattern. The twin refinement calculates the structure factor using expression (2), where ${F'_{hkl}}^2$ is the intensity calculated with the

$$F_{hkl} = \sqrt{p{F'_{hkl}}^2 + (1 - p){F''_{hkl}}^2} \qquad (2)$$

deuterium position having 100% occupancy and ${F''_{hkl}}^2$ is the intensity for the unsubstituted Nb_6I_{11}. The parameter p is a least-squares variable and represents the fraction of the sample which was DNb_6I_{11}.

Both models give the same result in that the deuterium atom occupies the central position in the Nb_6 octahedron, but the many improvements seen in the twin model when compared with the disorder model (see Table 2) clearly show that it is a superior description. In both the high- and low-temperature phases, the values for pairs of fractional co-ordinates calculated from the twin and disorder refinements are virtually identical. Most pairs are the same within one standard deviation, and all are within two standard deviations.

In general, the thermal parameters are also very similar, the exceptions being the U_{ii} for deuterium. In the LT phase, ΣU_{ii} for the twin and disorder refinements gives 0.045 and 0.036 Å^2, respectively; similarly for the HT phase, ΣU_{ii} for twin and disorder models gives 0.093 and 0.075 Å^2, respectively. This

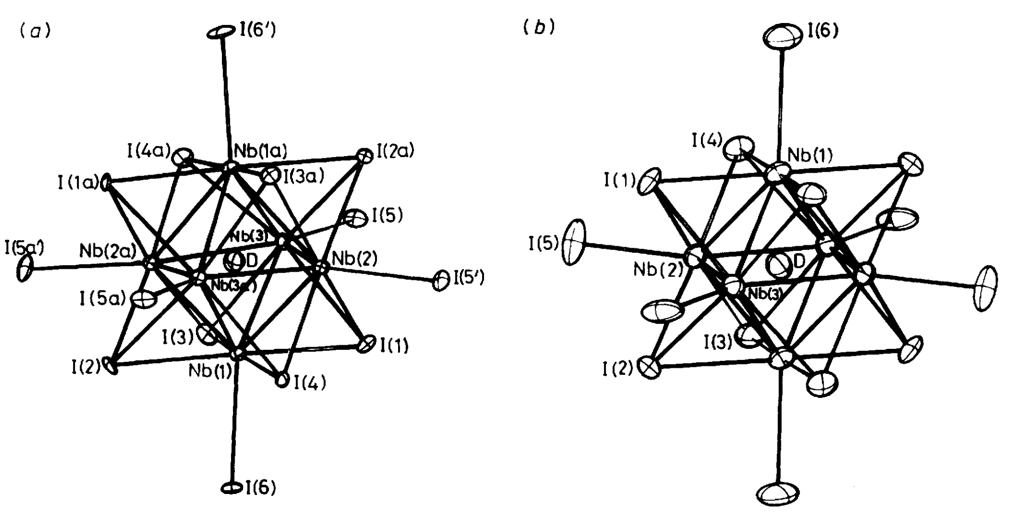

Figure. $DNb_6I^i_8I^{a-a}$ cluster from neutron diffraction data of a sample $D_{0.45}Nb_6I_{11}$. I^i denotes inner-sphere atoms, I^{a-a} interconnecting outer-sphere atoms. The atoms are drawn at a probability level of 50%. (*a*) 120 K (LT); (*b*) 350 K (HT)

Table 4. Bond lengths (Å) in $D_{0.45}Nb_6I_{11}$. The calculations use the lattice constants from *X*-ray (with neutron cell errors) and the atomic parameters from neutron experiments (see Table 1)

HT (350 K)			
D–Nb(1)	2.001(2)	D–Nb(2)	2.048(2)
D–Nb(3)	2.032(2)	Nb(1)–Nb(2)	2.825(3)
Nb(1)–Nb(3)	2.930(3)	Nb(2)–Nb(3)	2.886(3)
Nb(1)–Nb(2′)	2.901(3)	Nb(1)–Nb(3′)	2.771(3)
Nb(2)–Nb(3′)	2.884(3)	Nb(1)–I(1)	2.857(4)
Nb(1)–I(2)	2.879(4)	Nb(1)–I(3)	2.859(4)
Nb(1)–I(4)	2.881(3)	Nb(2)–I(1)	2.884(4)
Nb(2)–I(2′)	2.839(3)	Nb(2)–I(3′)	2.900(4)
Nb(2)–I(4)	2.838(4)	Nb(3)–I(1)	2.866(3)
Nb(3)–I(2′)	2.886(4)	Nb(3)–I(3)	2.868(4)
Nb(3)–I(4′)	2.869(3)	Nb(1)–I(6)	2.900(3)
Nb(2′)–I(5)	2.963(4)	Nb(3)–I(5)	2.927(4)
LT (120 K)			
D–Nb(1)	2.03(1)	D–Nb(1a)	1.98(2)
D–Nb(2)	2.07(2)	D–Nb(2a)	2.02(2)
D–Nb(3)	2.04(1)	D–Nb(3a)	2.02(2)
Nb(1)–Nb(2)	2.895(6)	Nb(1a)–Nb(2a)	2.855(5)
Nb(1)–Nb(3)	2.934(5)	Nb(1a)–Nb(3a)	2.948(6)
Nb(2)–Nb(3)	2.911(7)	Nb(2a)–Nb(3a)	2.929(6)
Nb(1)–Nb(2)	2.735(5)	Nb(1a)–Nb(2)	2.968(6)
Nb(1)–Nb(3a)	2.839(6)	Nb(1a)–Nb(3)	2.704(6)
Nb(2)–Nb(3a)	2.720(5)	Nb(2a)–Nb(3)	2.965(5)
Nb(1)–I(6)	2.902(6)	Nb(1a)–I(6)	2.823(7)
Nb(2)–I(5)	2.954(7)	Nb(2a)–I(5a)	2.963(7)
Nb(3)–I(5)	2.905(6)	Nb(3a)–I(5a)	2.923(6)
Nb(1)–I(1)	2.855(6)	Nb(1a)–I(1a)	2.854(6)
Nb(1)–I(2)	2.880(6)	Nb(1a)–I(2a)	2.878(6)
Nb(1)–I(3)	2.833(6)	Nb(1a)–I(3a)	2.853(7)
Nb(1)–I(4)	2.872(6)	Nb(1a)–I(4a)	2.869(7)
Nb(2)–I(1)	2.894(7)	Nb(2a)–I(1a)	2.902(7)
Nb(2)–I(2a)	2.850(7)	Nb(2a)–I(2)	2.823(7)
Nb(2)–I(3a)	2.895(6)	Nb(2a)–I(3)	2.893(6)
Nb(2)–I(4)	2.842(7)	Nb(2a)–I(4a)	2.838(7)
Nb(3)–I(1)	2.875(7)	Nb(3a)–I(1a)	2.870(7)
Nb(3)–I(2a)	2.871(7)	Nb(3a)–I(2)	2.883(6)
Nb(3)–I(3)	2.865(7)	Nb(3a)–I(3a)	2.853(6)
Nb(3)–I(4a)	2.870(7)	Nb(3a)–I(4)	2.859(7)

indicates that the contribution to the scattering by the deuterium atoms is too large for the disorder model, which responds by contracting the thermal parameters.

Although the refinement of the twin model is improved against the refinement of the disorder model, the validity rests on the assumption that the cell dimensions in the two compounds are the same. That this is not true is reflected in the large errors in the neutron cell dimensions. To perform the refinement of two independent structures simultaneously against one set of data is a very much more complicated affair than a twin refinement. However, if the cell dimensions were identical, both twin- and two-structure refinements would yield the same result. As the cell dimensions of Nb_6I_{11} and DNb_6I_{11} only differ by *ca.* 1% in *b* (and < 0.3% in *a* and *c*), we believe that they are sufficiently close to justify the twin refinement. The atomic parameters of the twin refinement are summarized in Table 3. Table 4 lists the interatomic distances calculated for the lattice constants in the footnote of Table 1. Single clusters in the LT and HT modifications of the specimen $D_{0.45}Nb_6I_{11}$ are shown in the Figure. The superposition of the structures of Nb_6I_{11} and DNb_6I_{11} does not lead to any significant changes of the thermal ellipsoids which are characteristic for Nb_6I_{11} and DNb_6I_{11}, especially concerning I(5) and I(6).

In spite of the unexpected experimental complication due to the heterogeneous nature of the investigated crystal our result gives clear evidence for the central position of the D atom in the Nb_6 cage both at 120 and 350 K. At 350 K the D atom is positioned in the centre of inversion with a sufficiently small Debye-Waller factor to exclude a time-averaged off-centre position. In the non-centrosymmetric low-temperature phase at 120 K the distance between the deuterium atom position and the centroid of the Nb_6 octahedron was calculated to be 0.04(6) Å, which is not significantly different from zero. This quantity includes error contributions from the cell dimensions.

The earlier result[3] indicating an off-centre position of the hydrogen atoms on the basis of a Rietveld type refinement with neutron powder data has to be revised. These data suffered from a contamination of the sample by β-NbD_x; in addition, the accuracy of the refined atomic positions was overestimated.[3] The positional parameters for the off-centre position found in the refinement deviated by less than 3σ from the cluster centre and the deviation became even less when the positions of Nb and I atoms were kept fixed to the values found in a single-crystal *X*-ray refinement.[4]

Acknowledgements

We are indebted to Dr. G. J. McIntyre of the Institut Laue-Langevin for valuable help with the twin refinements. Further-more, the support of this work from the Bundesminister für Forschung und Technologie is gratefully acknowledged.

References

1 A. Simon, *Z. Anorg. Allg. Chem.*, 1967, **355**, 311.
2 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn. (German transl.), Verlag Chemie, Weinheim, 1974, p. 999.
3 A. N. Fitch, S. A. Barrett, B. E. Fender, and A. Simon, *J. Chem. Soc., Dalton Trans.*, 1984, 501.
4 H. Imoto and A. Simon, *Inorg. Chem.*, 1982, **21**, 308.
5 H. Nohl and O. K. Andersen, *Inst. Phys. Conf. Ser.*, 1981, **55**, 61.
6 J. J. Finley, H. Nohl, E. E. Vogel, H. Imoto, R. E. Camley, V. Zevin, O. K. Andersen, and A. Simon, *Phys. Rev. Lett.*, 1981, **46**, 1472.
7 F. Dübler, H. Müller, and Ch. Opitz, *Chem. Phys. Lett.*, 1982, **88**, 467.
8 A. Simon, *Ann. Chim. (Paris)*, 1982, **7**, 539.
9 H. G. Fritsche, F. Dübler, and H. Müller, *Z. Anorg. Allg. Chem.*, 1984, **513**, 46.
10 A. Simon, H. G. v. Schnering, and H. Schäfer, *Z. Anorg. Allg. Chem.*, 1967, **335**, 295.
11 A. Simon and H. G. v. Schnering, *J. Less-Common Met.*, 1966, **11**, 31.
12 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.
13 G. M. Sheldrick, SHELX 78 program, Göttingen, 1978, unpublished work.
14 L. Koester, in 'Springer Tracts in Modern Physics,' ed. G. Höhler, Springer-Verlag, Heidelberg, 1977, vol. 80, pp. 1–55.
15 J-O. Lundgren, Crystallographic computer programs, Report UUIC-B13-04-05, University of Uppsala, Sweden, 1982.
16 J. M. Stewart, *X*-RAY 76, technical report TR-446, University of Maryland, 1976.
17 A. Simon, *J. Appl. Crystallogr.*, 1970, **3**, 11.

Received 24*th March* 1986; *Paper* 6/581