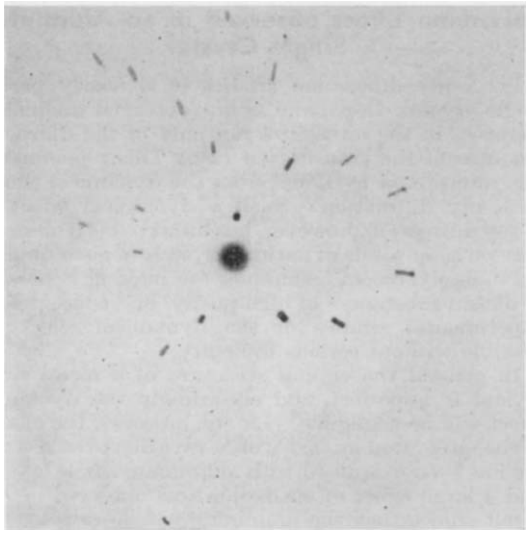

Fig. 2. X-ray photograph of an aluminium single crystal showing double spots

paper. It is clearly seen that each Laue spot is split into two parts. These correspond to an intense reflexion from the thin layer of either surface of the specimen[3]. The observation indicates a large extinction effect. Therefore it may be concluded that the Borrmann effect is also observable in an aluminium crystal of structurally good quality.

We are continuing our studies of the lattice defects of metals by using aluminium single crystals made by zone melting, and are expecting that the internal structure of the crystal will become observable more clearly with such materials of high purity.

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CHEMISTRY

The Silicon–Boron System

Recently the synthesis of a compound of the composition SiB_4 has been reported in two articles[1,2]. Concurrent with this work we have been investigating this compound as a part of our programme for studying high-temperature materials.

The compound was prepared in two different ways : (*a*) by sintering in an argon atmosphere a mixture of finely powdered boron (99 per cent purity) with amorphous silicon in an electrical resistance-type furnace ; (*b*) by melting a mixture of boron (about 10 per cent) and silicon (about 90 per cent) in a high-frequency induction furnace in an argon atmosphere. The last method usually gives very beautiful crystals of the new silicon boride (SiB_4) embedded in the silicon phase. The excess silicon was dissolved in a nitric acid–fluoric acid mixture.

By the first method of preparing the compound, we were able to study the behaviour of silicon–boron mixtures under various conditions. We have found that at temperatures between 1,200 and 1,380° C., the new compound is formed at first, but is then slowly decomposed into SiB_6 and silicon. At temperatures below 1,200° C. it is stable for long periods. The pure compound, apparently free from SiB_6 and silicon, has been prepared from the stoichiometric mixture heated at 1,200° C. for about three weeks in an argon atmosphere.

Several of our chemical analyses and density measurements indicate the formula SiB_4 (39·3 wt. per cent silicon). Some of our analyses, however, gave higher values of the silicon percentage (up to 48 wt. per cent silicon) and some density measurements also gave considerably higher values (up to 2·55 gm./cm.^{3}) than the one calculated for SiB_4 from our unit cell data : $a = 6{\cdot}319 \pm 0{\cdot}005$ Å. $b = 12{\cdot}713 \pm 0{\cdot}010$ Å. (2·43 gm./cm.^{3}). (Compare the result of Moissan's investigation[3] of apparently the same compound : formula SiB_3, density 2·52.) This suggests a fairly broad homogeneity range, which is also in accordance with the structural arrangements proposed by us. As a further support of this, we have noticed a small variation in relative line intensities from different samples.

From Weissenberg data a two-dimensional Patterson projection along the hexagonal *c*-axis was carried out. The result bears a close resemblance to the corresponding Patterson synthesis for CB_4 (ref. 4), and it would be reasonable to believe that the two compounds are isostructural. However, there are certain discrepancies, and therefore a three-dimensional Patterson synthesis was carried out. It shows that in the 0,0,*z*-position only two atoms are situated, about 2·4 Å. apart. The other atomic positions form icosahedrons in approximately the same manner as in CB_4. The atoms of an icosahedron are of two different sizes, the atoms forming the top and bottom of the icosahedron having higher electron density than the others.

A reasonable way to interpret these facts is the following. Consider the space group $R\bar{3}m$, formula SiB_4 with 9 molecules in the hexagonal cell. 6 of the 9 silicon atoms are placed in a 6c position, the other 3 silicon atoms and 15 boron atoms are statistically distributed over an $18h_1$ position ($x \approx 0{\cdot}11, z \approx 0{\cdot}87$), and 18 boron atoms are placed in an $18h_2$ position ($x = 1/6$, $z \approx 0{\cdot}02$). The remaining three boron atoms may be placed in interstitial positions or the composition may not be SiB_4. The presumed substitution of boron atoms by silicon atoms in $18h_1$ naturally gives room for a large variation of the composition.

In addition to the work on SiB_4, we have made some preliminary measurements on a part of the liquidus curve of the silicon–boron system. The result is given in Table 1. It is evident that there is a eutectic at about 3 per cent boron.

Table 1. Liquidus Temperatures of Silicon–Boron Mixtures

Weight per cent boron	Temperature of final disappearance of the solid phase (° C.)
0	1,420
1	1,415
2	1,408
3	1,403
4	1,411
5	1,414
6	1,420
7	1,432
8	1,431
9	1,421
10	1,431

The work on this liquidus curve and on the structure of SiB_4 will be continued. A three-dimensional Fourier synthesis is being carried out at the moment and the exact parameters will be published later.

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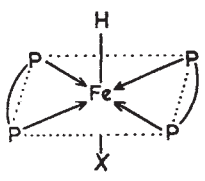
Some New Hydrides of Iron and Osmium

STABLE hydrido-complexes of the type *trans*-$[MHX(\text{phosphine})_n]$ (X = halogen or similar anionic ligand, phosphine = tertiary phosphine or chelate di-tertiary phosphine) containing the heavier transition metals ruthenium[1], osmium[1], palladium[2] and platinum[2] have been reported and a very unstable nickel derivative is also known[3]. Here we report the first stable derivatives containing a metal (iron) from the first transition series. These are interesting because the halo-hydrides (II) and (IV) show enormous chemical shifts in the proton resonance spectrum and because the hydride (I) was prepared from the metal and gaseous hydrogen. They have the *trans*-octahedral structure shown below and their properties are summarized in Table 1.

Table 1. PROPERTIES OF THE COMPLEX IRON HYDRIDES

Compound	m.p. (vacuum)	ν_{Fe-H}	δ_{Fe-H} ('Nujol' mulls)	ν_{Fe-D}	δ_{Fe-D}	Chemical shift (p.p.m., water standard)
(I)	248–252° dec.	1,726(*s*)	716(*m*)	1,259(*s*)	525(*m*)	+18·4 (C_6H_6)
(II)	154·5–155·5° dec.	1,849(*s*)	—	1,336(*s*)	—	+39·1 (C_6H_6)
(III)	180° dec.	1,810(*s*)	—	—	—	—
(IV)	dec. *c.* 220°	1,870(*s*)	—	—	—	+36·0 (C_6H_6)

Trans-$[FeH_2\{o\text{-}C_6H_4(PEt_2)_2\}_2]$ (I) is prepared by dissolving finely divided iron in the diphosphine, $o\text{-}C_6H_4(PEt_2)_2$, at 190° under hydrogen at atmospheric pressure, or by reducing *trans*-$[FeCl_2\{o\text{-}C_6H_4(PEt_2)_2\}_2]$ or $[FeCl_2\{o\text{-}C_6H_4(PEt_2)_2\}_2][FeCl_4]$ with excess lithium aluminium hydride. It is an orange crystalline substance, easily soluble in organic solvents, monomeric in boiling benzene, and thermally remarkably stable but very sensitive to air. The red crystalline hydrido-chlorides (II) and (III) are obtained by lithium aluminium hydride reduction of *trans*-$[FeCl_2(\text{diphosphine})_2]$, while (IV) is made by the reaction of *trans*-$[FeH_2\{o\text{-}C_6H_4(PEt_2)_2\}_2]$ with one equivalent of hydrochloric acid in dry ether.



(I) X = H, P—P = $o\text{-}C_6H_4(PEt_2)_2$
(II) X = Cl, P—P = $C_2H_4(PEt_2)_2$
(III) X = Cl, P—P = $C_2H_4(PMe_2)_2$
(IV) X = Cl, P—P = $o\text{-}C_6H_4(PEt_2)_2$

Trans-$[OsHCl\{C_2H_4(PEt_2)_2\}_2]$, which completes the first eutropic series of phosphino-hydrides, has also been prepared, and a comparison of properties is made in Table 2.

Table 2. SOME PROPERTIES OF *trans*-$[MHCl\{C_2H_4(PEt_2)_2\}_2]$ (M = FE, RU, OS)

M	m.p. (vacuum)	Colour	Dipole moment (±0·2 D)	ν_{M-H} ('Nujol' mull)	Chemical shift (p.p.m., water standard)
Fe	154·5–155·5 dec.	red	4·25	1,849	+39·1 (C_6H_6)
Ru	174·5–176	colourless	4·9	1,944	+27·1 ($CHCl_3$) +26·1 (C_6H_6)
Os	170·5–171·5	colourless	4·6	2,051	+31·3 ($CHCl_3$)

It will be noted that ν_{M-H} increases by 202 cm.$^{-1}$ on passing from M = iron to M = osmium, corresponding to about 24 per cent increase in bond-strength (force constant) on ascending the series. This is also the sequence of increasing thermal stabilities.

The chemical shift of the proton resonance in compound (II) is the largest ever recorded. It is even greater than the shift of the proton resonance in water relative to the unshielded proton (27 p.p.m.).

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Gas Liquid Chromatography of Conjugated Fatty Acids

THE heating of polyunsaturated fatty acids in strong alkali is known to cause re-arrangement of the double bonds to form a conjugated system[1]. The effect of this isomerization on the behaviour of polyunsaturated fatty acids in gas liquid chromatography has been studied in relation to linoleic and linolenic acids as found in wheat flour oil.

Oil was extracted by shaking the flour continuously for 2 hr. with carbon tetrachloride under nitrogen. The extract was filtered to remove flour particles and the solvent removed under vacuum in a rotary evaporator. Unconjugated fatty acids were prepared by saponification of the oil under nitrogen with 0·5 *N* methanolic potassium hydroxide, refluxing for 2 hr. Following acidification and ether extraction, the free fatty acids were methylated by reaction with diazomethane[2].

Conjugated fatty acids were prepared by an adaptation of the alkaline isomerization method[3] for analysis of unsaturated fatty acids. The oil was heated in a solution of 6·6 per cent potassium hydroxide in ethylene glycol at 180° C. for 25 min. under a stream of oxygen-free nitrogen. The mixture was cooled, diluted with water and acidified, when the isomerized free fatty acids were extracted with ether. The fatty acids were methylated as before by reaction with diazomethane.

The mixed methyl esters were analysed with a Pye argon chromatograph using a column packed with 2·3 per cent poly(ethyleneglycol adipate) as stationary phase on 60–100 mesh diatomaceous earth (M. and B. 'Embacel'). The chromatograms of the