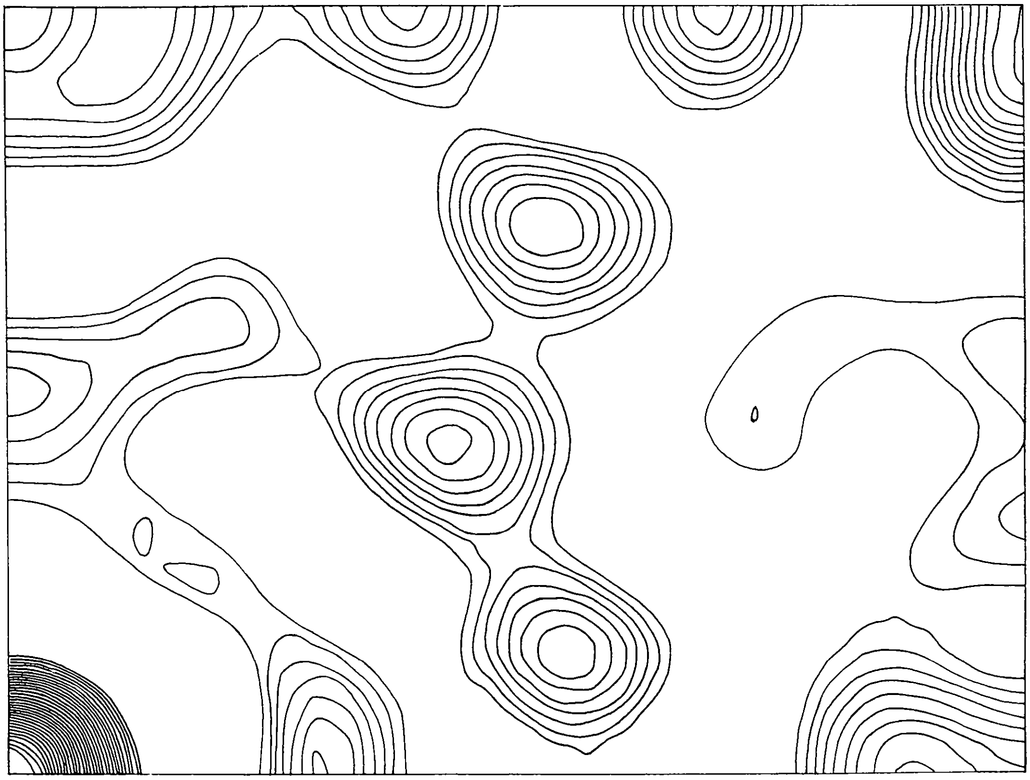

Fig. 2. Patterson function of a test structure.

tions shown in Fig. 1(*b*) may only be made on account of the use of linear interpolation in the determination of the points ϱ_c.

We give, as an example, the sharpened Patterson function of a test structure (*c* projection; $a = 8$, $b = 6$ Å; 4 C atoms, 1 Cl atom; space group $Pna2_1$) (Fig. 2). The calculation took 1·5 min for a lattice of 31 × 31 points and 33 different levels.

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X-ray evidence for $CrBO_3$, VBO_3 and $TiBO_3$ with calcite structure.

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In the course of preparations of boracites by gas phase transport reactions in sealed quartz tubes (Schmid, 1964) we also obtained several known and some new transition metal borates *via* the gas phase.

Here we want to report on a new chromium, vanadium, and titanium borate. The experimental conditions indicated in the following are not optimal for borate formation since they were chosen with a view to obtaining boracites. Nonetheless they may serve as a guide:

The chromium borate was obtained as follows: in a sealed quartz tube (volume 0·08 l) three quartz crucibles containing 0·76 g B_2O_3, 0·3 g (Cr_2O_3+Cr) and 0·67 g $CrCl_2$ respectively, were arranged, one above the other, and 175 mg H_2O in the form of H_3BO_3 was placed in the crucible containing Cr_2O_3+Cr. The sealed tube was heated in a vertical tubular furnace for four days in a small temperature gradient ($T_1 \sim 990$ °C, $T_2 \sim 1000$ °C) in such a way that the colder end of the tube was on top. The cooling to room temperature took 3 hours. In the crucible, containing B_2O_3, Cr–Cl–boracite had formed, and on the walls of the tube (coldest zone), hexagonal, grass-green platelets (about 0·05 mm thick and 0·5 mm in diameter) were detected. The crystals could easily be detached by dissolving the B_2O_3 film on the tube wall in boiling water.

The vanadium borate was formed as follows: three quartz crucibles containing 2·8 g B_2O_3, 1·34 g (V_2O_5+3V) and 2·54 g VCl_2 respectively, were placed in a quartz

Table 1. *Observed and calculated lattice spacings and visually estimated intensities for* $TiBO_3$, VBO_3, $CrBO_3$

Indices refer to the triply primitive hexagonal cell.
(The lattice spacings should be compared with those found by Bernal, Struck & White for $Fe_{0\cdot9}Ga_{0\cdot1}BO_3$: $a_H = 4\cdot631 \pm 0\cdot005$, $c_H = 14\cdot42 \pm 0\cdot01$, $a_R = 5\cdot496$ Å; $\alpha = 49° 38'$)

	$TiBO_3$			VBO_3			$CrBO_3$		
hkl	d_o	d_c	I_o	d_o	d_c	I_o	d_o	d_c	I_o
102	3·548	3·554	45	3·449	3·465	50	3·438	3·462	55
104	2·737	2·740	100	2·641	2·655	100	2·631	2·648	100
110	2·336	2·335	30	2·284	2·286	25	2·277	2·286	18
113	2·113	2·113	60	2·056	2·062	50	2·049	2·061	45
202	1·950	1·950	42	1·905	1·909	35	1·896	1·908	20
204	1·774	1·777	25	1·732	1·733	32	1·724	1·731	18
116	1·698	1·701	70	1·650	1·650	50	1·644	1·648	50
108		1·692		1·631	1·630	40	1·621	1·624	40
212	1·480	1·497	5	1·464	1·465	25	1·465	1·465	20
214	1·415	1·414	10	1·380	1·381	30	1·380	1·380	28
1,0,10	—	1·398	—	1·347	1·348	1	1·339	1·341	5
208	1·370	1·370	5	1·327	1·328	25	1·323	1·324	80
300	1·349	1·348	40	1·320	1·320	70	1·320	1·320	
119		1·351		1·306	1·306	35	1·301	1·301	10
0,0,12	1·242	1·242	30	1·194	1·193	60	1·187	1·187	60
2,0,10	1·200	1·200	10	1·162	1·160	20	1·157	1·156	25
218	1·181	1·181	40						

$TiBO_3$	VBO_3	$CrBO_3$
$a_H = 4\cdot670 \pm 0\cdot008$ Å	$a_H = 4\cdot573 \pm 0\cdot005$ Å	$a_H = 4\cdot573 \pm 0\cdot005$ Å
$c_H = 14\cdot90 \pm 0\cdot05$ Å	$c_H = 14\cdot32 \pm 0\cdot01$ Å	$c_H = 14\cdot23 \pm 0\cdot01$ Å
$a_R = 5\cdot65$ Å	$a_R = 5\cdot453$ Å	$a_R = 5\cdot434$ Å
$\alpha = 48° 48'$	$\alpha = 49° 24'$	$\alpha = 49° 46'$

tube (as above). The H_2O-dosis was 45 mg. The sealed tube was heated for 12 hours in a small gradient (5° per 20 cm) at about 900 °C, the colder end being on top. Cooling took 2 hours. In the quartz crucible, originally containing B_2O_3, hexagonal red brown (in transmitted light) platelets (dimensions like those of the chromium borate) had formed. No boracite was obtained, but small V_2O_3 crystals had formed on the walls of the tube.

The titanium borate was obtained as follows: the three quartz crucibles (as above) contained 2·8 g B_2O_3, 1·3 g TiO and 6·0 g TiI_2 respectively. The water dosis was 175 mg. The whole tube was maintained isothermal for 48 hours at 900 °C. Cooling took 3 hours. In the crucible, containing B_2O_3, hexagonal platelets, red brown in transmitted light and greenish dark brown as a bulk in reflected light, had formed. The crystal dimensions were like those of the chromium compound.

Chromium *Kα* powder diagrams of all new phases and Cu *Kα*-Weissenberg photographs of the chromium compound were made. We could show that all three compounds are isostructural and belong to the calcite type, as do the recently discovered iron borates with the general formula $Fe_{1-x}M_xBO_3$ (Bernal, Struck & White, 1963).

Although there was not sufficient substance for chemical analysis, the calculated and observed *d*-values and the visually estimated intensities (Table 1), compared with those of the iron borate, leave no doubt that we had to do with the borates $CrBO_3$, VBO_3 and $TiBO_3$.

The mechanisms of the transport of the oxides are not yet clear; probably halides and oxyhalides (*cf.* Schäfer, 1962) of higher metal valency than two, formed by disproportionation of the halides MX_2, were involved. As to further experimental details and a discussion of the B_2O_3 transport, the cited paper on boracites should be referred to.

The synthesis principle is quite generally applicable to borates, provided that a suitable transport reaction of the involved metal oxide can be found. An elaboration of the method seems therefore very promising for obtaining both single crystals and yet unknown compounds, *e.g.* $AlBO_3$, $GaBO_3$, *etc.*

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