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Abstract

The structure of three rare earth hexaborides, NdB_6 , EuB_6 and YbB_6 , was studied by single-crystal X-ray diffraction. The refinements indicated boron vacancies for EuB_6 and YbB_6 , but the site occupancies of NdB_6 were strongly model dependent, showing either boron or metal vacancies. No impurity atoms could be detected in the structures. Refinements of a model allowing anharmonic thermal motion of atoms gave small but significant fourth-order anharmonic thermal parameters for NdB_6 . Static displacements of both the rare earth and boron atoms were considered and tested as an alternative representation. It was concluded that the observed features in the difference density maps were due to charge asphericity.

Keywords: Rare-earth hexaborides; X-ray diffraction; Crystal structure; Boron vacancies; Charge asphericity

1. Introduction

In continuation of our studies of rare earth hexaborides [1–4], the crystal structure of NdB_6 , EuB_6 and YbB_6 has been refined from single-crystal X-ray diffraction data. These compounds have a crystal structure with cubic symmetry ($Pm\bar{3}m/O_h^1$). They consist of a three-dimensional skeleton of boron octahedra B_6 , the interstices of which are filled by rare earth atoms. The rare earth hexaborides exhibit a wide variety of interesting magnetic, electrical and transport properties, which are reviewed in Ref. [5]. NdB_6 is a metal with the Nd ion in a trivalent state [6], while EuB_6 and YbB_6 are narrow gap semiconductors with Eu and Yb ions in a divalent state [6,7]. NdB_6 is reported to have a homogeneity region with compositions ranging from $\text{NdB}_{6.01}$ to $\text{NdB}_{8.2}$ owing to the Nd atom vacancies [8]. EuB_6 and YbB_6 appear to be essentially stoichiometric [5,9]. However, it has been shown that a substantial amount of carbon can be incorporated in the lattice of EuB_6 and YbB_6 (presumably substituting for boron in the octahedron), giving rise to a noticeable decrease in the lattice parameter with increasing carbon content [10,11]. Thus such subtle details of the crystal structure as the occurrence of vacancies and the incorporation of foreign atoms, as well as the relations between structure and properties, are far from being understood and have remained a subject of controversy. This sit-

uation calls for high precision single-crystal structure determinations.

2. Experimental details

The single-crystal samples were prepared at the A.F. Ioffe Institute by the high temperature solution growth method from aluminium, as described in Ref. [9]. The compositions of the samples (in mass per cent), determined by wet chemical analysis, are presented in Table 1. The boron in NdB_6 was enriched with the ^{11}B isotope (for neutron diffraction measurements).

The data collections were carried out on NdB_6 and YbB_6 single crystals ground to approximately spherical shape and on a cubical EuB_6 sample. The lattice parameters from the single-crystal samples were determined by a least-squares refinement for the centred setting angles ($\text{Ag } K\alpha_1$) of 24 Friedel reflection pairs

Table 1
Chemical compositions (in mass per cent) of samples

Compound	RE ^a	B	Al	C	Total
NdB_6	67.0	32.2	0.22	0.00	99.42
EuB_6	69.6	29.9	0.09	<0.05	<99.64
YbB_6	71.6	27.4	0.30	0.50	99.80

^aRE, rare earth metal.

($\pm 2\theta$). The sizes of the samples and the measured lattice parameters are given in Table 2.

Intensity data were collected at 296 ± 1 K on a Huber 5042 four-circle diffractometer at the University of Helsinki. Pd-filtered Ag $K\alpha$ radiation was used. Measurements of the diffraction profiles were performed using coupled ω - 2θ step scans. A detailed description of the experimental procedures for the measurements has been given previously [3]. Data were collected to maximum $\sin \theta/\lambda = 1.26 \text{ \AA}^{-1}$ in one half of the available reciprocal space. The total numbers of measured and non-equivalent reflections in the data collections for each crystal are given in Table 2.

Intensity data were reduced to F^2 values with the programs REFPK and BGLP [12] using the algorithm presented by Lehmann and Larsen [13] for the determination of the background level and applying corrections for Lorentz and polarization effects. The intensities of three test reflections, measured every 50 reflections, did not show any systematic time dependence during the data collections. The intensity variations were within $\pm 1\%$. Absorption corrections for the naturally cubical crystal were calculated with the computer program DATAP [14] using the gaussian numerical integration method, and absorption factors for the spherical crystals were interpolated from the tabulated values of Weber [15]. The values of the linear absorption coefficients given in Table 2 were calculated by assuming no vacancies either in the boron or in the metal lattice. Averaging the symmetry-equivalent reflections and rejecting discordant reflections led to internal R factors

of 0.028, 0.030 and 0.033 for NdB_6 , EuB_6 , and YbB_6 respectively. Unlike in Refs. [3,4], corrections for thermal diffuse scattering were not applied.

3. Refinements

Refinements were carried out using the least-squares program PROMETHEUS [16]. All the measured reflections were included in the analyses. The quantities varied in the refinements were the scale and extinction parameters, the thermal parameters and site occupancies for metal and boron atoms and the positional parameter of boron. The lattice is of CaB_6 type (space group no. 221) and the boron atoms occupy special positions of $4m.m$ site symmetry, giving the following constraints for the thermal parameters: $U_{11}, U_{22} = U_{33}, U_{12} = U_{13} = U_{23} = 0$. The symmetry of the metal atom sites is $m\bar{3}m$, which implies that the thermal vibrations of the metal atoms are isotropic and can be described with one parameter U_{iso} .

The values adopted for the calculated atomic scattering factors and for the anomalous dispersion corrections were those given in Ref. [17]. Applying the dispersion corrections presented in Ref. [18], as in Refs. [3,4], yielded slightly lower boron occupancies than presented in the following. Both the neutral atom and the ionic (Nd^{3+} , Eu^{2+} , Yb^{2+}) scattering factors were applied in the refinements. The ionic model gives a clearly lower R factor for NdB_6 (the same was true for CeB_6), but only a slightly lower R for YbB_6 and

Table 2
Final structure data and refinement characteristics

Parameter	NdB_6	EuB_6	YbB_6
Crystal shape	Sphere	Cube	Sphere
Crystal size (mm)	$\varnothing = 0.130 \pm 0.005$	$d = 0.120 \pm 0.005$	$\varnothing = 0.125 \pm 0.005$
Lattice parameter a (\AA)	4.1269(1)	4.1849(1)	4.1479(1)
Absorption coefficient μ (cm^{-1})	95.9	111.9	174.4
Number of measured reflections	3679	3839	3721
Number of non-equivalent reflections, N	158	163	160
Agreement factor $\omega R(F^2)$ (%)	1.86	1.29	1.59
Goodness of fit	0.52	0.33	0.33
<i>Boron</i>			
Occupancy q_{B} (%)	97.9(1.0)	98.0(7)	97.7(9)
Coordinate x_{B}	0.1989(2)	0.2027(2)	0.2012(2)
U_{11} (\AA^2)	0.0033(3)	0.0033(2)	0.0032(3)
U_{22} (\AA^2)	0.0047(2)	0.0046(2)	0.0054(2)
<i>Metal</i>			
U_{iso} (\AA^2)	0.00710(4)	0.00662(2)	0.01035(3)
Extinction parameter g (10^{-4})	0.401(11)	0.172(3)	0.114(3)

The temperature factor expression is $\exp(-2\pi^2 \sum_{ij} h_i h_j a_i^* a_j^* U_{ij})$. The crystallographic agreement factor is defined as $\omega R(F^2) = [\sum w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2 / \sum w F_{\text{obs}}^4]^{1/2}$. F_{obs} and F_{calc} are the observed and calculated structure factors, $w = 1/\sigma^2(F_{\text{obs}}^2)$ is the weight and $\sigma(F_{\text{obs}}^2)$ is the standard deviation of the scaled intensity. The goodness of fit is defined as $[\sum w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2 / (N - n)]^{1/2}$, where n is the number of independent parameters.

a slightly higher R for EuB_6 . The questionable thing is that by using the ionic scattering factors only for the rare earth metal [3,4], we totally remove three or two electrons from the calculated structure. In the final refinements neutral atom scattering factors were used.

Refinement of the extinction parameters was performed following the theory of Becker and Coppens [19]. Refinements of anisotropic extinction parameters using the non-averaged data did not converge. The EuB_6 and YbB_6 data showed only moderate extinction effects, which could best be modelled as isotropic secondary extinction of type I, with a lorentzian distribution function (as in our previous refinements of the $\text{Ce}_{1-x}\text{La}_x\text{B}_6$ data). The NdB_6 data showed more severe extinction and, unfortunately, the extinction model correlated with the structure model. Either by including primary extinction in addition to secondary extinction (model A) or by refining the secondary extinction of type III (model B), the R factors can be decreased significantly. If the occupancies are fixed to 100%, model B is slightly better than model A. If we refine the occupancies too, model A is better than model B. The interesting point, however, is that if the site occupancy of the metal (or boron) is refined simultaneously with the extinction parameters, both these models yield vacancies on the metal site. If we use Nd^{3+} scattering factors instead of neutral atom factors, we get slightly higher metal site occupancies. Model B yields full occupancies on both sites (metal, boron), but still model A is slightly (but not significantly) better. The above discussion is valid for the simple structure model. If the features found in the difference density maps are modelled, e.g. by including static displacements of atoms, parameters describing the asphericity of the charge distribution or anharmonic thermal parameters, the situation is different. The choice of extinction model will have a smaller influence on the occupancy values, the metal atom deficiency disappears and the boron site becomes slightly underoccupied.

4. Results and discussion

4.1. Structure

Because of the model dependence of the extinction correction and the occupancy factors, we adopted the isotropic secondary extinction of type I into the basic model of all our compounds. The obtained structure data are presented in Table 2. They indicate the occurrence of vacancies at the boron site for all compounds, as in our previous studies on LaB_6 [1,2], CeB_6 [3] and their solid solutions [4]. The fractional coordinate x_B of boron in NdB_6 is close to the values observed for other hexaborides of trivalent metals, e.g. LaB_6 [1,2], CeB_6 [3] and SmB_6 [20]. The coordinates x_B for EuB_6

and YbB_6 , where the rare earth metal is in the divalent state, are clearly higher. The lengths of the two types of B–B bonds and the metal–boron distances are presented in Table 3.

The thermal parameters show the same general features as those of various other hexaborides reported in previous studies, thus supporting the model of a rigid boron network and metal ions vibrating relatively freely in the interstitial positions. The isotropic thermal parameter of the rare earth atoms is clearly greater than the equivalent isotropic thermal parameter of the boron atom in all the studied compounds, although the boron atom mass is less than one-tenth of the metal atom masses. The fact that the usual mass dependence of the thermal vibration amplitude [21] is not observed is mainly due to the decoupled vibrations of the rare earth atoms [22,23]. The isotropic thermal parameters of the rare earth metals in the hexaborides tend to increase with increasing atomic number. This is possibly related to the filling of the core 4f shell from $4f^0$ (La) to $4f^{14}$ (Yb). The temperature factors of the boron atom do not display such a dependence. The boron atom vibrations are anisotropic and the parameter U_{22} ($=U_{33}$) is greater than U_{11} . The anisotropy of the boron vibrations is related to the different strengths of the two types of B–B bonds and correlates with the force constants of these bonds: the interoctahedral bonds are stronger than the intraoctahedral ones (e.g. Ref. [24]).

In the case of NdB_6 (and CeB_6 [3]) the model of the thermal parameters can be expanded to include anharmonicity (Gram–Charlier formalism up to the fourth order). The results, given in Table 4, and the corresponding results for the harmonic model, given in Table 2, are surprisingly similar to the results of Trounov et al. [20] for SmB_6 . However, while they reported that the difference density maps for both the anharmonic and the harmonic model were similar to each other, we observed a clearly visible depletion in the difference density around the metal atom. Trounov et al. observed distinctive positive peaks of $1.3 \text{ e } \text{Å}^{-3}$ in the $\langle 100 \rangle$ direction, 0.75 Å distant from the Sm atom. In our map (harmonic model) a more complicated positive surrounding was found, with a diffuse maximum of $0.86 \text{ e } \text{Å}^{-3}$, at 0.74 Å from the Nd atom and more spread towards the $\langle 110 \rangle$ and $\langle 111 \rangle$ directions than

Table 3
Interatomic distances (Å). Only the nearest-neighbour distances are tabulated. B–B is the intraoctahedral distance and B–B' the interoctahedral distance

Distance	NdB_6	EuB_6	YbB_6
B–B	1.7574(12)	1.7596(12)	1.7525(12)
B–B'	1.6415(17)	1.6964(17)	1.6695(17)
B–metal	3.0314(3)	3.0783(3)	3.0495(3)

Table 4

Structure data and refinement characteristics for NdB₆ with anharmonic thermal vibrations of Nd; $d_{1111} = d_{2222} = d_{3333}$ and $d_{1122} = d_{1133} = d_{2233}$

<i>Boron</i>	
Occupancy μ_B (%)	97.1(8)
Coordinate x_B	0.1989(2)
U_{11} (Å ²)	0.0026(2)
U_{22} (Å ²)	0.0041(2)
<i>Metal</i>	
U_{iso} (Å ²)	0.00589(11)
d_{1111} (10 ⁻⁸)	-19(2)
d_{1122} (10 ⁻⁸)	-6.0(6)
Extinction parameter g (10 ⁻⁴)	0.317(10)
Agreement factor $wR(F^2)$ (%)	1.43
Goodness of fit	0.40

along $\langle 100 \rangle$. Anharmonic treatment decreased the maximum to 0.40 e Å⁻³ and applying the secondary extinction model of type III led to a further decrease to 0.20 e Å⁻³. The anharmonic treatment did not significantly change the values of the site occupancies, but changing the extinction model yielded full occupancies to both atoms.

Refinements using the Gram–Charlier model converged also for the EuB₆ and YbB₆ data. However, in the case of YbB₆ only the parameter d_{1122} differed significantly from zero in the case of EuB₆ the refinement yielded practically zero values for both anharmonic parameters.

The question remains as to whether this model is physically and/or chemically reasonable for our compounds at room temperature. Furthermore, the mathematical basis of this formalism is such that it may model properties other than thermal motion, in particular deviations of the static atomic electron density from spherical symmetry. Nd³⁺ has a 4f⁵ shell and should display an aspherical charge distribution, while Eu²⁺ and Yb²⁺ have half-filled (4f⁷) and filled (4f¹⁴) shells and a spherical charge distribution is expected. It has been shown in Ref. [25] that the Gram–Charlier formalism can successfully represent bonding effects in the valence charge density. On the other hand, if it is used as a thermal motion formalism for X-ray data, atomic asphericity should be included in the scattering formalism. However, our compounds are not ideal for charge density studies and extremely careful and precise diffraction data would be required.

An alternative model where the metal atoms are displaced from their average site (0,0,0) can also be applied successfully. In comparison with the model mentioned above, it leads to equal values of all parameters (except the metal atom thermal parameter, which is, of course, significantly decreased) and to equal R factors. Placing Nd (or Ce) atoms on (0, y , z) or (x , x , z) sites and Eu and Yb on (x ,0,0) sites will give the best

R factors, but, especially in the latter case, correlation between the positional and thermal parameters is very high. Also the boron atom position could be split to multiple positions with partial occupancies. However, the R factors did not show any significant improvement. Static displacements of the boron atom in the rare earth hexaborides have recently been considered by Korsukova [26] and Malyshev et al. [27].

4.2. Lattice parameters and impurity atoms

In order to establish the possible existence of impurity atoms in the structure, refinements with extra atoms either in the boron or in the metal lattice were tried. Although the results of the chemical analysis presented in Table 1 do not necessarily represent the individual single-crystal samples of our study, they can be used as a starting point. If it is assumed that all of the rare earth metal and the boron (but no other elements) are included in the crystal structure, the compositions NdB_{6.30}, EuB_{6.04} and YbB_{6.13} (or Nd_{0.95}B₆, Eu_{0.99}B₆ and Yb_{0.98}B₆) can be calculated. This could imply (a) metal vacancies, (b) irregularities in the network of boron octahedra or (c) replacement of some of the boron by heavier element(s). Another possibility is that all detected boron is not included in the crystal structure. Aluminium is sometimes found as inclusions in some of the hexaborides [9] and we may assume that most of the aluminium detected in the chemical analysis originates from them. However, some attempts to include Al in the structure model were made, without success. Since the refinements generally tend to yield partial occupancy of the boron site, placing a heavier element (such as C), with a larger scattering factor, on this site seems not worth trying unless the total site occupancy is less than 100%. All attempts to include carbon in the structure failed.

There seems to be a qualitative agreement between the lattice parameter value and the boron occupancy as measured by us for NdB₆ and as presented by Storms [8] for polycrystalline samples. However, a cautious attitude should be taken in regard to the latter results. It seems that the samples with compositions B/Nd = 4.42, 5.50 and 6.05 may not be interpreted as compounds of NdB_{4.42}, NdB_{5.50} and NdB_{6.04}, but rather as mixtures of two structural phases, NdB₄ and NdB₆. There seems to be some correlation between the lattice parameter and the B/Nd ratio when the ratio is less than 6, while for ratios greater than 6 the lattice parameter is almost constant (the experimental error is not given). However, this apparent correlation might rather reflect the existence of two different lattice parameters from two different phases than different degrees of boron vacancies within a single phase. Furthermore, the constancy of the lattice parameter when the B/Nd ratio is greater than 6 may be due to (by X-ray methods)

undetectable elementary boron. The lattice parameter measured for the crystal of our study is just the same as for the compound $\text{NdB}_{6.1}$ of Aivasov et al. [28] and the compound $\text{NdB}_{5.50}$ of Storms [8], so we cannot make any firm conclusions on this basis.

The results of the chemical analysis of EuB_6 (Table 1) indicated the presence of some carbon in the crystals. However, even the maximum amount is so small that within the limits of experimental accuracy the sample can be considered as carbon free [10,11]. Further, the obtained lattice parameter is very close to the values reported in Refs. [29,30] for stoichiometric EuB_6 . The value of the lattice parameter of YbB_6 obtained in our study (4.1479(1) Å) is close to that of $\text{YbB}_{5.97}\text{C}_{0.03}$ (4.1476(5) Å [11]), but within experimental error limits it is also close to the lattice parameter of stoichiometric YbB_6 (4.1486(5) Å [11]). The value of $x=0.03$ in $\text{YbB}_{6-x}\text{C}_x$ would mean about 0.15% (by weight) of carbon. On the other hand, the result from the chemical analysis was 0.5% (by weight) of carbon, which would imply a value of 0.10 for x if all that carbon were included in the structure. In conclusion, it seems probable that the samples of our study are almost free of any impurity atoms.

5. Conclusions

Refinements of the structure of EuB_6 and YbB_6 indicated boron vacancies in accordance with several previous X-ray diffraction studies on other hexaboride compounds. The site occupancies of NdB_6 were found to correlate strongly with the extinction model. It has to be emphasized, however, that the refinement of the common basic model for all compounds (isotropic secondary extinction of type I) yielded boron vacancies for NdB_6 too. Although the chemical analyses indicated the possible existence of carbon atoms, no impurity atoms in the structures could be observed from the X-ray diffraction data. Refinements allowing anharmonic thermal motion or static atomic displacements were successfully applied for modelling the observed features in the difference electron density maps, especially in the case of NdB_6 . However, comparison of the electronic states of the studied compounds indicates that the observed discrepancies with the basic model are rather due to charge asphericity around the neodymium nucleus.

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