Finally, we reiterate that the quantities referred to both here and in the ACA report as $|F|^2$ are uncorrected for extinction. Unlike the Lorentz and polarization factors and the correction for absorption, the correction for extinction is not calculable since it is a function of the unknown degree of perfection of the particular crystal being measured. Comparison of the mean values of $|F|^2$ in Table 4 with the data of Togawa (1964) and of Weiss *et al.* shows that the extinction correction for the strongest reflexions is a factor of about 5. For those contemplating an accuracy of ± 5% in $|F|^2$ this is indeed a sobering thought.

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Mean Square Vibration Displacements and Atomic Scattering Factors of Aluminum Nitride Ions

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Absolute values of the squares of the structure amplitudes of AlN were measured with monochromatic Cu $K\alpha$ radiation in the temperature interval 85–670°K in order to determine the mean square vibration displacements and atomic scattering factors of Al and N ions. From the F^2 data, the parameter U_0/c controlling the separation of Al and N ions along the c axis was determined as $0{\cdot}386 \pm 0{\cdot}001$ compared with 0·375 for the case of the ideal structure ($c/a = 1{\cdot}633$) and 0·380 for the case of equality of all the nearest interatomic distances (at $c/a = 1{\cdot}600$). Temperature studies have shown that in AlN anisotropy of mean square vibration displacements ($\overline{U^2}$) occurs. Thus, $\overline{U^2_{xy}} = (0{\cdot}30 \pm 0{\cdot}02)\,10^{-2}$ Å^2, $\overline{U^2_z} = (0{\cdot}65 \pm 0{\cdot}03)10^{-2}$ Å^2 for Al ion and $\overline{U^2_{xy}} = (0{\cdot}52 \pm 0{\cdot}02)10^{-2}$ Å^2, $\overline{U^2_z} = (1{\cdot}00 \pm 0{\cdot}03)10^{-2}$ Å^2 for N ion at room temperature. The coefficient of linear expansion (α) is also anisotropic. In the temperature range 298–670°K $\alpha_z = (3{\cdot}0 \pm 0{\cdot}2)10^{-6}$ deg^{-1} and $\alpha_{xy} = (3{\cdot}8 \pm 0{\cdot}2)10^{-6}$ deg^{-1}. The values of F^2_{exp} at absolute zero are given and compared with F^2_{theor}.

The intensity of X-ray diffraction spectra of AlN has been measured in the temperature interval 85–670°K with the purpose of determining the mean square vibration displacements and atomic scattering factors of Al and N ions. Monocrystal aluminum nitride was prepared in the form of 'whiskers' by the method of gas transport reaction with ammonia. Transparent single crystals ground in the jasper mortar were used for X-ray investigation. The transparency of the selected single crystals (whiskers) of AlN was indicative of the nearness of their composition to the stoichiometric one.

The investigations were carried out on flat polycrystal samples with particle sizes 2–3μ in a vacuum chamber. The total intensity of the X-ray primary beam was compared with the integrated intensities of reflexions. Intensities of X-ray diffraction spectra of aluminum nitride were measured with the use of monochromatic Cu $K\alpha$ radiation and a scintillation counter with discriminator. Monochromatization of the radiation was realized by means of a bent single crystal of germanium. The measurements were made by determining the pulse amount at counting rate for point-by-point displacement of the counter.

Absolute squares of structural amplitudes (Table 1) were determined from the data for the integrated intensities of reflexions related to the total intensity of the primary beam. The square of the structural amplitude is expressed in terms of the atomic scattering factor of ions of the compound investigated and the parameter U_0/c by

$$F^2=\left(f_{\mathrm{Al}}^2+f_{\mathrm{N}}^2+2f_{\mathrm{Al}}f_{\mathrm{N}}\cos 2\pi\frac{U_0}{c}l\right)$$
$$\times\frac{2}{3}\left\{3+(-1)^l\left[4\cos\frac{2\pi}{3}\,\frac{h-k}{2}\right.\right.$$
$$\left.\left.\times\cos\frac{2\pi}{3}\,\frac{2h+k}{2}\cos\frac{2\pi}{3}\,\frac{h+2k}{2}-1\right]\right\}$$
$$=\tilde{F}^2\,.\,n\,, \qquad (1)$$

where F^2 is the square of the structural amplitude, U_0 is the separation (in Å) of Al and N ions along the c axis, l is the Miller index, $\tilde{F}^2=F^2/n$ is the square of the reduced structural amplitude,

$$n=\frac{2}{3}\left\{3+(-1)^l\left[4\cos\frac{2\pi}{3}\,\frac{h-k}{2}\right.\right.$$
$$\left.\left.\times\cos\frac{2\pi}{3}\,\frac{2h+k}{2}\cos\frac{2\pi}{3}\,\frac{h+2k}{2}-1\right]\right\}.$$

In Fig. 1 the values of the squares of the reduced structure amplitude have been represented. They coincide well with the corresponding smooth curves at $l=0$, $l=1$, $l=3$ *etc.*

The value of the reduced-amplitude square is dependent on the atomic scattering factors of Al and N ions, f_{Al}, f_{N}, on U_0, the interatomic distance between the ions along the c axis, and on the l index, the difference ratio of the reduced structure amplitude value squares being a function only of U_0 for the indices $l=0$, $l=1$, $l=2$ and $l=3$:

$$\frac{\tilde{F}^2_{l=0}-\tilde{F}^2_{l=1}}{\tilde{F}^2_{l=2}-\tilde{F}^2_{l=3}}=\frac{1-\cos 2\pi\dfrac{U_0}{c}}{\cos 2\pi\dfrac{2U_0}{c}-\cos 2\pi\dfrac{3U_0}{c}}\,. \qquad (2)$$

The expression obtained is sensitive enough to the value of the parameter U_0 to allow the determination of U_0 without recourse to the complex procedure of Fourier series summation. The parameter U_0/c was determined by plotting U_0/c *versus*

$$\frac{1-\cos 2\pi U_0/c}{\cos 2\pi 2U_0/c-\cos 2\pi 3U_0/c}\,.$$

The values of $\tilde{F}^2$ for equation (2) were determined from the curves of Fig. 1 in the middle range of $H=2\sin\theta/\lambda$.

As the calculation showed, according to formula (2), U_0/c is equal to $0{\cdot}386\pm0{\cdot}001$ and is temperature independent within the experimental accuracy in the interval under investigation. Jeffrey, Parry & Mozzi (1956) quote the value 0·385. $U_0/c=0{\cdot}380$ for the case of equality of all the nearest distances between the atoms at $c/a=1{\cdot}600$, and for an ideal case ($c/a=1{\cdot}633$) it equals 0·375. It follows that the ion lying inside the tetrahedron in the AlN lattice is somewhat displaced to the base of the unit cell. The nearest spacing between Al and N ions calculated for $a=3{\cdot}111$ Å and $c=4{\cdot}978$ Å

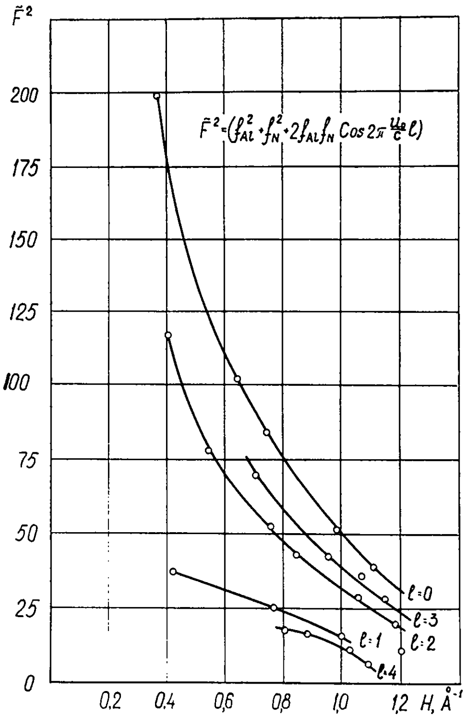

Fig. 1. The values of the squares of the reduced structure amplitudes of AlN at 19 °C ($H=2\sin\theta/\lambda$).

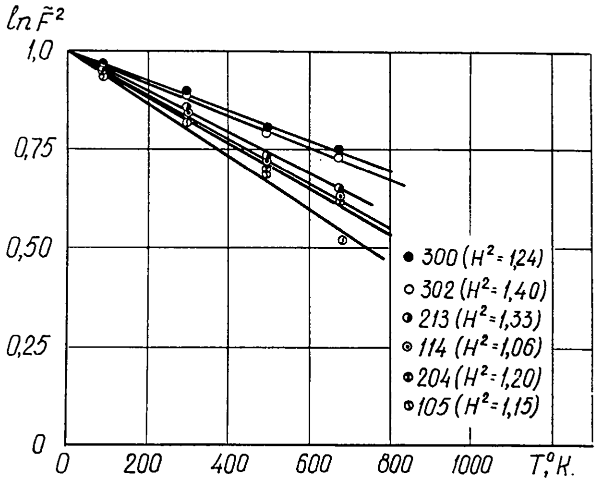

Fig. 2. Change of the reduced $\tilde{F}^2$ values with temperature ($H=2\sin\theta/\lambda$).

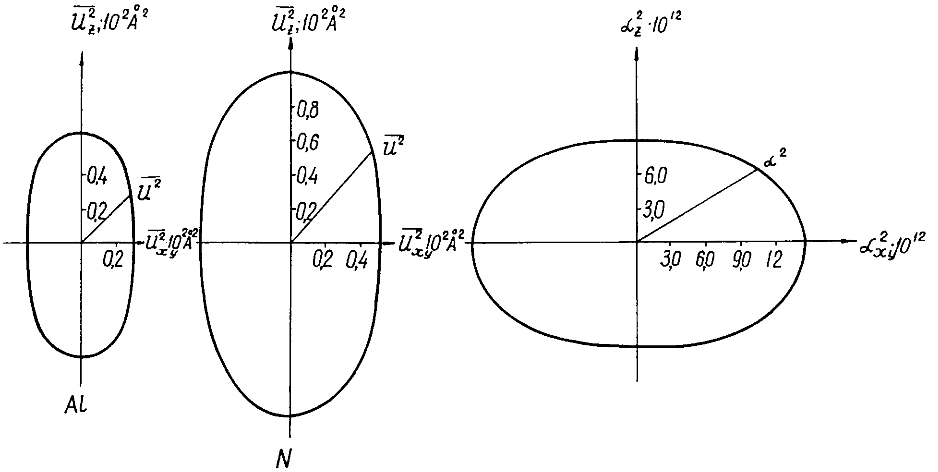

Fig. 3. Ellipsoids of mean square vibration displacements of (*a*) Al and (*b*) N ions (at 19 °C) and (*c*) of the square of the coefficient of linear expansion.

amount to 1·922 Å along the *c* axis and 1·883 Å in the three other directions. The parameters *a* and *c* of the unit cell measured by us turned out to be close to the data of Jeffrey *et al.*, being accurate to the third place of decimals.

Measurements of diffraction spectra intensity at different temperatures have shown that anisotropy of ion vibrations exists in the lattice of aluminum nitride. The lines with high value of the Miller index l have the maximum temperature effect and those at $l=0$ the minimum one (Fig. 2). This shows that ions oscillate with a larger amplitude in the *c* axis directions than in the base plane.

From the values of F^2 measured at different temperatures, mean square displacements of Al and N ions were calculated in two directions: along the *c* axis and in the base plane (Fig. 3).

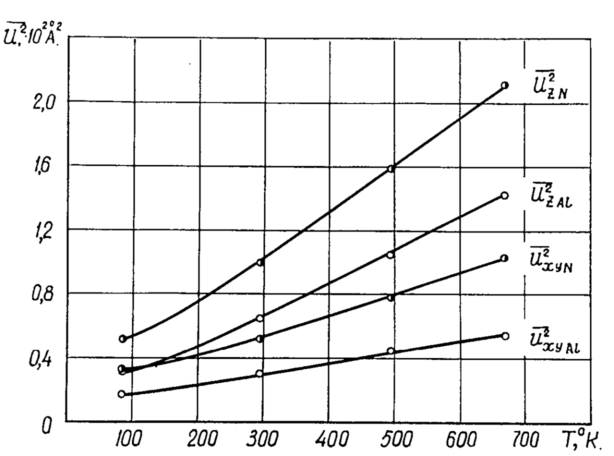

Fig. 4. Dependence of mean square vibration displacements of Al and N ions in the AlN lattice on temperature.

The values of the mean square displacements of the ions along the *c* axis are about twice as large as in the base plane. At room temperature

$$\left.\begin{aligned}\bar{U}_{xy}^2 &= 0{\cdot}30 \pm 0{\cdot}02 \times 10^{-2}\ \text{Å}^2\\ \bar{U}_z^2 &= 0{\cdot}65 \pm 0{\cdot}03 \times 10^{-2}\ \text{Å}^2\end{aligned}\right\}\quad \text{for Al}$$

and

$$\left.\begin{aligned}\bar{U}_{xy}^2 &= 0{\cdot}52 \pm 0{\cdot}02 \times 10^{-2}\ \text{Å}^2\\ \bar{U}_z^2 &= 1{\cdot}00 \pm 0{\cdot}03 \times 10^{-2}\ \text{Å}^2\end{aligned}\right\}\quad \text{for N}.$$

These correspond to the following values of the characteristic temperatures in Debye theory approximation:

$$\Theta_{xy} = 790\,,\ \Theta_z = 510 \quad \text{for aluminum;}$$
$$\Theta_{xy} = 850\,,\ \Theta_z = 580\,^\circ\text{K} \quad \text{for nitrogen}.$$

The temperature dependence of mean square vibration displacements is shown in Fig. 4. It should be noted that the ratios $\overline{U_z^2}/\overline{U_{xy}^2}$ increase with increasing temperature for Al and N ions. The measurement of the coefficient of linear expansion (α) by X-ray methods has shown that this coefficient, as well as the mean square vibration displacements, is anisotropic. In the temperature range 298–670 °K the coefficient of linear expansion (α_z) is equal to $(3{\cdot}0 \pm 0{\cdot}2)10^{-6}$ deg^{-1} along the *c* axis and $\alpha_{xy} = (3{\cdot}8 \pm 0{\cdot}2)10^{-6}$ deg^{-1} in the base plane. For the square of the coefficient of linear expansion the ellipsoid is elongated in the base plane [Fig. 3(*b*)].

Having determined the values of mean square vibration ion displacements of aluminum nitride, we have calculated the values of structure amplitudes at the absolute zero of temperature (Table 1); the values are shown in Fig. 5. The theoretical values calculated from f curves according to Hartree–Fock for Al and N neutral atoms (*International Tables for X-ray Crystallography*, 1962) are presented there for comparison.

Table 1. *Reduced values of the structure-amplitude square of aluminum nitride*

hkl	F^2 19°C	$\tilde{F}^2$ 19°C	*n*	$\tilde{F}^2$ 0°K	$\tilde{F}^2_{\text{theor}}$	$\frac{\lvert\tilde{F}^2_{\text{obs}}-\tilde{F}^2_{\text{theor}}\rvert\,100\%}{\tilde{F}^2_{\text{obs}}}$
010	199·0 ± 1·0	199·0 ± 1·0	1	203·0 ± 1·0	204·77	0·87
002	449·2 ± 2·8	112·3 ± 0·7	4	115·3 ± 0·7	115·96	0·58
011	113·1 ± 1·5	37·7 ± 0·5	3	37·8 ± 0·5	40·55	7·30
012	78·2 ± 0·8	78·2 ± 0·8	1	85·1 ± 0·9	87·40	2·70
110	411·6 ± 4·4	102·9 ± 1·1	4	111·7 ± 1·1	113·85	1·93
013	210·0 ± 2·1	70·0 ± 0·7	3	80·9 ± 0·7	82·61	2·11
020	84·3 ± 2·0	84·3 ± 2·0	1	92·9 ± 2·0	94·09	1·28
112	210·0 ± 0·8	52·5 ± 0·2	4	58·9 ± 0·2	60·25	2·28
021	76·5 ± 0·6	25·5 ± 0·2	3	27·8 ± 0·2	28·06	0·93
004	74·0 ± 7·6	18·5 ± 1·9	4	21·3 ± 2·0	20·30	4·58
022	43·2 ± 1·0	43·2 ± 1·0	1	48·6 ± 1·0	50·11	3·11
014	17·0 ± 1·3	17·0 ± 1·3	1	19·6 ± 1·3	17·94	8·15
023	128·4 ± 1·5	42·8 ± 0·5	3	51·6 ± 0·5	52·71	2·14
120	51·8 ± 0·7	51·8 ± 0·7	1	60·3 ± 0·7	60·84	0·90
121	50·1 ± 0·9	16·7 ± 0·3	3	18·6 ± 0·3	18·21	2·20
114	46·8 ± 1·6	11·7 ± 0·4	4	13·7 ± 0·4	13·70	0·0
122	29·2 ± 0·7	29·2 ± 0·7	1	35·3 ± 0·7	35·68	1·08
015	108·6 ± 2·1	36·2 ± 0·7	3	50·6 ± 0·7	50·25	0·69
024	9·5 ± 0·4	9·5 ± 0·4	1	11·4 ± 0·4	12·65	11·0
030	156·4 ± 3·2	39·1 ± 0·8	4	48·5 ± 0·8	48·02	0·99
123	86·4 ± 1·8	28·8 ± 0·6	3	38·6 ± 0·6	37·28	3·41
032	80·4 ± 1·6	20·1 ± 0·4	4	25·4 ± 0·4	28·34	11·5
006	44·8 ± 5·6	11·2 ± 1·4	4	16·4 ± 1·5	18·32	11·7

As can be seen from Table 1, good agreement is observed between them on the whole. However, it should be noted that the experimental value of F^2 for the 011 reflexion is somewhat lower than the theoretical one. Deviation of the experimental value of F^2 from the theoretical one for the 011 reflexion exceeds the measurement error by a factor of 5·5. For other reflexions the deviation is much smaller and does not exceed the doubled experimental error.

F^2 for the 011 reflexion is practically determined by the difference between the atomic scattering factors of Al and N ions and is observed at comparatively small values of $H=2\sin\theta/\lambda$, and it is therefore sensitive to the state of ions in the crystalline lattice. The observed difference in $\tilde{F}^2_{011}$ is probably due to the partial transition of the valence electron in the aluminum nitride lattice from aluminum to nitrogen (Sirota, Gololobov, Olekhnovich & Seleg, 1966).

The data obtained on vibration displacements of ions in AlN, as well as the value of structure factors, should be taken into account in considering the problem of interatomic bonding in aluminum nitride.

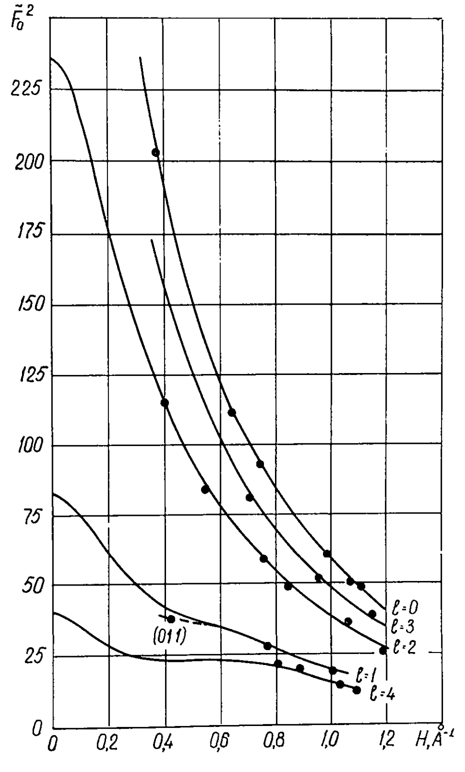

Fig. 5. The values of the square of the reduced structure amplitude at 0°K. Points represent experimental values, continuous lines the theoretical ones. ($H=2\sin\theta/\lambda$).

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