220. *High-temperature Phase Equilibria in the System Dicalcium Silicate–Tricalcium Phosphate.*

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High-temperature phase equilibria in the system $2CaO,SiO_2$—$3CaO,P_2O_5$ have been investigated by high-temperature microscopy and *X*-ray analysis. The system presents a continuous series of solid solutions with a melting-point maximum at 2240°, contradicting earlier findings. A new high-temperature form of $3CaO,P_2O_5$ has been discovered which does not survive quenching to room temperature, but is completely miscible with the α form of $2CaO,SiO_2$. At lower temperatures two compounds are formed by solid-state reactions, the known silicocarnotite stable below 1450° and a new phase, denoted as " A," stable below 1125°, having the approximate composition $7CaO,P_2O_5,2SiO_2$. Powder *X*-ray measurements are given for each phase in the system, either as obtained in a specially designed high-temperature *X*-ray camera or, where appropriate, as recorded at room temperature in a focusing camera.

The section $2CaO,SiO_2$—$3CaO,P_2O_5$ in the ternary system $CaO–SiO_2–P_2O_5$, which is relevant to processes in the steel, cement, and fertiliser industries, has been examined [1-5] with widely differing conclusions. This divergency can be attributed to the experimental

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[1] Trömel, *Stahl und Eisen*, 1943, **63**, 21.
[2] Barrett and McCaughey, *Amer. Mineralogist*, 1942, **27**, 680.
[3] Bredig, *J. Phys. Chem.*, 1942, **46**, 747.
[4] Trömel, Harkort, and Hotop, *Z. anorg. Chem.*, 1948, **256**, 253.
[5] Berak and Wojciechowska, *Roczniki Chem.*, 1956, **30**, 757.

difficulties. There are two main problems. First, as the liquidus temperatures over a large part of the system exceed 2000° C, accurate temperature measurement and detection of the liquidus are difficult. For instance, observation of external collapse of a specimen during heating, while a guide to the solidus temperature in the absence of impurities, provides a very unreliable indication of the liquidus. Trömel *et al.*[4] tried to obtain a more exact indication of the liquidus by stirring their melts with an iridium wire, but they make no pretensions to very great accuracy with this method. Secondly, reliance was placed on *X*-ray identification of quenched materials in the belief that rapid cooling would preserve the equilibrium products present at high temperature. At the outset it became apparent that this technique, although widely employed, is not applicable to the system $2CaO,SiO_2$—$3CaO,P_2O_5$ since some of the phases do not survive quenching. These difficulties were overcome.

EXPERIMENTAL

We adopted a method of high-temperature microscopy, which permits continuous observation of the behaviour of melts, described by Welch.[6] It employs a small electrically heated thermocouple to serve as specimen holder, heater, and thermometer. The couple is mounted on the stage of a polarising microscope used to study the material at the junction. The highest temperature attainable with the original apparatus with platinum–rhodium thermocouples (20% Rh, 80% Pt/40% Rh, 60% Pt) is 1880°, which is below the liquidus temperature in much of the present system.

Much higher temperatures were achieved with a tungsten–molybdenum thermocouple but although such couples are easily made, and oxidation can be prevented by use of an argon atmosphere, these highly reactive metals are attacked by the materials to be examined. The technique finally adopted was basically that described by Welch and Gutt,[7] the thermocouple being replaced by a heating element of pure iridium in a gas-tight cell through which dry argon circulated.

Further improvements concern the method of measuring the temperature of the heater. This was recorded in terms of r.m.s. current through it, the relation between current and temperature being established at the m. p.s of pure compounds such as Al_2O_3, MgO,Al_2O_3, and CaO,SiO_2. The use of optical pyrometry was explored but the disappearing filament pyrometer had to be sighted through the glass window of the cell housing the heater, and even slight clouding of this by volatilised substances seriously affected the measurements. However, this method was used to check the accuracy of the current calibration as follows: the brightness temperature at the m. p. (taken as 2454° * [8]) of the iridium heater, as observed through the glass window, was measurod, and the effective spectral emissivity calculated by the relationship:

$$\frac{1}{T} - \frac{1}{S} = \frac{\lambda\ (\log e_\lambda)}{0{\cdot}4343c_2}$$

where T = true temperature (°K), S = brightness temperature (°K), $\lambda = 0{\cdot}65\ \mu$, $c_2 = 14{,}320\ \mu$ deg., e_λ = spectral emissivity at wavelength λ. If we assume that over the measurable range of brightness temperature this value of emissivity remains constant, the corresponding true temperature could similarly be derived from any brightness temperature. It was thus possible to check directly the m. p.s of a number of pure oxides, and for the great majority the agreement was within ±10° of the values in the literature. This check confirmed the validity of assuming a constant value of emissivity for the iridium heater, and at the same time indicated which of the pure oxide preparations gave the most reproducible m. p.s for calibration.

Volatilisation was considered; depending on the initial composition differential loss of either P_2O_5 or CaO could occur during thermal treatment. For instance, after several minutes' heating, $2CaO,P_2O_5$ changes into $3CaO,P_2O_5$ through loss of P_2O_5, but in a few hours' heating $4CaO,P_2O_5$ loses lime, also becoming $3CaO,P_2O_5$. $3CaO,P_2O_5$ appeared to be particularly

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* All temperatures given in this paper refer to the International Temperature Scale of 1927.

[6] Welch, *J. Sci. Instr.*, 1954, **31**, 458.
[7] Welch and Gutt, *J. Amer. Ceramic Soc.*, 1959, in the press.
[8] Henning and Wensel, *Bur. Stand. J. Res.*, 1933, **10**, 809.

stable. To test the volatilising behaviour of the $3CaO,P_2O_5$–$2CaO,SiO_2$ mixes, specimens of composition close to the highest-melting mixes were melted on the iridium wire, and maintained above the m. p. for a period considerably exceeding that needed for liquidus determination. By repetition enough material was collected for analysis which showed that the composition had not changed.

The dynamic method of optical examination used permitted the determination of the liquidus, that is, the temperature at which the smallest observable crystal could be maintained in the melt without growth or decay. It was also possible to recognise the occurrence of polymorphic transformations and optical changes occurring during cooling or heating of compositions within the system. There remained however the problem of identifying the unquenchable phases and of exploring the temperature region below about 1000° where some of the materials became opaque and changes occurring on further cooling could not be followed optically. In order to follow more closely the sub-solidus phase relations the heated stage equipment was adapted to form the basis of an *X*-ray camera capable of recording powder diffraction patterns up to 1850°. This has been described fully elsewhere;[9] essential data are under Table 1.

TABLE 1. *Characteristic X-ray powder measurements for the high-temperature continuous solid solution series* $2CaO,SiO_2$—$3CaO,P_2O_5$.

$2CaO,SiO_2$ ...	100		94·4		91·6		83·3		80		75·9		69·0	
$3CaO,P_2O_5$ ...	0		5·6		8·4		16·7		20		24·1		31·0	
Temp.	1550°		1450°		1350°		1500°		1500°		1500°		1500°	
	d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
	4·00	1	4·03	1	4·00	1	4·03	1	4·00	2	3·97	2	3·95	2
	3·63	1	3·67	1	3·69	1			3·71	2	3·69	4	3·69	1
	2·89	5	2·91	8	2·91	8	2·91	5	2·91	4	2·90	8	2·90	6
	2·74	4	2·76	8	2·77	8	2·75	4	2·75	5	2·73	7	2·73	6
	1·99	1	2·00	4					2·00	3	1·99	4	1·99	2

$2CaO,SiO_2$ ...	66·0		62·5		56·4		50·7		45·6		40·4	
$3CaO,P_2O_5$ ...	34·0		37·5		43·6		49·3		54·4		59·6	
Temp.	1200°		1500°		1500°		1500°		1500°		1500°	
	d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
	3·95	3	4·00	2	4·03	2	3·99	3	3·99	3	4·00	3
	3·64	2	3·74	1	3·78	1	3·75	2	3·77	1	3·80	1
	2·88	8	2·93	8	2·97	6	2·94	8	2·95	8	2·94	8
	2·72	7	2·74	2	2·76	5	2·73	7	2·73	7	2·72	7
			1·99	2			2·00	5	2·00	4	1·99	1

$2CaO,SiO_2$ ...	34·9		27·4		19·2		12·2		5·8		0	
$3CaO,P_2O_5$ ...	65·1		72·6		80·8		87·8		94·2		100	
Temp.	1500°		1550°		1400°		1500°		1500°		1500°	
	d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
	3·98	4	4·03	4	3·98	3	3·97	4	3·96	4	3·96	8
			3·83	1	3·81	1			3·83	1	3·84	1
	2·94	6	2·97	7	2·94	8	2·95	6	2·95	8	2·96	10
	2·70	4	2·73	5	2·71	7	2·69	5	2·67	6	2·68	9
	1·99	3	1·96	1			1·98	1	1·98	2	1·98	6

Compositions are % w/w. The high-temperature camera had diam. 102 mm., and Cu-K_α radiation was used. Interplanar spacings (*d*) are given in Å. Relative intensities (*I*) are estimated visually on an arbitrary scale from 1 (very weak) to 10 (very strong).

The mixes were prepared from crushed quartz (99·95% pure), calcium carbonate (99·9% pure), and $2CaO,P_2O_5$ ($\nless$99·9% pure) made from "AnalaR" phosphoric acid and $CaCO_3$. The powdered materials, which had been screened through a 100-mesh sieve, were mixed dry and ignited in platinum boats at 1000° and subsequently at 1550° in an electric furnace for 20 hr.

RESULTS AND DISCUSSION

The liquidus curve, determined with the thermocouple up to 1880° and on the iridium wire at higher temperatures, is shown in the Figure. In contradiction to the views of earlier

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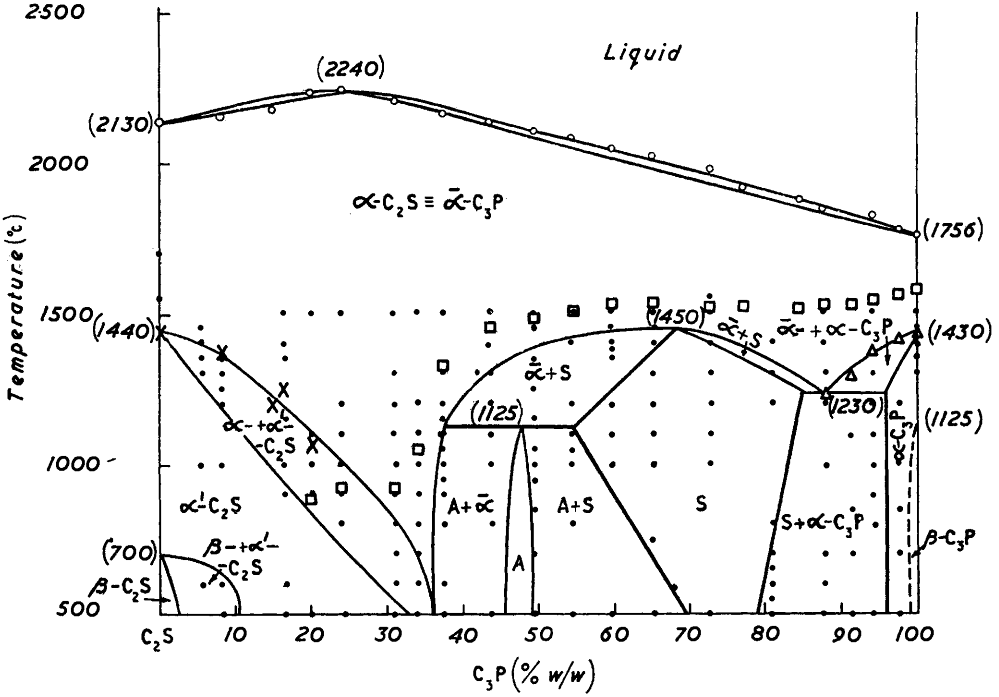
[9] Aruja, Welch, and Gutt, *J. Sci. Instr.*, 1959, **36**, 16.

workers already mentioned, the system presents a continuous series of solid solutions with a m. p. maximum of 2240° at 24% of $3CaO,P_2O_5$. The solidus curve was more difficult to establish. First, it is known that traces of impurity depress the temperature of initial melting far more markedly than the liquidus temperature; secondly, the readiness with which the first traces of liquid could be observed made it difficult to distinguish between slight initial liquid formation due to impurities, and the onset of a major degree of melting, signifying that the real solidus temperature had been reached. In addition, the calibration curve of the iridium heater was based on temperatures at which the last surviving crystals could be maintained at the centre of the melt, whereas the temperature gradient in the specimen first formed liquid at points closest to the wire. This problem was dealt with by Welch and Gutt,[7] who described a possible method of correction. However, we have not included the experimental determinations of the solidus as they were not considered to be sufficiently reproducible. Accordingly a hypothetical solidus curve is shown on the phase diagram. The maximum in the liquidus curve indicates a tendency towards compound formation and the X-ray investigation at lower temperatures confirms the existence of two compounds.

The system $2CaO,SiO_2(C_2S)$–$3CaO,P_2O_5(C_3P)$.



○ Liquidus temperature. □ Temperature of minimum birefringence.
△ Temperature of $\bar{\alpha} \longrightarrow \alpha$ transition of $3CaO,P_2O_5$, by optical determination.
× Temperature of $\alpha \longrightarrow \alpha'$ transition of $2CaO,SiO_2$, by optical determination.
● Points at which determinations were made with the high-temperature X-ray camera.

A is a new phase, and S is silicocarnotite.

Also shown in the Figure are certain optical observations made during heating and cooling below the m. p. When $3CaO,P_2O_5$ cooled from the m. p. (1756°) the birefringence first decreased to a minimum (1577°) whereat the specimen appeared isotropic and the sign of elongation changed. On further cooling the birefringence increased slowly until an abrupt increase took place at about 1430°. This was followed by a further gradual increase usually accompanied by cracking due to thermal shock as room temperature was approached. The temperatures of the minimum and the sudden increase in birefringence were fully reproducible. Examination of compositions lying on the join $2CaO,SiO_2$–$3CaO,P_2O_5$ revealed that the sudden increase in birefringence could be observed up to 12% of $2CaO,SiO_2$ at successively lower temperatures. The minimum birefringence stage was observable with all compositions up to 80% of $2CaO,SiO_2$. At this composition the temperature of the minimum was lower than for pure $3CaO,P_2O_5$. There was a continuous tendency for the temperature of the minimum to fall as the $2CaO,SiO_2$ content increased. Its value for individual compositions was fully reproducible and was best determined after cooling the specimen from above the liquidus as rapidly as possible, in order to prevent fractional recrystallisation. This method of cooling also minimised cracking; when this occurred the birefringence minimum was less easily seen in the fragments.

With pure $2CaO,SiO_2$ the polymorphic inversions from α to α' and then to β could be seen. The former was particularly striking, being accompanied by an overall contraction of the material as well as by a marked change in birefringence. The α' to β inversion was characterised by a slight increase in birefringence readily observable provided the orientation of the crystals was favourable. The β—γ transformation, when it occurred, was characterised by abrupt opacification and distintegration. As $3CaO,P_2O_5$ was added the temperature of the α—α' inversion was lowered, reaching the lowest value observable with certainty at 20% of $3CaO,P_2O_5$. This composition was also the richest in $2CaO,SiO_2$ which exhibited the minimum in birefringence (Figure).

The sudden increase in birefringence for $3CaO,P_2O_5$ is regarded as coincident with a transformation from a hitherto unobserved higher-temperature form (hereafter called super-α-$3CaO,P_2O_5$) into what was previously regarded as the highest-temperature form (α-$3CaO,P_2O_5$). Super-α-$3CaO,P_2O_5$ cannot be preserved at room temperature. In order not to cause confusion with the $2CaO,SiO_2$ series of inversions this new $3CaO,P_2O_5$ phase will be written as $\bar{\alpha}$-$3CaO,P_2O_5$.

The minimum birefringence is not considered as indicating a polymorphic transformation, but as arising through a differential thermal expansion in two crystallographic directions. Its significance was that in the early stages of this work it suggested that a continuous phase existed over a portion of the system represented by all previous investigators as having a discontinuity of the solid phase. These views are supported by *X*-ray analysis in the high-temperature camera. The patterns obtained at 1500° with all the compositions lying on the join $2CaO,SiO_2$–$3CaO,P_2O_5$ were consistent with the behaviour of a continuous series of solid solutions. These patterns, which were essentially of the same type, were characterised by two strong lines whose separation increased systematically as $2CaO,SiO_2$ was added to $3CaO,P_2O_5$. The *d* values for the five strongest lines recorded at high temperatures over the entire composition range are given in Table 1. Two additional lines, of medium intensity at 3·1 Å and 3·5 Å (not shown), were also observed over the limited composition range 49—72% of $3CaO,P_2O_5$.

Apart from the inversions already described, dusting of the material during cooling was observed on the hot stage in the composition range 50—90% of $3CaO,P_2O_5$, the specimen simultaneously becoming opaque. *X*-Ray analysis of the dust showed that this change was associated with the formation of silicocarnotite. To establish the phase relations at the lower temperatures a systematic *X*-ray analysis was carried out in the high-temperature camera, the temperatures and compositions being chosen on the basis of the microscopical information. Additional high-temperature powder diffraction data for the intermediate polymorphs of pure $2CaO,SiO_2$ and $3CaO,P_2O_5$ are given in Table 2.

In order to ensure the closest possible approach to equilibrium, the *X*-ray analysis was pursued through successively higher temperatures, preparations heated at 1550° for 20 hr. and then annealed at 500° for 70 hr. being used as starting materials. It was realised that this procedure might incur risk of superheating if the inversions were sluggish, but there was no evidence that this occurred. The ignition for 20 hr. at 1550° made most mixes homogeneous, but in the region of highest liquidus temperatures there were indications of inhomogeneity in the final product. Therefore, for mixes in this region ignition at 1550° was followed by melting on the iridium wire and quenching when fully molten before annealing at 500°. Before *X*-ray analysis in the high-temperature camera all the mixes were *X*-rayed at room temperature in a focusing camera.

TABLE 2. *High-temperature camera powder measurements for intermediate polymorphs of* 2CaO,SiO$_2$ *and* 3CaO,P$_2$O$_5$.

α'-2CaO,SiO$_2$ at 1350°		β-2CaO,SiO$_2$ at 600°		α-3CaO,P$_2$O$_5$ at 1400°		α'-2CaO,SiO$_2$ at 1350°		β-2CaO,SiO$_2$ at 600°		α-3CaO,P$_2$O$_5$ at 1400°	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
3·91	1	3·82	1	7·44	4	2·32	2	2·42	1 *	2·96	7
3·42	1	3·21	1	6·40	1	2·27	1	2·28	2	2·91	1
3·20	2	3·07	1	5·28	1	2·23	1	2·18	2	2·66	5
2·91	2	2·88	2	4·05	1	2·22	2	2·02	1	2·62	4
2·88	2	2·82	1	3·95	6			2·00	1	2·21	1
2·79	8	2·78	8	3·86	1			1·80	1	1·97	1
2·76	8	2·74	7	3·74	5					1·93	1
2·40	1	2·64	6	3·05	1						

* Broad line. Camera data and symbols as for Table 1.

In general the establishment of equilibrium below 500° required inordinately long heat treatment, and the investigation at lower temperatures was not continued.

The Figure shows that both silicocarnotite and a new phase " A " exist as homogeneous solid solutions over a range of composition that varies with temperature. Above 1450° silicocarnotite inverts without decomposition into an $\bar{\alpha}$-3CaO,P$_2$O$_5$ solid solution, and the previously accepted composition 5CaO,P$_2$O$_5$,SiO$_2$ for silicocarnotite lies close to the composition range now determined for this phase.

Phase " A " has the approximate composition 7CaO,P$_2$O$_5$,2SiO$_2$, but should not be confused with the mineral of the same composition identified by Nagelschmidt.[10] Lea and Nurse [11] obtained from a quenched preparation of 7CaO,P$_2$O$_5$,2SiO$_2$ an *X*-ray pattern which they identified with nagelschmidtite, but which can now be recognised as also containing a minority of the " A " phase. After annealing this preparation they observed a change in relative intensities in the *X*-ray pattern which they ascribed to the partial formation of a low-temperature phase. The *X*-ray pattern of their annealed preparation shows it to be a mixture of the " A " phase with some unchanged nagelschmidtite. Nagelschmidtite and Trömel's phase " R " both have the structure associated with the continuous high-temperature solid-solution series α-2CaO,SiO$_2$—$\bar{\alpha}$-3CaO,P$_2$O$_5$, and to avoid confusion in nomenclature the term nagelschmidtite could be extended to describe the entire α-2CaO,SiO$_2$—$\bar{\alpha}$-3CaO,P$_2$O$_5$ solid solution range. In the region of 35% of 3CaO,P$_2$O$_5$ these solid solutions are stable as low as 700°; in the presence of impurities the stability field may well extend to room temperature.

Although the highest-temperature form of both the end-members of the solid solution series, *i.e.*, pure α-2CaO,SiO$_2$ or pure $\bar{\alpha}$-3CaO,P$_2$O$_5$, do not survive quenching to room temperature, it is possible to quench the highest-temperature form of the solid solution substantially free from other phases within a very narrow region of composition at about 35% of 3CaO,P$_2$O$_5$ in the present system; focusing-camera measurements for this material are given in Table 3. Compositions slightly richer in 2CaO,SiO$_2$ yield mainly the α'-2CaO,SiO$_2$ phase after quenching, while appreciable quantities of the " A " phase are present after quenching compositions slightly richer in 3CaO,P$_2$O$_5$. The " A " phase decomposes above 1125° into an $\bar{\alpha}$-3CaO,P$_2$O$_5$ solid solution richer in 2CaO,SiO$_2$, and silicocarnotite. Included in Table 3 are focusing-camera measurements for the " A " phase and

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[10] Nagelschmidt, *J.*, 1937, 865.

[11] Lea and Nurse, Ministry of Supply Monograph No. 11/108, 1951, p. 72.

for silicocarnotite. Below 500° there must be a region in which α'-$2CaO,SiO_2$ and " A " co-exist, which could not be determined because crystallisation rates are too slow.

The inversion from β- to α-$3CaO,P_2O_5$ at 1125° was determined from heating curves. The course of the β—α inversion curve could not be detected experimentally, but it must fall steeply with increasing $2CaO,SiO_2$ content since the mix containing 2·8% of $2CaO,SiO_2$ was stabilised in the α-form after the standard annealing at 500°. The polymorphic transformation temperatures for pure $2CaO,SiO_2$ shown in the Figure are those deduced from earlier work by Welch (see Nurse [12]). The stability field for γ-$2CaO,SiO_2$ above 500° is too small to be reproduced satisfactorily, and is omitted. The stability relations between the γ-, β-, and α'-modifications of $2CaO,SiO_2$ have already been discussed by Nurse [12] and by Roy.[13]

TABLE 3. *Room-temperature X-ray powder measurements for $\bar{\alpha}$-type, "A," and silicocarnotite phases respectively, of the compositions indicated.*

34% $3CaO,P_2O_5$ 66% $2CaO,SiO_2$		49·3% $3CaO,P_2O_5$ 30·7% $2CaO,SiO_2$		72·6% $3CaO,P_2O_5$ 27·4% $2CaO,SiO_2$		72·6% $3CaO,P_2O_5$ 27·4% $2CaO,SiO_2$	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
3·931	5	4·26	1	8·56	2	2·37	1
3·582	3	4·04	1	7·82	1	2·29	3
3·500	3 *	3·49	4	5·65	1	2·27	3
2·910	1	3·14	6	5·29	1	2·22	1
2·843	10	3·00	8	4·55	2	2·17	3
2·710	10	2·91	4	4·05	2	2·03	2
2·342	2	2·64	5	3·92	3	2·01	2
2·226	5	2·52	4	3·87	2	1·96	3
1·959	7	2·37	2	3·80	1	1·94	2 *
1·912	1 *	2·31	1	3·59	2	1·88	4
1·863	1 *	2·29	1	3·29	3	1·87	2
1·784	4	2·23	1 *	3·19	4	1·85	2
1·760	1	2·21	1	3·09	2	1·81	3
1·667	3	2·02	1	3·02	3	1·80	1
1·588	5	1·88	6 †	2·96	4	1·78	2
1·563	4	1·86	4	2·82	8	1·75	4
1·489	4	1·78	3	2·80	2	1·68	1
1·431	1	1·72	1	2·72	1	1·64	1
1·420	1	1·62	1	2·60	5	1·53	3
1·352	3	1·40	1	2·58	4	1·50	2
1·267	2			2·53	2	1·45	1
1·221	2 *			2·46	1		

Measurements obtained in a Guinier type focusing camera, 114 mm. diam. with Cu-K_α radiation.
* Broad line. † Doublet. Other symbols as for Table 1.

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[12] Nurse, " Proc. 3rd Intern. Symposium on the Chemistry of Cement 1952," Cement and Concrete Association, London, 1954, p. 56.
[13] Roy, *J. Amer. Ceramic Soc.*, 1958, **71**, 293.