higher free energy than $MgAl_2O_4$ from the nitrate solution. The higher free energy will have higher surface energy and surface area is shown in Equation 2. This note shows that the higher sinterability of $MgAl_2O_4$ powder from the sulfate solution as opposed to nitrate solution is attributed to the higher surface area (smaller particle size), which predominantly controls the sintering of $MgAl_2O_4$, as shown in Equation 1.

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The structure of the X phase in the Si–Al–O–N alloys

Recently, several works [1–3] have been published concerning the question of the X (or X1) phase, which appears in hot-pressed Si–Al–O–N compounds within a considerably large part of the high temperature (1760° C) isothermal section of the phase diagram. The pure X phase is hard to obtain. The exact composition of the X phase is controversial – the concentration values obtained by different authors (e.g. [2–4]) range between 12 to 20 wt% Si, 19 to 26 wt% Al, 44 to 52 wt% O and 6 to 16 wt% N. There are, however, reasons to assume that this is a definite stoichiometric compound. Several attempts have been made to determine its crystal structure. The following results were published:

(i) Triclinic [1] with $a = 9.9$ Å, $b = 9.7$ Å, $c = 9.5$ Å, $\alpha = 109°$, $\beta = 95°$, $\gamma = 95°$
(ii) Orthorhombic [2] with $a = 7.85$ Å, $b = 9.12$ Å, $c = 7.965$ Å
(iii) Monoclinic [3] with $a = 9.728$ Å, $b = 8.404$ Å, $c = 9.572$ Å, $\beta = 108.96°$, in addition to some earlier, less definite suggestions.

Suggestions (ii) and (iii) were worked out by X-ray diffraction, while (i) was deduced tentatively from TEM data. Most interestingly, the three suggested structures have many low-index reflections in common. Table I shows the lists of lattice spacings (*d*-spacings) calculated from the given parameters. If we compare only the few low-index lines that could be observed by X-rays, we may assume that all the results actually belong to the same structure, which was interpreted wrongly in several different ways because insufficient data were used. This is actually proved below.

We examined hot-pressed specimens which were prepared from Si_3N_4, SiO_2 and Al_2O_3 powders (about 18, 32 and 50 wt% respectively) by pressing at 30×10^6 N m^{-2} and 1780° C for 90 min. They lie close to the compositions suggested by Gauckler [4] and Naik *et al.* [5] and have a nearly pure X structure (Fig. 1). Specimens for transmission electron microscopy were prepared by the conventional methods for ceramics (e.g. [1]). After ion milling they were coated on one side by sputtering with a gold layer (6 nm thick), for the purpose of enhancing the electrical conductivity of the specimen and for camera-constant calibration. The specimens were examined in a JEM 200A electron microscope operated at 200 kV.

Sets of consecutive electron diffraction patterns from an individual X grain could never be indexed to fit any of the suggested structures. The triclinic structure [1] gave a close match for some diffractions but could not explain a complete set of results. We shall now examine the method of deducing the lattice constants from basic electron diffractions. Using the three basic patterns ([1 0 0], [0 1 0] and [0 0 1] zone axes) with their

TABLE I d-values and indexing of the X phase according to three former suggestions and the structure published in this paper

Triclinic* [1]		Orthorhombic† [2]		Monoclinic‡ [3]		Triclinic – present work	
$a = 9.9$ Å, $\alpha = 109°$ $b = 9.7$ Å, $\beta = 95°$ $c = 9.5$ Å, $\gamma = 95°$		$a = 7.85$ Å $b = 9.12$ Å $c = 7.965$ Å		$a = 9.728$ Å, $\beta = 108.96°$ $b = 8.404$ Å $c = 9.572$ Å		$a = 8.56$ Å, $\alpha = 70°$ $b = 9.85$ Å, $\beta = 81°$ $c = 9.69$ Å, $\gamma = 81°$	
d (Å)	$h\,k\,l$	d (Å)	$h\,k\,l$	d (Å)	$h\,k\,l$	d (Å)	$h\,k\,l$
9.82	1 0 0						
9.11	0 1 0	9.12	0 1 0	9.20	1 0 0	9.20	0 1 0
				9.053(a)	0 0 1	9.05	0 0 1
8.95	0 0 1	See footnote(c)		8.404(c)	0 1 0	8.40	1 0 0
		7.965(a)	0 0 1				
7.81	$0\,1\,\bar{1}$	7.85(a)	1 0 0	7.853(a)	$1\,0\,\bar{1}$	7.853	0 1 1
7.11	$1\,\bar{1}\,0$						
7.03	$1\,0\,\bar{1}$						
						6.577	1 1 0
						6.526	1 0 1
						6.376	1 1 1
6.29	1 1 0						
6.22	1 0 1			6.205	1 1 0		
				6.159	0 1 1		
6.11	$1\,1\,\bar{1}$						
		5.999	0 1 1				
		5.950	1 1 0				
		5.90(b)				5.887	$1\,\bar{1}\,0$
						5.840	$1\,0\,\bar{1}$
				5.738	$1\,1\,\bar{1}$		
5.51	0 1 1	5.591(a)	1 0 1	5.606(a)	1 0 1	5.602	$0\,1\,\bar{1}$
						5.258	$\bar{1}\,1\,1$
5.14	$\bar{1}\,1\,1$						
4.75	$0\,2\,\bar{1}$	4.747	1 1 1	4.775	$2\,0\,\bar{1}$	4.776	$0\,2\,\bar{1}$

*calculated from parameters of [1].

†calculated from parameters of [2].

‡observed and calculated data from [3], with some additional reflections calculated from the same parameters.

(a) a calculated value which was also closely observed by X-ray diffraction in the respective work.

(b) 5.90 Å reflection was considered to fit (0 1 1) and (1 1 0). It seems to be too far from them, but in good agreement with ($1\,\bar{1}\,0$) of the new structure.

(c) 2.805 = 8.415/3 Å observed also by [2]; (0 3 0) line = 2.803 Å observed by [3].

measured α^*, β^* and γ^* angles† together with the well-known formula for angles between lattice planes in a triclinic structure [6], one gets a set of three symmetric equations of the form

$$\frac{\cos\beta\cos\gamma - \cos\alpha}{\sin\beta\sin\gamma} = \pm\cos\alpha^* \qquad (1)$$

for the unknown α, β, and γ angles. For a trial-and-error simultaneous solution of this set one should handle two cases which yield two different solutions. "Solution I" is obtained by taking all cosines (of α, β and γ) as negative or one of them negative and two positive. This solution was used by [1] and gave $\alpha = 109°$, $\beta = 95°$ and $\gamma = 95°$, when the measured values of α^*, β^* and γ^* were used (109, 96 and 96° respectively). "Solution II" is obtained by taking all cosines as positive or two of them as negative and it results in $\alpha = 70°$, $\beta = 81°$, $\gamma = 81°$ (or 110, 99, 81° etc.). The two solutions are not equivalent and not physically related, which means that only one of them is correct, while the other results from the use of insufficient data. Each solution, when combined

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†These are angles of the reciprocal unit cell, measured in the three basic diffraction patterns.

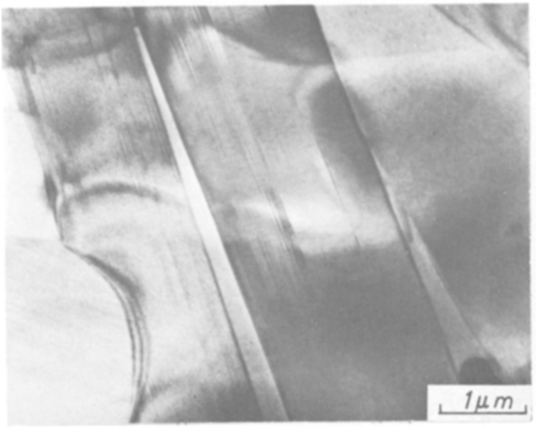

Figure 1 A typical X-phase microstructure (transmission electron micrograph).

with the measured basic d-spacings, results in different lattice parameters and a list of different d-spacings. Clearly, both solutions fit the basic diffraction patterns and, incidentally, to some additional patterns, but only the correct solution can fit all the observed data.

The present results, which were calibrated with the aid of the thin gold layer on the specimens, were

$$\frac{1}{|a^*|} = 8.4\,\text{Å}, \frac{1}{|b^*|} = 9.2\,\text{Å}, \frac{1}{|c^*|} = 9.05\,\text{Å}$$

$$\alpha^* = 109°, \beta^* = 96°, \gamma^* = 96° \dagger$$

Fig. 2 shows a [0 0 1] zone axis diffraction pattern with superimposed gold rings for calibration. Numerous other diffraction patterns, containing reflections also from planes with 3 non-zero indices, proved that "Solution II" is the correct one for the X phase. It yields, as mentioned above,

$$\alpha = 70°, \quad \beta = 81°, \quad \gamma = 81° (\pm 0.5°).$$

The respective lattice parameters are found, with the aid of the formula for interplanar spacings [6], to be‡

$$a = 8.56\,\text{Å}, \quad b = 9.85\,\text{Å}, \quad c = 9.69\,\text{Å}$$

A series of electron diffractions, which were all taken from the same X-phase grain by tilting the specimen around an axis perpendicular to the (0 1 0) plane, is given in Fig. 3. All the expected patterns appeared in such series, in the correct order and with the correct angles between their zone axes. Table II shows the good agreement between measured and calculated angles between the zone axes of Figs. 3a to e. The deviations were usually around 1° and did not exceed 2.5°.

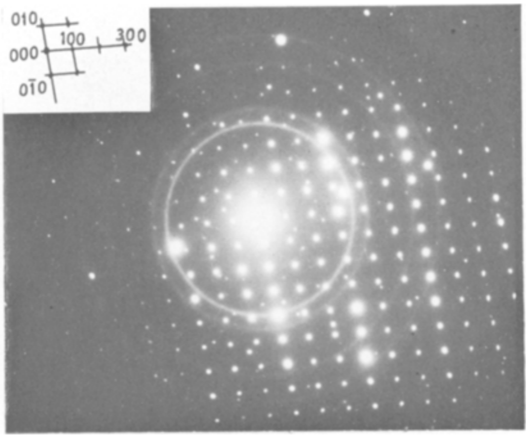

Figure 2 [0 0 1] zone axis electron diffraction pattern from an X-phase grain. The selected area includes a neighbouring (less reflecting) grain to incorporate the gold diffraction rings.

The upper part of the d-spacings list for the new structure is given in the last column of Table I. If we examine the X-ray observed diffraction lines, such as 9.05, 7.85, 5.90 and 5.60 Å, along with the structure found above, we can conclude that all the four works (the close correspondence of our data with those of Drew and Lewis was already noted above) definitely deal with the same X phase having the same triclinic crystal structure. This should suggest that X is a stoichiometric stable phase and that only one "second" phase exists in the phase diagram region in question.

TABLE II Measured angles between zone axes of consecutive diffraction patterns (Fig. 3), compared with calculated values

Pair of zone axes	Measured angle	Calculated angle
[1 0 0] – [4 0 $\bar{1}$]	17.0 ± 1°	16.3°
[4 0 $\bar{1}$] – [3 0 $\bar{1}$]	5.5 ± 1°	5.3°
[3 0 $\bar{1}$] – [2 0 $\bar{1}$]	10.0 ± 1°	9.9°
[2 0 $\bar{1}$] – [1 0 $\bar{1}$]	22.5 ± 1°	22.1°

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†In spite of the apparent differences in the values of the reciprocal parameters, one can show that these data are compatible with the basic diffraction patterns given in Fig. 1 of [1], which actually belong to the same phase.

‡These parameters, although not in accordance with the convention of negative cosines, were found to be convenient for further structure considerations of the phase. Reduction of the unit cell according to usual procedures yielded only other triclinic cells. One example is: $a = 11.21$ Å, $b = 9.69$ Å, $c = 8.56$ Å, $\alpha = 99°$, $\beta = 90°$ and $\gamma = 124°$ (± 0.5°).

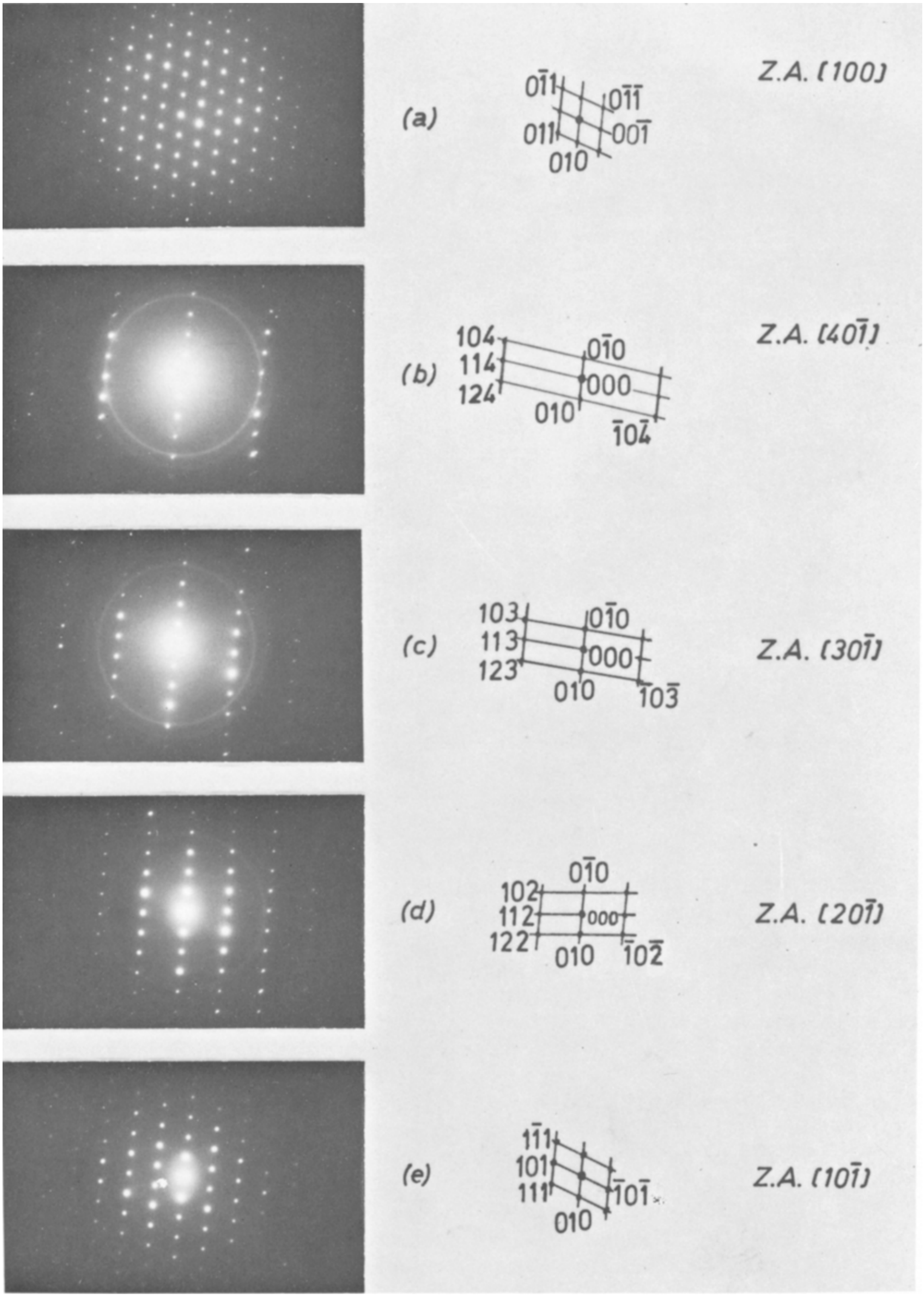

Figure 3 A series of electron diffraction patterns obtained from a single X grain by tilting around an axis perpendicular to (0 1 0). The "*x* tilt" and "*y* tilt" positions of the two tilting axes perpendicular to the beam were, respectively: (a) 21°50′, – 40°20′; (b) 12°30′, – 25°20′; (c) 9°30′, – 20°45′; (d) 3°30′, – 12°40′ and (e) – 124° (± 0.5°).

The twins which were reported by Drew and Lewis [1] were also observed in the present work (Fig. 1). They resulted in the appearance of typical twin diffraction patterns which could sometimes be interpreted as belonging to (0 1 1) twins. The observable types of 2-dimensional defects (probably twins) in the structure and also the atoms' arrangement in the structure are still under investigation. The strong (3 0 0) reflection (2.8 Å) which was observed in all the reported investigations (see Fig. 2 in this work and footnote under Table I) may lead to the assumption that a stacking of 3 layers, each containing $3n$ formula units, is involved ($n = 1, 2, 3\ldots$). This implies that $3n$ formula units should fit into the new 754 Å^3 unit cell. One adequate solution could be $Si_{10}Al_{15}O_{32}N_7$ recently found [5]. This composition can fit 3 times into the unit cell if a specific density of 2.9 is assumed. However, no definite conclusion concerning the possible compositions can be drawn at present.

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Solubility of hydrogen and bulk modulus in transition metals

Recently, the author [1] has shown that by correlating the heat of solution of hydrogen with spectroscopic data of neutral gaseous atoms, the solution process of hydrogen in the transition metals involves transfer of an s electron from the metal to hydrogen, or vice versa with changes in the electronic configuration of the metals.

There is, however, still controversy as to whether or not hydrogen dissolved in a metal has any effective size or whether chemical bonding effects are important. McQuillan [2] has suggested that interstitial atoms are too small to have any meaningful size. Ebisuzaki and O'Keeffe [3] has expressed a similar view. In contrast, however, several authors [4–7] have considered the size factor to be important. Oriani [8] has shown, from the calculation of partial molar volume of hydrogen in various metals, that the disturbance produced by the hydrogen can be very large, and that it varies from one lattice to another. The importance of considering volume changes in connection with the thermodynamic behaviour of solid solutions as a function of solute atom concentration has been pointed out by Wagner [9]. Armoult and McLellan [10] have measured the variation of Young's modulus of austenite produced by increasing the carbon content. The decrease in the Young's modulus was contrasted with the recent work of Wriedt and Oriani [11] on the effect of dissolved hydrogen on the Young's modulus of Ta, Nb, and V, in which the presence of interstitial species was found to increase linearly.

The purpose of this letter is to show that the heats of solution of hydrogen in metals can be correlated to the bulk modulus, which is a direct measure of the strength of bonding in metals. Considering the solubility of hydrogen in a metal, we write the equation of solution in the form