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CRYSTAL STRUCTURE REFINEMENT OF AlN AND GaN

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We have refined the structure parameters of AlN and GaN using X-ray intensities from single crystals collected with an automatic single crystal diffractometer. The lattice constants and the u values are $a = 3.110$ Å, $c = 4.980$ Å, $u = 0.3821$ for AlN and $a = 3.190$ Å, $c = 5.189$ Å, $u = 0.377$ for GaN. The final R-values for anisotropic temperature factors are equal to 0.015 for AlN and 0.026 for GaN. The effective atomic charges in these compounds are estimated.

1. INTRODUCTION

SPHALERITE-TYPE solid solutions $Al_{1-x}Ga_xX$ with X = P, As, Sb have been reported in literature. No convincing data* have been published for the corresponding nitrides which crystallize in the wurtzite structure. Although the existence of wurtzite-type solid solutions have been published for $Ga_{1-x}In_xN$ [2], all attempts to grow (Al, Ga) N mixed crystals have failed.† This situation stimulated the single crystal structure investigations reported below.

For the ideal wurtzite structure, $c/a = 1.633$ and $u = 0.375$. In contrast to the cubic sphalerite structure, the wurtzite structure offers two possibilities to deviate from the ideal arrangement, by changing the c/a ratio and by changing the u value. Such deviations are often observed in wurtzite-type structures [3].

The crystal structure of AlN was determined by Ott [4] using rotation photographs of single crystals and Debye–Scherrer diagrams: AlN belongs to the wurtzite-type structures with $c/a = 1.60$, $u = 0.38$ and equal Al–N distances. In addition, Ott concluded from intensity relations that AlN does not contain Al^{3+} and N^{3-} ions, but uncharged Al and N atoms, which form nonpolar bonds. Similar results were derived for GaN [5, 6].

More recently, the structures of these compounds have been investigated using polycrystalline samples [7–10]. The structure parameters given in these papers agree: AlN deviates more than GaN from the ideal c/a and u values.

There exists a strong correlation between the c/a ratio and the u parameter for all wurtzite-type structures: if c/a decreases, then u increases in such a way that the four tetrahedral distances remain nearly constant and the tetrahedral angles are distorted [11]. The bond lengths would be equal if

$$u = \frac{1}{3}\frac{a^2}{c^2} + \frac{1}{4}.$$

The reported u values usually deviate more from the ideal u value than from the value calculated by this equation.

The c/a ratio correlates also with the differences of the electronegativities: the compounds with the greatest differences show the largest departure from the ideal c/a ratio [8]. The distortions were explained by long-range polar interactions. In this way the crystal gains polar energy in the presence of ionic charges [12].

From literature values it was concluded that only wurtzite structures with c/a ratios lower than the ideal value of 1.633 are stable. Compounds with c/a greater than this value form stable sphalerite modifications. Within a group of MX compounds with common M atoms the c/a ratio decreases with decreasing ionic radius ratio $R(M)/R(X)$ [13].

* Lyutaya and Bartnitskaya [1] have reported a continuous series of solid solutions in the system of Ga–Al–N, but did not describe the preparation of the polycrystalline samples. The samples were investigated by X-ray phase analysis, but the authors did not describe the line shape of the so-called (Al, Ga) N mixed crystals. Stoeger (personal communication) found only very broad lines in X-ray photographs of polycrystalline samples of Al, Ga, N. On annealing these samples, the lines split into double lines which could be indexed as GaN and AlN.

The lattice constants reported by Lyutaya and Bartnitskaya for $Al_{0.5}Ga_{0.5}N$ do not agree with the expected ones, but have only small deviations from the GaN lattice constants.

† Unpublished data of J. Burmeister, P. Eckerlin, I. Maak, A. Rabenau and J. Stoeger.

Table 1. Details of the intensity measurement

	AlN	GaN
Number of measured reflections	362	2870
Number of averaged reflections	186	188
θ (max) [°]	50	50
a [Å]	3.110(1)	3.190(1)
c [Å]	4.980(1)	5.189(1)
μ [cm^{-1}]	12.1	305

Table 2. Structure parameters of AlN *and* GaN

	AlN			
	$z\ (=u)$	U	U_{11}	U_{33}
Al	0	0.38 (2)	0.37 (2)	0.40 (2)
N	0.3821 (3)	0.44 (2)	0.44 (2)	0.46 (4)
R		0.015	0.015	
$R(w)$		0.021	0.020	
	GaN			
	$z\ (=u)$	U	U_{11}	U_{33}
Ga	0	0.43 (2)	0.52 (2)	0.27 (2)
N	0.377 (1)	0.51 (7)	0.70 (8)	0.24 (9)
R		0.041	0.026	
$R(w)$		0.053	0.033	

The following equations have been used for the temperature factors:

isotropic: $T = \exp -8\pi^2 \cdot U \cdot (\sin\theta/\lambda)^2$

anisotropic: $T = \exp -2\pi^2 \cdot [U_{11}(h \cdot a^*)^2 + U_{12}hka^*b^* \ldots]$.

a^*, b^*, c^* are the basic vectors of the reciprocal lattice. The U-values are multiplied by 100.

The following relations hold:

$x = -1/3 \qquad y = -2/3$

$U_{11} = U_{22} = 2U_{12} \quad U_{13} = U_{23} = 0.$

The numbers in brackets are the standard deviations related to the last digit.

R and $R(w)$ are the normal and the weighted R-values:

$$R = \frac{\Sigma\,|F_0 - F_c|}{\Sigma\,F_0} \qquad R(w) = \frac{\Sigma\,w(F_0 - F_c)^2}{\Sigma\,wF_0^2}.$$

F_0, F_c are the observed, and the calculated structure amplitudes. w are the weights calculated from the counting statistics.

Table 3. Interatomic distances and angles

	AlN	
Al–N	1.9029	(14) Å
Al–N′	1.8891	(7) Å
N–Al–N′	110.80	(3)°
N′–Al–N′	108.11	(4)°
Mean	108.78	(2)°
	GaN	
Ga–N	1.952	(4) Å
Ga–N′	1.951	(1) Å
N–Ga–N′	109.24	(11)°
N′–Ga–N′	109.70	(8)°
Mean	109.59	(4)°

The numbers in the brackets are the standard deviations related to the last digit.

Atom designation: N : $-1/3 \quad -2/3 \quad z$

N′: $\left.\begin{matrix} -2/3 & -1/3 \\ -2/3 & -4/3 \\ 1/3 & -1/3 \end{matrix}\right\} z + \frac{1}{2}$

2. EXPERIMENTAL

The reflection intensities of an AlN and GaN crystal were collected with an automatic single crystal diffractometer. The lattice parameters were determined from the diffractometer angles of 25 reflections by a least squares program. The absorption was corrected by the Gaussian integration with the crystal shape described by its faces. The intensities and the X-ray paths in the crystal of symmetry equivalent reflections were averaged. Further details are listed in Table 1.

3. STRUCTURE REFINEMENT

The scattering curves of the neutral atoms and corrections of the anomalous dispersion were used for the structure refinements [14, 15]. The isotropic extinction was refined using the averaged X-ray paths [16]. The X-ray system has been used for the calculations [17].

The following weight system has been used:

$1/w$ = maximum of $[1/\sigma(F_0); 0.01F_0]$

where F_0 is the observed structure factor and $\sigma(F_0)$ is the standard deviation of F_0 calculated from the counting statistics of the intensity measurement. The R-values, atomic parameters, interatomic distances and angles are listed in Tables 2 and 3.

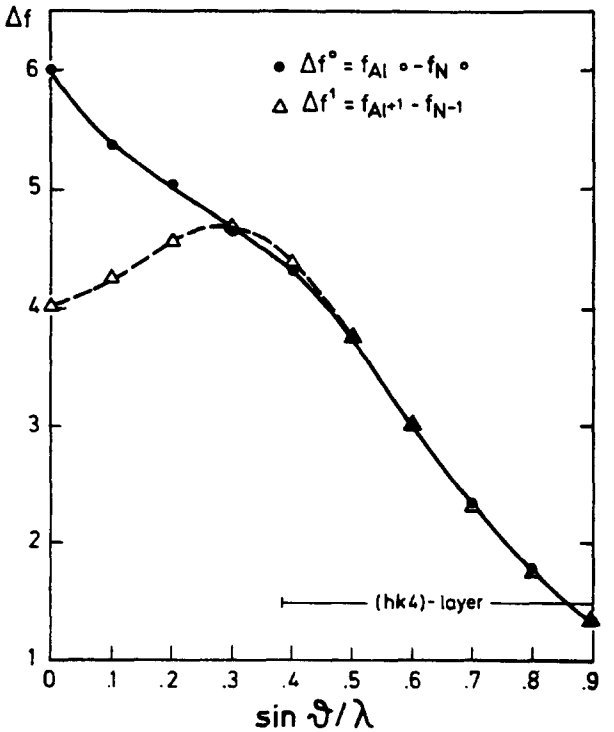

Fig. 1. The differences of the X-ray scattering curves for Ga and N are shown. The curves refer to the neutral and the one-fold charged atoms.

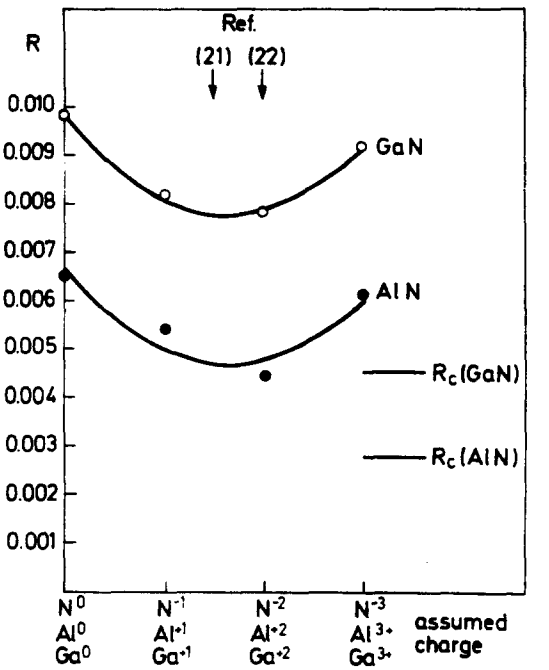

Fig. 2. Values of the reliability factors (R-factors) for the ($hk4$) reflections with $\sin\theta/\lambda < 0.7$ in dependence of the different scattering curves for Al^0N^0 to $Al^{3+}N^{3-}$ and Ga^0N^0 to $Ga^{3+}N^{3-}$. R has been calculated by $R = \Sigma|F_0 - F_c|/F_0$ where F_0 and F_c are the observed, and calculated structure amplitudes, respectively. The expected R-values (R_c) are calculated by replacing $|F_0 - F_c|$ by the standard deviations of the observed structure factors. The arrows mark the charges calculated in references [21] and [22].

4. DISCUSSION

For GaN we found nearly the ideal structure parameters [$c/a = 1.627\ (3)$, $u = 0.377\ (1)$]. The deviations are in the range of only two standard deviations. The u_c value calculated for equal tetrahedral distances is $u_c = 0.376$ (cf. Introduction). Therefore, the GaN distances have equal length and also the bond angles agree within three standard deviations with the values for a regular tetrahedron. AlN deviates significantly from the ideal parameters and its u [0.3821 (3)] is larger than the corresponding $u_c = 0.380$. Consequently the interatomic distances and angles differ significantly from each other by 0.01 Å and 3°, respectively (Table 3). Compared to the earlier investigations of c/a and u, there is a good agreement on the lattice constants, but there are significant differences between the u values [7, 10, 18]. Our u values are closer to the corresponding u_c values than those previously reported.

The thermal motion of the N atoms are higher than those of Al or Ga atoms. However, the differences between the isotropic mean square displacements are not very significant if their standard deviations are considered (Table 2). But there is an essential difference between the anisotropic temperature factors of AlN and GaN: whereas AlN shows an isotropic thermal motion, the mean square displacements in GaN are about two times larger when perpendicular than parallel to the c-axis. Anisotropic temperature factors for AlN and GaN were also determined by Sirota *et al.* [9, 10], and they are in disagreement with our results. They found a mean square displacement two to three times larger when parallel than perpendicular to the c-axis.

There seems to be a simple possibility to determine the static effective charge of the atoms in wurtzite-type structures which has already been mentioned by Ott [4]. The structure factors of the ($hk4$) layer are determined mainly by the difference of the scattering factors of the M and X atoms and by their temperature factors:

$$F_c(hk4) = f(M)T(M) - f(X)T(X)$$

where $f(M)$ and $f(X)$ are the atomic scattering factors of the M and X atoms, respectively and $T(M)$ and $T(X)$ are the temperature factors of the M and X atoms, respectively.

In Fig. 1 the differences Δf of the atomic scattering factors for Al^0-N^0 and $Al^{+1}-N^{-1}$ are shown. In addition, the sin θ/λ range of the ($hk4$) layer is marked.

In this range the maximum difference between these two curves is $df = 0.05e$ and the corresponding relative change $df/\Delta f = 0.012$. An expected agreement factor of the $l = 4$ layer can be calculated by

$$R_c = \sum \sigma(F_0) / \sum F_0$$

where F_0 are the observed structure amplitudes and $\sigma(F_0)$ is the standard deviation of F_0. R_c equals 0.011 and, therefore, for the $(hk4)$ layer

$$R_c \approx \Delta f / [f(\mathrm{Al}) - f(\mathrm{N})].$$

This situation is still more difficult for GaN: $\Delta f / [f(\mathrm{Ga}) - f(\mathrm{N})]$ is lower than for AlN.

In spite of these difficulties we refined our data with the scattering curves for Al^0–Al^{3+}, Ga^0–Ga^{3+} and N^0–N^{3-}. The atomic scattering factors for Al, N^0 and N^- were taken from Fukamachi [19]. The factors for N^{2-} and N^{3-} were calculated by extrapolation from N and N^-. The scattering factors for Ga were taken from the *International Tables for X-ray Crystallography* [20]. We used only the $(hk4)$ structure amplitudes with $\sin\theta/\lambda < 0.7$. We rescaled these F_0 and F_c values and calculated the R-values for the different scattering curves:

$$R = \frac{\sum^N |F_0 - F_c|}{\sum^N F_0}$$

where F_0 and F_c are the observed and calculated structure amplitudes and N is the number of observations.

The results are shown in Fig. 2 together with the corresponding R_c values. We have fitted these R-values by parabolic curves. They have their minimas at charges of 1.66 for AlN and 1.65 for GaN with an estimated error of 0.5. These results are in agreement with the static charges for AlN (1.36) and GaN (1.48) calculated by Harrison and Ciraci [21]. They agree also with the charges of about two for several II–VI and III–VI compounds, which were derived by Kunc and Bilz [22] from Raman spectra.

Looking over all results discussed in this section, we see no significant differences between the structures of AlN and GaN which can explain why these substances do not form mixed crystals.

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