

The Crystal Structure of Nb_7P_4

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The crystal structure of Nb_7P_4 has been determined by single-crystal methods. The symmetry is monoclinic (space group $C2/m$) and the cell dimensions are $a = 14.950 \text{ \AA}$; $b = 3.440 \text{ \AA}$; $c = 13.848 \text{ \AA}$; $\beta = 104.74^\circ$. The unit cell contains 28 niobium and 16 phosphorus atoms. Two sets of 2 niobium atoms are situated in positions $2a$ and $2d$, respectively, while the remaining atoms occupy $4i$ positions. The structure can be described as a complex array of interconnected Nb_3P triangular prisms with additional niobium atoms situated in approximately cubic holes between the prisms. Various features of the structure are discussed in terms of size-factor principles. An interesting correlation between coordination number and thermal vibration for the niobium atoms is pointed out.

When mixtures of niobium and phosphorus are heated at temperatures below 1000°C the only intermediate phases formed are NbP and NbP_2 .¹⁻⁵ It was recently discovered, however, that several new phases are formed when mixtures of niobium and NbP are arc-melted.⁵

Unfortunately, the arc-melting process is accompanied by some loss of phosphorus, and the resulting ingots are generally inhomogeneous. It is therefore hardly possible to determine the phase relationships at high temperatures in the $\text{Nb}-\text{P}$ system solely by studies of arc-melted alloys. In order to examine the equilibrium conditions more closely, an investigation has been started at this Institute employing well-controlled annealing and quenching techniques at temperatures up to 2000°C , and the results will be reported later.

While the arc-melted alloys are less suitable for phase-analytical purposes, they may well serve as material for crystallographic studies, since they often contain well-developed single-crystals of the new phases. It was already mentioned in Ref. 5 that the compound Nb_3P has been identified in metal-rich alloys. A single-crystal structure refinement of Nb_3P has now been completed, and the results will soon be published.⁶

A structure determination of a new, monoclinic niobium phosphide is described in the present paper. Small, well-developed crystals of this compound were obtained from arc-melted alloys containing 30-40 at % phosphorus. It was not possible to collect crystals in sufficient amounts for ordinary chemical

analysis. The structure determination showed, however, that the ideal crystallographic formula is Nb_7P_4 . The structure analysis did not indicate any appreciable deviation from this formula, and, within experimental error, no changes of the unit cell dimensions were observed for material taken from alloys of different compositions. The new monoclinic phase is therefore denoted Nb_7P_4 .

THE STRUCTURE DETERMINATION OF Nb_7P_4

A preliminary X-ray investigation of the Nb_7P_4 crystals showed that the symmetry is monoclinic. The crystals were generally needle-shaped with the needle-axis coincident with the monoclinic axis. For the structure determination, a single-crystal fragment was cut from a long needle. The fragment was bounded by well-developed (100), (001), and (10 $\bar{2}$) planes, and by two rather smooth surfaces almost parallel to (010). The crystal measured approximately $0.05 \times 0.07 \times 0.08$ mm in the a , b , and c directions, respectively. It was mounted in a Weissenberg camera with the b axis as the rotation axis. The intensity material was recorded photographically with niobium-filtered MoK radiation. The multiple-film technique was used with thin iron foils interleaved between successive films. The intensities were estimated visually by comparison with an intensity scale prepared from timed exposures of one reflexion from the crystal.

Approximate unit cell dimensions were determined from the Weissenberg films. The cell was found to be centered. Using the symmetry information and the approximate unit cell dimensions obtained from the single crystal films, the lines were indexed on powder diffraction films taken with Guinier-Hägg type focussing cameras. Silicon ($a = 5.43054$ Å) was used as the internal calibration standard, and films were taken both with $\text{CuK}\alpha_1$ and $\text{CrK}\alpha_1$ radiation. After a least-squares refinement of the powder diffraction data (for details of the computer and the programmes used, see Table 1) the following unit cell dimensions and standard deviations were obtained:

$$a = 14.9503 \pm 0.0009 \text{ \AA}; b = 3.4398 \pm 0.0003 \text{ \AA}; c = 13.8478 \pm 0.0009 \text{ \AA}; \\ \beta = 104.743^\circ \pm 0.006^\circ.$$

Table 1. Programs used in performing the crystallographic calculations on a CDC 3600 computer. (All programs are written in FORTRAN IV).

Program	Authors
Least squares refinement of unit cell dimensions	J. Tegenfeldt, Uppsala, Sweden.
Lorentz-polarization and absorption corrections	P. Coppens, L. Leiserowitz and D. Rabinovich, Rehovoth, Israel; modified by O. Olofsson, Uppsala, Sweden.
Fourier summations, structure factor calculations	A. Zalkin, Berkeley, U.S.A.; modified by R. Liminga and J. O. Lundgren, Uppsala, Sweden.
Least squares refinements of positional parameters and temperature factors	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A.; modified by A. Zalkin, Berkeley, U.S.A. and by C.-I. Brändén, R. Liminga and J. O. Lundgren, Uppsala, Sweden.
Interatomic distances	A. Zalkin, Berkeley, U.S.A.

The only systematic extinctions observed among the reflexions were those arising from the *C*-centering. The possible space-groups are therefore *C2*, *Cm* or *C2/m*. Since the length of the *b* axis is only 3.440 Å, the position $4b$ in space group *Cm* as well as the positions $8j$ and $4e-4h$ in space group *C2/m* can be excluded for spatial reasons. After a careful visual inspection of the Weissenberg films it was concluded that the intensity ratio between corresponding (*hkl*) and (*hk + 2l*) reflexions was constant, allowing for the influence of the *Lp*-factor. This observation indicates that the atoms are confined to two planes perpendicular to the unique axis and spaced $b/2$ apart. If this restriction is imposed on the positions in space group *C2*, these positions must conform to the higher symmetry *2/m*. The space group problem is thus reduced to the choice between the two alternatives *Cm* (non-centrosymmetric) and *C2/m* (centrosymmetric). A statistical test according to Wilson⁷ gave no conclusive answer as to the presence of a centre of symmetry or not.

At this stage of the structure analysis, the composition of the compound was known only very approximately. A comparison of the unit cell volume with the cell volumes for Nb₃P, NbP, and Mo₄P₃ indicated a cell content of about 44 atoms, and the most likely composition seemed to be Nb₂₈P₁₆.

By using the intensity material from the two layer lines (*h0l*) and (*h1l*), the section *P(x0z)* of the Patterson function was calculated. (In this, and all further calculations mentioned below, a CDC 3600 computer was used employing programs listed in Table 1.) If all the atoms are distributed in two planes perpendicular to *b* and spaced $b/2$ apart, the section *P(x0z)* should contain all relevant maxima of the whole three-dimensional Patterson function.

In view of the result of the statistical test, and also on account of the extreme difficulties in locating possible Harker peaks, the Patterson section was analyzed without introducing any assumption of centrosymmetry. Only simple superposition methods were tried, and an arrangement of 14 twofold sets of niobium atoms was eventually found to explain the largest maxima in the Patterson map satisfactorily. This arrangement was, however, found to be centrosymmetric, and the 28 niobium atoms could be arranged in 2 twofold and 6 fourfold positions of the space group *C2/m*. By analysis of the available space, 4 fourfold positions for the phosphorus atoms were derived, and these positions were well confirmed by the presence of appropriate maxima in the Patterson function. At this stage, no significant maxima in the Patterson function remained to be explained.

The electron density section $\rho(x0z)$ was computed on the basis of the structure proposed, and maxima appeared with the expected locations and heights. It was therefore decided to proceed directly to a least squares refinement of the structure.

Before starting the refinement, the 845 *h0l* and the 779 *h1l* intensities measured were corrected for absorption (see Table 1). Absorption coefficients were obtained from Ref. 8. After a few preliminary refinement cycles it was found that the intensity material suffered severely from extinction effects. (These effects are probably to a certain extent responsible for the inconclusive result from the statistical test for centrosymmetry.) In order to decrease the influence of extinction, the 80 strongest low-angle reflexions were excluded from the subsequent refinements. For the remaining reflexions, weights were

assigned according to the formula $w = 1/(a + |F_o| + c |F_o|^2)$, following a suggestion by Cruickshank.⁹ After some adjustments based on weight analyses calculated after each cycle of refinement, the constants were finally given the following values: $a = 40$ and $c = 0.0070$. Atomic scattering factors (including the real part of the anomalous dispersion correction) were taken from Ref. 8. The following 34 parameters were refined: one scale factor for each of the $h0l$ and $h1l$ sets of reflexions, 20 positional parameters, and 12 isotropic temperature factors. The refinement converged rapidly, and after the last cycle, the remaining shifts were less than 5 % of the calculated standard deviations. The final R -value for the 1624 reflexions was 0.15, and, with the omission of the 80 strongest reflexions, the R -value was 0.101.

In view of the strong extinction effects, the agreement between observed and calculated structure factors was considered very satisfactory. The good agreement, and the rather uniform and normal magnitude of the temperature factors, indicate that the $C2/m$ symmetry is most probably correct. No attempt to refine the structure on the basis of a lower symmetry (Cm or $C2$) was therefore considered necessary. Furthermore, the results of the refinement show that the true composition of the crystal probably deviates very little from the ideal crystallographic formula Nb_7P_4 .

The final structure data for Nb_7P_4 are given in Table 2.

Table 2. Nb_7P_4 .

Space group $C2/m$; $Z = 4$.

$a = 14.9503 \pm 0.0009$ Å; $b = 3.4398 \pm 0.0003$ Å; $c = 13.8478 \pm 0.0009$ Å;
 $\beta = 104.743^\circ \pm 0.006^\circ$.

		x	$\sigma(x)$	z	$\sigma(z)$	B (Å ²)	$\sigma(B)$
Nb _I	in 2 a	—	—	—	—	0.175	0.015
Nb _{II}	in 2 d	—	—	—	—	0.175	0.015
Nb _{III}	in 4 i	0.43126	0.00008	0.82675	0.00009	0.268	0.012
Nb _{IV}	in 4 i	0.19530	0.00008	0.31188	0.00008	0.197	0.011
Nb _V	in 4 i	0.20981	0.00008	0.80030	0.00008	0.216	0.012
Nb _{VI}	in 4 i	0.33760	0.00008	0.02775	0.00009	0.271	0.012
Nb _{VII}	in 4 i	0.00322	0.00008	0.66537	0.00008	0.209	0.012
Nb _{VIII}	in 4 i	0.17502	0.00009	0.54042	0.00009	0.348	0.013
P _I	in 4 i	0.17403	0.00026	0.11243	0.00028	0.360	0.038
P _{II}	in 4 i	0.37360	0.00027	0.60229	0.00028	0.366	0.038
P _{III}	in 4 i	0.36956	0.00025	0.33571	0.00027	0.303	0.036
P _{IV}	in 4 i	0.06355	0.00025	0.84915	0.00026	0.270	0.035

Interatomic distances in Nb_7P_4 are given in Table 3. Lists of observed and calculated structure factors can be obtained from the Institute of Chemistry, Uppsala, on request.

DESCRIPTION AND DISCUSSION OF THE Nb_7P_4 STRUCTURE

A projection of the structure along the monoclinic axis is illustrated in Fig. 1. All the phosphorus atoms have a triangular prismatic environment of six niobium atoms, with 1—3 additional niobium neighbours situated outside

Table 3. Interatomic distances and their standard deviations (Å units) in Nb₇P₄. Distances shorter than 4 Å listed.

		Dist.	S.d.			Dist.	S.d.
Nb _I	— 2 P _{IV}	2.505	0.003	Nbv _{II}	— 1 Nb _{IV}	3.063	0.002
	— 2 P _I	2.671	0.004		— 1 Nb _V	3.177	0.002
	— 4 Nb _{III}	2.918	0.001		— 2 Nb _{III}	3.215	0.001
	— 4 Nb _{VI}	3.078	0.001		— 1 Nb _{VIII}	3.370	0.002
	— 2 Nb _I	3.440	0.000		— 2 Nb _{VII}	3.440	0.000
Nb _{II}	— 2 P _{III}	2.592	0.004	— 1 Nb _{VIII}	3.443	0.002	
	— 2 P _{II}	2.634	0.004	Nbv _{III}	— 2 P _{II}	2.581	0.003
	— 4 Nb _{VII}	2.855	0.001		— 2 P _{III}	2.632	0.003
	— 4 Nb _{VIII}	3.061	0.001		— 1 P _{II}	2.873	0.004
	— 2 Nb _{II}	3.440	0.000		— 2 Nb _{IV}	2.980	0.001
Nb _{III}	— 2 P _{IV}	2.579	0.003		— 2 Nb _{II}	3.061	0.001
	— 2 P _I	2.611	0.003	— 2 Nb _{VIII}	3.243	0.002	
	— 2 Nb _{IV}	2.894	0.001	— 1 Nb _{IV}	3.255	0.002	
	— 2 Nb _I	2.918	0.001	— 1 Nb _{VII}	3.370	0.002	
	— 1 P _{II}	3.007	0.004	— 2 Nb _{VIII}	3.440	0.000	
	— 2 Nb _{VII}	3.215	0.001	— 1 Nb _{VII}	3.443	0.002	
	— 1 Nb _V	3.237	0.002	— 1 Nb _V	3.503	0.002	
	— 1 Nb _{VI}	3.419	0.002	P _I	— 2 Nb _V	2.523	0.003
	— 2 Nb _{III}	3.440	0.000		— 2 Nb _{VI}	2.566	0.003
	— 1 Nb _{VI}	3.529	0.002		— 2 Nb _{III}	2.611	0.003
Nb _{IV}	— 2 P _{II}	2.461	0.003		— 1 Nb _I	2.671	0.004
	— 1 P _{III}	2.541	0.004		— 1 Nb _{IV}	2.699	0.004
	— 1 P _I	2.699	0.004	— 1 Nb _{VI}	2.969	0.004	
	— 2 Nb _{III}	2.894	0.001	— 2 P _I	3.440	0.000	
	— 2 Nb _V	2.916	0.001	— 1 P _{IV}	3.599	0.005	
	— 2 Nb _{VIII}	2.980	0.001	— 1 P _{III}	3.675	0.005	
	— 1 Nb _{VII}	3.063	0.002	— 1 P _{IV}	3.723	0.005	
	— 1 Nb _{VIII}	3.255	0.002	P _{II}	— 2 Nb _{IV}	2.461	0.003
	— 2 Nb _{IV}	3.440	0.000		— 2 Nb _{VII}	2.572	0.003
	— 1 P _{IV}	3.944	0.004		— 2 Nb _{VIII}	2.581	0.003
Nb _V	— 1 P _{IV}	2.448	0.004		— 1 Nb _{II}	2.634	0.004
	— 2 P _I	2.523	0.003		— 1 Nb _{VIII}	2.873	0.004
	— 2 P _{III}	2.603	0.003	— 1 Nb _{III}	3.007	0.004	
	— 2 Nb _{IV}	2.916	0.001	— 2 P _{II}	3.440	0.000	
	— 2 Nb _{VI}	3.160	0.001	— 1 P _{III}	3.677	0.005	
	— 1 Nb _{VII}	3.177	0.002	— 1 P _{III}	3.715	0.005	
	— 1 Nb _{III}	3.237	0.002	P _{III}	— 1 Nb _{IV}	2.541	0.004
	— 1 Nb _{VI}	3.242	0.002		— 2 Nb _{VII}	2.567	0.003
	— 2 Nb _V	3.440	0.000		— 1 Nb _{II}	2.592	0.004
	— 1 Nb _{VIII}	3.503	0.002		— 2 Nb _V	2.603	0.003
Nb _{VI}	— 2 P _I	2.566	0.003		— 2 Nb _{VIII}	2.632	0.003
	— 2 P _{IV}	2.601	0.003	— 2 P _{IV}	3.437	0.004	
	— 1 P _I	2.969	0.004	— 2 P _{III}	3.440	0.000	
	— 2 Nb _{VI}	3.063	0.002	— 1 P _I	3.675	0.005	
	— 2 Nb _I	3.078	0.001	— 1 P _{II}	3.677	0.005	
	— 2 Nb _V	3.160	0.001	— 1 P _{II}	3.715	0.005	
	— 1 Nb _V	3.242	0.002	P _{IV}	— 1 Nb _V	2.448	0.004
	— 1 Nb _{III}	3.419	0.002		— 1 Nb _{VII}	2.474	0.004
	— 2 Nb _{VI}	3.440	0.000		— 1 Nb _I	2.505	0.003
	— 1 Nb _{III}	3.529	0.002		— 2 Nb _{III}	2.579	0.003
Nb _{VII}	— 1 P _{IV}	2.474	0.004		— 2 Nb _{VI}	2.601	0.003
	— 2 P _{III}	2.567	0.003	— 2 P _{III}	3.437	0.004	
	— 2 P _{II}	2.572	0.003	— 2 P _{IV}	3.440	0.000	
	— 2 Nb _{II}	2.855	0.001	— 1 P _I	3.599	0.005	
				— 1 P _I	3.723	0.005	
			— 1 Nb _{IV}	3.944	0.004		

the quadrilateral faces of the prisms. The triangular faces of the P_I , P_{II} , and P_{III} prisms are parallel to (010), while the triangular faces of the P_{IV} prisms are perpendicular to this plane. The structure can be regarded as an array of interconnected Nb_6P triangular prisms (indicated by broken lines in Fig. 1) with additional niobium atoms (Nb_I and Nb_{II}) situated in slightly distorted cubic holes between the prisms. A very similar structural architecture is found for Ta_2P , the structure of which was recently determined by Nylund.¹⁰

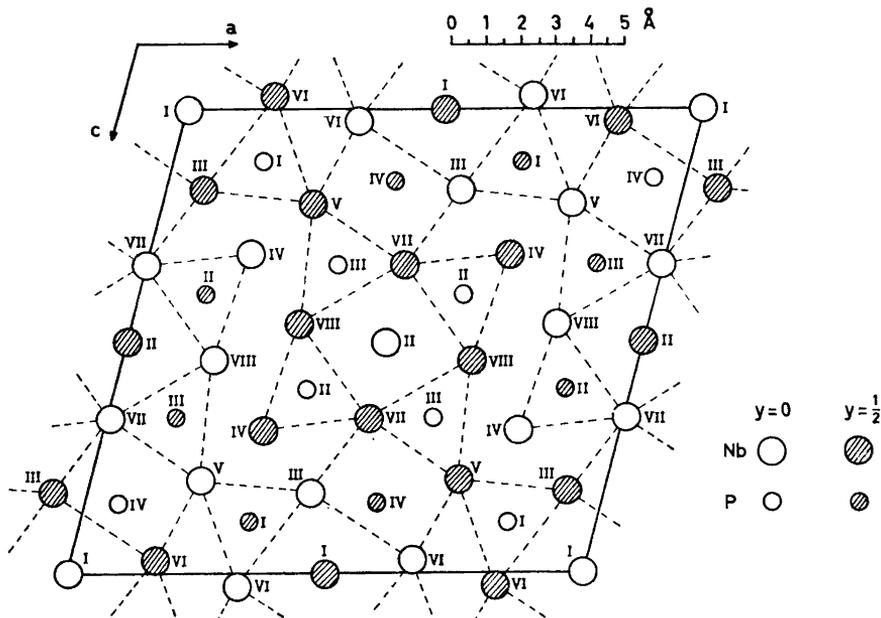


Fig. 1. The crystal structure of Nb_7P_4 projected on (010). The Nb_6P triangular prisms are indicated by broken lines.

The linkage of the prisms provides large distances between the phosphorus atoms, the shortest P—P distance exceeding 3.4 Å. The triangular prismatic metal coordination about phosphorus, and the large P—P distances, are both characteristic features for metal-rich transition metal phosphides. Some structural properties of these compounds have been discussed previously by the author¹¹ in terms of size-factor principles. In particular, the nine-coordination of metal atoms about phosphorus (the tetrakaidecahedral type of coordination) has been thoroughly analyzed on the basis of the radius ratio concept. In Nb_7P_4 , the two phosphorus atoms P_I and P_{II} possess this type of coordination, and a closer inspection of the various interatomic distances in the P_I and P_{II} coordination polyhedra reveals the features expected.

The radius of the niobium atoms is assumed to be 1.47 Å (the Goldschmidt metal radius for 12-coordination) and the radius of the phosphorus atoms 1.10 Å (the tetrahedral covalent radius). Using these values, and following the geo-

metrical reasoning as developed in Ref. 11, the average Nb—P distance within each Nb₆P prism (d_{AC}) should be 2.57 Å, while the average distance (d_{BC}) between the phosphorus atoms and the niobium atoms situated outside the quadrilateral faces should be 2.88 Å. The observed values for d_{AC} are 2.57 and 2.54 Å for the P_I and P_{II} polyhedra, respectively, and the corresponding values for d_{BC} are 2.78 and 2.84 Å. For P_{III} and P_{IV}, having eight and seven niobium neighbours, respectively, the Nb—P distances are more evenly distributed, ranging between 2.45 and 2.63 Å, and the average Nb—P distances, 2.59 Å for P_{III} and 2.54 Å for P_{IV}, are close to the radius sum of 2.57 Å. The nine shortest Nb—Nb distances within each Nb₆P prism should on average be about 14 % larger than the Goldschmidt diameter, and the observed values are 3.35, 3.30, 3.40, and 3.34 Å for the four different prisms as compared with the expected value of 3.36 Å. The niobium atoms situated outside the quadrilateral prism faces are expected to be in direct contact with the four niobium atoms at the corners of each face, and the average distance, 3.00 Å, is only 2 % larger than the Goldschmidt diameter of 2.94 Å. The distribution of interatomic distances in Nb₇P₄ is evidently largely in conformity with the size-factor principle.

The shortest Nb—Nb distances range between 2.86 and 3.53 Å; further Nb—Nb distances are larger than 4 Å. If, in the coordination spheres about the niobium atoms, Nb—Nb distances shorter than 3.6 Å and Nb—P distances shorter than 3.1 Å are taken into account, the coordination numbers for the niobium atoms in Nb₇P₄ are rather high, ranging from 14 to 17. Coordination numbers larger than 15 are not common with transition metal phosphides, and probably occur only for metal atoms from groups IV and V. An interesting correlation between the coordination number and the value B for the isotrop-

Table 4. Correlation between isotropic temperature factor values and atomic coordination for the crystallographically non-equivalent atoms in Nb₇P₄.

The standard deviations for the B values are less than 0.015 for the niobium atoms and less than 0.04 for the phosphorus atoms.

d_{Nb} = average distance between the central atom and its niobium neighbours; d_P = average distance between the central atom and its phosphorus neighbours. Nb—Nb distances shorter than 3.6 Å and Nb—P distances shorter than 3.1 Å are taken into account.

Central atom	Isotropic temperature factor B (Å ²)	Coordination number	d_{Nb} (Å)	d_P (Å)
Nb _{VIII}	0.348	17	3.252	2.660
Nb _{VI}	0.271	16	3.243	2.661
Nb _{III}	0.268	16	3.192	2.677
Nb _V	0.216	15	3.219	2.540
Nb _{VII}	0.209	15	3.207	2.550
Nb _{IV}	0.197	14	3.078	2.540
Nb _I	0.175	14	3.086	2.588
Nb _{II}	0.175	14	3.054	2.613
P _{II}	0.366	9	2.638	—
P _I	0.360	9	2.638	—
P _{III}	0.303	8	2.592	—
P _{IV}	0.270	7	2.541	—

ic temperature factor is shown by the values in Table 4. The B values may to a certain extent be influenced by the extinction effects mentioned in the description of the structure refinement. However, the results from least squares refinements carried out either with the inclusion or with the omission of the strong, low-angle reflexions, indicated that the temperature factors were very little affected by the extinction effects. When the strong reflexions were omitted, all B values increased by 0.03 \AA^2 or less, leaving their order relative to one another unchanged. This observation, and the fact that the intensity material was properly corrected for absorption, makes it reasonable to assume that the B values for Nb_{III} , Nb_{VI} , and Nb_{VIII} are in fact significantly larger than those for the remaining niobium atoms. Nb_{III} , Nb_{VI} , and Nb_{VIII} have the largest coordination numbers among the atoms in the structure. It is furthermore evident from the values in Table 4, that the average distances between these atoms and their neighbours are larger than those for the remaining niobium atoms. It thus appears that Nb_{III} , Nb_{VI} , and Nb_{VIII} are less tightly bound in the structure and are therefore more susceptible to thermal vibrations.

The correlation between coordination number and thermal vibration, which seems to have received very little attention previously, has also been observed in the case of the Mn_2P and Ni_2P structures,¹² and it is clearly manifested in the Fe_2P structure as indicated by the results from a study of the Mössbauer effect¹³ for Fe_2P .

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