opals, apart from glass-clear hyalites of low water content, showed discrete areas composed of close-packed aggregates of silica spheres of uniform size (Figs. 3 and 4). The diameter of the spheres is commonly in the range of 1500 Å–3500 Å.

The evidence presented here indicates a distinct break in structural properties between the two major groups of opals. It is believed that sufficient samples have been examined to indicate that this division is real, and may reflect differences in the genesis of the opals.

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CRYSTALLOGRAPHY

TiAs₂-type Phases

THE structure of $TiAs_2$, which is of a new type, has[8] recently been determined by Wenglowski *et al.*[1]. The orthorhombic unit cell contains eight formula units which comprise two kinds of titanium and four kinds of arsenic atoms. The co-ordination of Ti_I and Ti_{III} is very similar. Both have six As neighbours forming a trigonal prism and three more neighbours lying at the corners of a triangle perpendicular to the prism axis. The corners of this triangle are occupied by 3As in the case of Ti_I and by 2As + 1Ti_{III} in the case of Ti_{III}. As_I is located at the centre of a tetrahedron formed by 1Ti_{II} + 2Ti_{III} + 1As_I. As_{II} and As_{III} lie at the centre of a distorted tetrahedron of 3Ti_I + 1Ti_{III}. Finally, As_{IV} is placed at the centre of a trigonal prism of 2Ti_I + 4Ti_{III}, a co-ordination which is also found in α-TiAs (TiP type) and β-TiAs (NiAs type). This co-ordination immediately reveals that $TiAs_2$ must be metallic though its composition would suggest the possibility of a semi-conductor of ionic formula $Ti^{4+}(As_2)^{4-}$. However, only one of the four different arsenic atoms forms pairs, but half the cations are connected as well. Assuming single bonds between Ti_{II}–Ti_{II} and As_I–As_I, we are left with 44 anion valence electrons per unit cell for the cation-anion bonds which cannot be balanced by the 28 available cation electrons and thus induce metallic conductivity. My resistivity measurements in fact confirm these conclusions.

$TiAs_2$ seems to be the only arsenide of this structure type, $ZrAs_2$ (ref. 2) and $HfAs_2$ (ref. 3) crystallizing in the $C23$ type of structure. We found this structure, however, in two antimonides, $ZrSb_2$ and α-$HfSb_2$ (low-temperature modification). Their lattice constants are listed in Table 1 together with the data derived for $TiAs_2$. Though Wenglowski *et al.*[1] deduced from their tensimetric analysis the existence of a broad homogeneity range for $TiAs_2$, we could not detect a difference in the X-ray patterns of different samples of all three compounds. $ZrSb_2$ and $HfSb_2$ also show metallic conduction and a small p-type thermoelectric power. Since no localized d electrons are left on the cations, a temperature-independent dia- or para-magnetism is to be expected in these compounds.

There is little doubt that $ZrBi_2$, the lattice constants of which have been reported by Bykov and Kazarnikov[4],

also crystallizes in this structure. Our bismuthide samples did not allow a determination of the lattice constants but Guinier patterns give some indication that $HfBi_2$ is isostructural with $ZrBi_2$.

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Note added in proof. For $HfBi_2$, which in powder form is as strongly pyrophoric as $ZrBi_2$, I obtained the following lattice constants: $a = 15.7$ Å, $b = 10.1$ Å, $c = 3.93$, which are nearly the same as those of $ZrBi_2$ (ref. 4).

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CHEMISTRY

Chlorine Hyperfine Splittings in Phenoxy Free Radicals

HOLLOCHER *et al.*[1] have presented evidence for chlorine hyperfine splittings of the electron spin resonance spectrum of 2-hydroxy-1,4-naphthosemiquinone chloroderivatives. The observed splitting was quite small (0·28 gauss) and no attempt was made to present a value for a chlorine splitting constant. In order to obtain a larger splitting from the chlorine nuclear spin and perhaps also to obtain an estimate of the splitting constant, an electron spin resonance investigation of the chloroderivatives of phenoxy radicals was made. The electron spin resonance spectrum of the unsubstituted phenoxy radical has been obtained by Stone and Waters[2], using a flow apparatus[3] in order to detect this short-lived free radical. The electron spin resonance spectra of the free radicals of phenol, p-chlorophenol, 2,6-dichlorophenol and 2,4-dichlorophenol have been detected using a similar system and are reported here.

The compounds were obtained from K. and K. Laboratories and from Eastman Kodak, and were used without further purification as 10^{-3} molar aqueous solution. Free radicals were generated by oxidizing these compounds with an acidic solution of ceric ammonium sulphate, and detected with a Varian 4,500 X-band spectrometer.

The electron spin resonance spectra obtained are shown in Fig. 1, and the hyperfine splittings assigned to these spectra are listed in Table 1.

Table 1. HYPERFINE SPLITTINGS (GAUSS)

Radical	Doublet	Triplet	Sextet
Phenoxy	10·1	6·6	
		1·8	
p-Chlorophenoxy		6·6	1·9
2,6-Dichlorophenoxy	9·7		
2,4-Dichlorophenoxy	7·9		1·9

A comparison of the hyperfine splittings enables us to assign them to specific protons or chlorine atoms in the different ring positions. For example, the large doublet splitting (~ 10 gauss) occurs in the electron spin resonance spectra of the phenoxy, and 2,6-dichlorophenoxy, radicals but not in the other two. Hence, we can assign the 10 gauss splitting to the 4 position proton of the phenoxy radical.

Similarly, in the phenoxy and p-chlorophenoxy radicals, we have triplet splittings of 6·5 gauss, but in the splittings for the 2,4-dichlorophenoxy radical we have a doublet of 7·9 gauss. Although these are somewhat different, we feel that it is reasonable to assign this splitting to the 2 and 6 position protons.

We have then assigned splittings to each of the ring protons in the phenoxy radical; the next step is to evaluate

Table 1. LATTICE CONSTANTS OF TiAs₂-TYPE PHASES

	a (Å)	b (Å)	c (Å)
$ZrSb_2$	14.974 ± 14	9.968 ± 5	3.878 ± 3
α-$HfSb_2$	14.981 ± 12	9.869 ± 5	3.848 ± 3
$TiAs_2$	13.220 ± 8	8.915 ± 4	3.478 ± 2
	13·27 (ref. 1)	8·96 (ref. 1)	3·50 (ref. 1)