An X-ray investigation of synthetic pyroxenes in the system acmite–diopside–water at 1000 kg/cm² water-vapour pressure

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Summary.—An X-ray investigation has been made of synthetic pyroxenes in the system acmite–diopside, crystallized at 750° C and 1000 kg/cm² water-vapour pressure. Lattice parameters of these pyroxenes have been determined by least squares analyses of powder diffraction patterns and show an approximately linear relationship with composition, plotted as weight per cent. A rapid X-ray method has also been devised for the determination of the compositions of pyroxenes of this series.

T HE lattice parameters of synthetic pyroxenes in the system acmite–diopside have been determined at a water-vapour pressure of 1000 kg/cm² and a temperature of 750° C. This system has been previously investigated by Yagi (1958) who has shown on the basis of optical data that these pyroxenes form a complete solid solution series. Pure diopside was first synthesized by Allen and White (1909). More recently indexed d values of synthetic diopside have been published by Yoder (1950), and the lattice parameters by Sakata (1957). Acmite was first synthesized pure by Bowen and Schairer (1929) but to the author's knowledge no reliably indexed pattern of pure acmite has yet been published.

This paper presents the results of an investigation of the lattice parameters of pyroxenes varying in composition from pure acmite $(NaFeSi_2O_6)$ to pure diopside $(CaMgSi_2O_6)$ as determined from X-ray diffraction patterns. A least squares analysis, performed on a Mercury computer, has been used to calculate the parameters.

The results show that an approximately linear relationship exists between the lattice parameters and composition (weight per cent) in this series. An X-ray method based on the separation between prominent peaks on the diffraction patterns has been devised for the rapid determination of synthetic pyroxenes in this series; at first sight it would appear that the determinative curves could provide a simple method of obtaining the approximate compositions of natural alkali pyroxenes that contain a significant amount of the acmite component, but since the effect of the hedenbergite component on the lattice parameters of acmite is similar to that of diopside, and most natural alkali pyroxenes contain some hedenbergite, the curves given cannot be used to determine the composition of the natural minerals.

Experimental methods. Compositions were made up at 10 weight per cent intervals between the two end members. The method used for preparing homogeneous powders of the required composition was a modification of that proposed by Roy (1956). The materials used were:

SiO_2. Tetra ethyl orthosilicate, $(C_2H_5)_4SiO_4$, was kindly provided by Monsanto Chemicals Ltd. Several experiments were carried out to determine the average yield of SiO_2 by gelling a known weight of $(C_2H_5)_4SiO_4$ with 0·88 ammonia solution, the average yield being 99·7 % of the calculated amount. The deficiency is probably due to a small amount of ethyl alcohol; a correction was made to the required weight of $(C_2H_5)_4SiO_4$ to allow for this.

Na_2O. Sodium carbonate of 'Analar' grade was used as a source of Na_2O.

CaO. 'Analar' calcium carbonate was used as a source of CaO.

Fe_2O_3. 'Pure Iron' No. 260/1 British Chemical Standards was used for the preparation of Fe_2O_3.

MgO. 'Pure magnesium metal' was kindly provided by Magnesium Elektron Ltd.

The only modification of the method for preparing powders concerns compositions containing Fe_2O_3. As ferric nitrate decomposes readily, this solution is not evaporated to dryness, but only to a small volume, and then added to the other nitrates and the $(C_2H_5)_4SiO_4$ and gelled with 0·88 ammonia solution, the gelling being completed in a matter of minutes.

Apparatus. All the crystallization experiments were carried out using Tuttle 'cold-seal' pressure vessels (Tuttle, 1949), and using the sealed tube technique (Goranson, 1931), the capsules being made of gold. Temperature measurements were made by chromel-alumel thermo-

couples and continuously recorded on a Honeywell-Brown recording potentiometer. The thermocouples were calibrated at the melting-point of zinc (419·5° C) and the melting-point of sodium chloride (801° C). All experiments described here were held for five days at 750° C and at a water-vapour pressure of 1000 kg/cm² and the temperatures are estimated to have been within ±5° C of 750° C. Water pressure was measured by a Bourdon-tube pressure gauge and the pressure is estimated to have been within ±4 % of the stated value.

X-ray methods. Before any X-ray investigations were made the charges were examined using a petrographic microscope to make sure that only one phase was present. A Philips high angle diffractometer that had previously been calibrated with a silicon standard was used throughout this work.

Smear mounts of the charges were prepared for obtaining the X-ray diffraction patterns of the pyroxenes and the region from 13° 2θ to 70° 2θ was scanned using Ni-filtered Cu radiation and 1° slits. The recording settings were: scale factor 4, time constant 4. The diffractometer was set to scan at $\frac{1}{4}$° 2θ per minute and the chart speed set to record at 400 mm per hour.

The position of the reflections from each pyroxene specimen were measured using a specially constructed rule with a vernier capable of measuring to 0·001° of 2θ. From these observations the cell parameters a, b, c, and β were determined using a least squares programme written by M. T. Frost of this Department for the Mercury computer; this programme does not involve the use of an internal standard but instead incorporates the use of a 'drift constant' to allow for errors in the alignment of the smear mount in the goniometer. A comparison was made between the values of lattice parameters obtained in this way and those obtained using the more conventional method involving an internal standard and the results agreed within ±0·005 Å for a, b, and c and about 0·05° for β. Thereafter the drift constant technique was adopted for the determination of cell parameters.

Diffraction peaks for synthetic pyroxenes shown in fig. 2 were indexed by calculation of all possible 2θ values; using approximate cell parameters computation was performed using a Mercury computer programme written by M. T. Frost.

From the inspection of the X-ray data it was found that the separations of the 221 and 002 and of the 13$\bar{1}$ and 002 reflections gave almost linear relationships with composition as shown in fig. 3. These results were obtained by scanning the region between 34·5° 2θ and 36·5° 2θ on

the diffractometer six times and the mean of the six readings of $2\theta_{221} - 2\theta_{002}$ and $2\theta_{13\bar{1}} - 2\theta_{002}$ taken. The diffractometer settings used were identical with those described for determining the cell parameters.

Results. The indexed 2θ values for pure synthetic acmite and pure synthetic diopside are given in table I, together with the observed and

TABLE I. 2θ (observed), d (observed), and d (calculated) for pure synthetic acmite and pure synthetic diopside. Cu–$K\alpha$ radiation with internal standard

		Acmite					Diopside		
hkl	I	$2\theta_{obs}$	d_{obs}	d_{calc}	hkl	I	$2\theta_{obs}$	d_{obs}	d_{calc}
110	90	13·897°	6·37 Å	6·36 Å	021	13	26·621°	3·346 Å	3·343 Å
020	45	20·186	4·40	4·40	220	47	27·573	3·232	3·231
111	10	24·670	3·606	3·610	22$\bar{1}$	100	29·853	2·990	2·989
220	20	28·033	3·180	3·181	310	29	30·274	2·950	2·948
22$\bar{1}$	90	29·924	2·983	2·985	31$\bar{1}$	37	30·882	2·893	2·891
310	100	30·819	2·899	2·900	13$\bar{1}$	21	34·944	2·565	2·564
13$\bar{1}$	30	35·255	2·544	2·545	002*	—	—	—	—
002	20	35·513	2·526	2·526	221*	—	—	—	—
221	45	36·325	2·458	2·458	311	25	39·106	2·300	2·298
112	10	41·052	2·197	2·197	330	19	41·881	2·155	2·154
33$\bar{1}$	30	42·659	2·118	2·118	33$\bar{1}$	17	42·381	2·131	2·132
42$\bar{1}$	15	43·153	2·095	2·095	041	13	44·361	2·040	2·040
150	20	52·957	1·728	1·728	150	17	52·098	1·754	1·753
53$\bar{1}$	25	57·158	1·610	1·610	53$\bar{1}$	19	56·617	1·624	1·624
440	20	57·930	1·591	1·591					
531	17	67·065	1·394	1·394					

* Peaks not resolved.

calculated d values for each reflection; the variations between observed and calculated d values are small. The 021 and 31$\bar{1}$ reflections are too weak to be observed in acmite-rich compositions, and the 110, 200, 112, 42$\bar{1}$, and 440 reflections are too weak to be observed in diopside-rich compositions.

The lattice parameters a, b, c, and β have been determined at 10 weight per cent intervals between pure acmite and pure diopside; they are listed in table II and plotted on fig. 1. The parameters vary approximately linearly with composition, although the line representing variation in the b parameter shows slight curvature toward the diopside-rich end of the series; the variation of the β parameter is best represented by a curved line. A plot of the lattice parameters versus mole per cent composition produces only a very slight modification of these curves as the molecular weights of diopside and acmite are similar. These results are further proof that there is complete solid solution between the two end-members.

The X-ray diffraction patterns for selected pyroxenes of this series are reproduced in fig. 2. These patterns indicate the major intensity changes and 2θ variations with composition. Table III lists the d-spacings and observed 2θ values for the intermediate pyroxenes. The second column

TABLE II. The lattice parameters a, b, c, and β of synthetic pyroxenes in the system acmite–diopside. Compositions in weight %

			Acmite	$Ac_{90}Di_{10}$	$Ac_{80}Di_{20}$	$Ac_{70}Di_{30}$	$Ac_{60}Di_{40}$	$Ac_{50}Di_{50}$
a	...	...	9·658 Å	9·662	9·669	9·678	9·688	9·698
b	...	...	8·795 Å	8·805	8·823	8·825	8·854	8·868
c	...	...	5·294 Å	5·284	5·280	5·275	5·273	5·271
β	...	...	107·42°	107·16	106·99	106·86	106·62	106·46
Volume	...	...	429·1 Å³	429·5	430·7	431·1	433·4	434·7

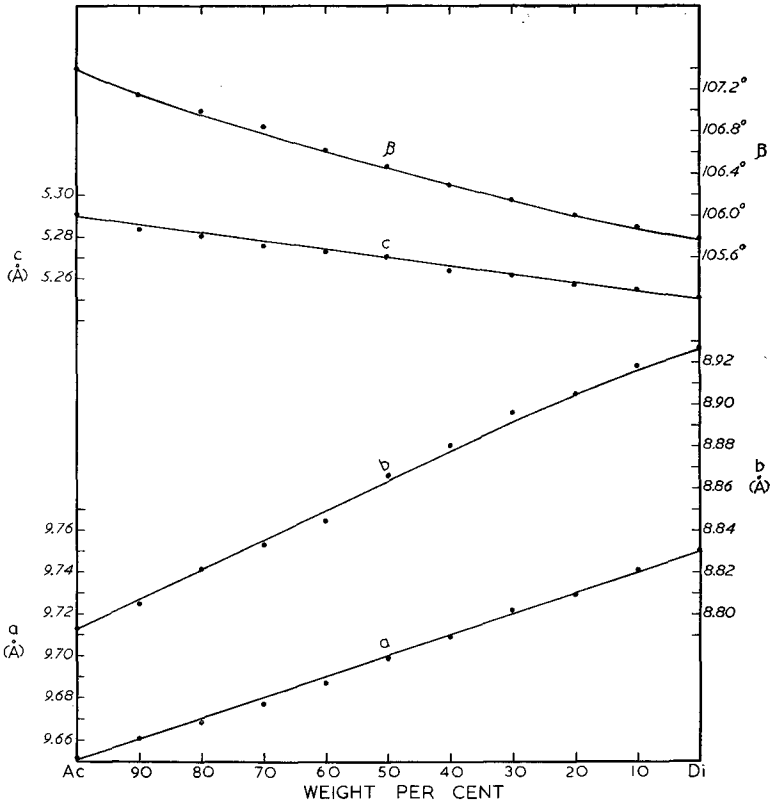|			$Ac_{40}Di_{60}$	$Ac_{30}Di_{70}$	$Ac_{20}Di_{80}$	$Ac_{10}Di_{90}$	Di_{100}
a	...	...	9·709 Å	9·722	9·730	9·741	9·748
b	...	...	8·880 Å	8·896	8·904	8·919	8·924
c	...	...	5·264 Å	5·261	5·257	5·255	5·251
β	...	...	106·29°	106·15	106·04	105·90	105·79
Volume	...	...	435·6 Å³	437·1	437·7	439·1	439·5

FIG. 1. Lattice parameters a, b, c, and β plotted against composition for synthetic pyroxenes in the system acmite–diopside.
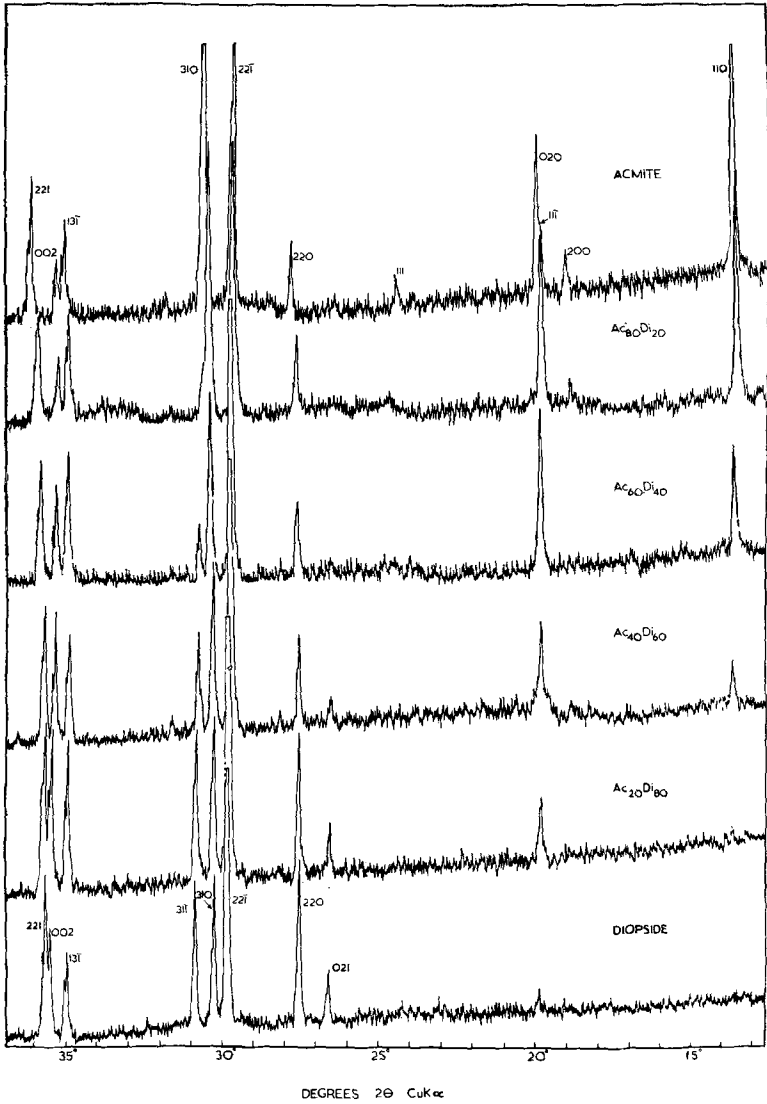
FIG. 2. Indexed X-ray diffraction patterns for synthetic pyroxenes in the system acmite–diopside.

TABLE III. 2θ (observed), 2θ (calculated), and d (observed) for intermediate pyroxenes in the system acmite–diopside. Compositions in weight %

	$Acmite_{80}Diopside_{20}$			$Acmite_{60}Diopside_{40}$			$Acmite_{40}Diopside_{60}$			$Acmite_{20}Diopside_{80}$		
	$2\theta_{obs}$	$2\theta_{calc}$	d	$2\theta_{obs}$	$2\theta_{calc}$	d	$2\theta_{obs}$	$2\theta_{calc}$	d	$2\theta_{obs}$	$2\theta_{calc}$	d
110	13·87	13·88	6·38 Å	13·77	13·79	6·43 Å	13·78	13·77	6·42 Å	not measured		
020	20·13	20·13	4·407	20·02	20·02	4·431	19·99	19·99	4·440	19·94	19·93	4·449 Å
021	not measured			not measured			26·72	26·71	3·333	26·68	26·67	3·338
220	27·96	27·95	3·188	27·81	27·80	3·205	27·73	27·74	3·214	27·66	27·65	3·222
$22\bar{1}$	29·95	29·94	2·981	29·89	29·88	2·986	29·90	29·90	2·986	29·88	29·88	2·988
310	30·72	30·72	2·908	30·55	30·55	2·924	30·47	30·47	2·931	30·36	30·37	2·942
$31\bar{1}$	not measured			not measured			30·92	30·92	2·890	30·91	30·91	2·890
$13\bar{1}$	35·21	35·21	2·546	35·10	35·09	2·554	35·06	35·07	2·557	35·01	35·01	2·561
002	35·54	35·54	2·524	35·48	35·48	2·528	35·51	35·51	2·526	35·52	35·52	2·525
221	36·20	36·19	2·479	35·99	35·98	2·493	35·87	35·87	2·501	35·75	35·76	2·510
311	not measured			not measured			not measured			39·23	39·23	2·295
$33\bar{1}$	42·64	42·63	2·119	42·53	42·52	2·124	42·50	42·49	2·125	42·42	42·42	2·129
$4\bar{2}1$	43·15	43·14	2·095	43·04	43·04	2·100	43·02	43·01	2·101	42·96	42·95	2·104
041	44·82	44·82	2·020	44·63	44·63	2·029	44·56	44·55	2·032	44·45	44·44	2·036
150	52·78	52·79	1·733	52·54	52·54	1·740	52·40	52·41	1·745	52·25	52·25	1·749
$5\bar{3}1$	57·08	57·09	1·612	56·92	56·92	1·616	56·83	56·83	1·619	56·71	56·71	1·622

of this table, $2\theta_{calc}$, lists the 2θ values as obtained from the least squares computation using the 'drift constant'. These values are therefore not absolute 2θ values but have been included to show the approximate magnitude of experimental error.

Curves for the rapid determination of the compositions of synthetic pyroxenes of this series are given in fig. 3. Experimental data for these
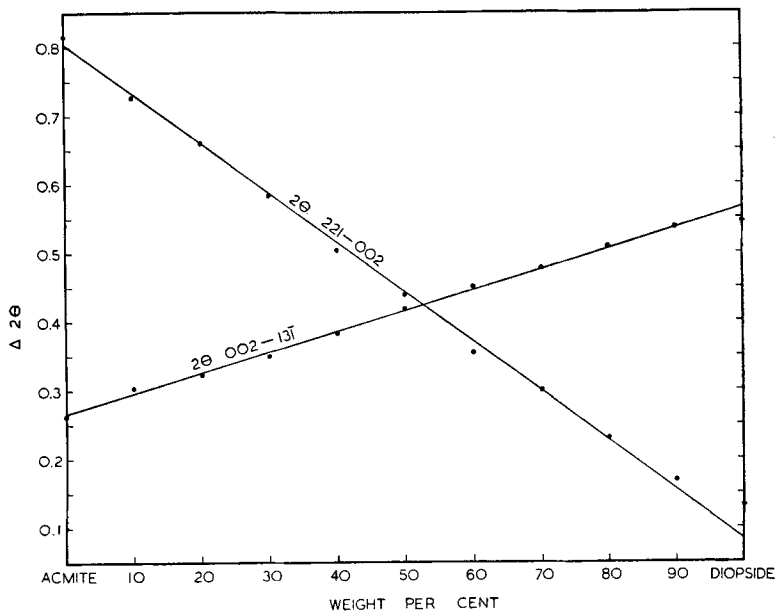

FIG. 3. $\Delta\ 2\theta_{221-002}$ and $\Delta\ 2\theta_{002-13\bar{1}}$ plotted against composition for synthetic pyroxenes in the system acmite–diopside.

curves are listed in table IV. Within experimental error these curves are linear between pure acmite and 90 weight per cent diopside. Anomalous values for pure diopside are caused by the lack of resolution of the 002 and 221 peaks for this end-member.

Discussion of results. From the previous data of Yagi (1958) and Ostrovsky (1946) and from the present investigation it is evident that there is a complete solid solution series between acmite ($NaFeSi_2O_6$) and diopside ($CaMgSi_2O_6$) under the experimental conditions used in this study. This is borne out by the fact that there is only one pyroxene phase throughout the series, and also by the approximately linear relationships between the cell parameters and composition as shown in fig. 1.

These curves cannot be used to determine the compositions of natural alkali pyroxenes because the effects of the hedenbergite component and the possible effect of Al_2O_3 substituting for Fe_2O_3 are not taken into consideration. Table V shows the cell parameters of the three main components found in natural alkali pyroxenes; on the assumption that

TABLE IV. Values of $2\theta_{002} - 2\theta_{13\bar{1}}$ and $2\theta_{221} - 2\theta_{002}$ in the system acmite–diopside. Compositions in weight %

Composition	$2\theta_{002} - 2\theta_{13\bar{1}}$	Standard deviation	$2\theta_{221} - 2\theta_{002}$	Standard deviation
Acmite	0·264	0·002	0·816	0·003
Acmite$_{90}$Diopside$_{10}$	0·303	0·018	0·726	0·018
Acmite$_{80}$Diopside$_{20}$	0·323	0·013	0·660	0·013
Acmite$_{70}$Diopside$_{30}$	0·349	0·01	0·584	0·01
Acmite$_{60}$Diopside$_{40}$	0·383	0·003	0·503	0·002
Acmite$_{50}$Diopside$_{50}$	0·419	0·008	0·438	0·009
Acmite$_{40}$Diopside$_{60}$	0·451	0·002	0·354	0·003
Acmite$_{30}$Diopside$_{70}$	0·479	0·006	0·300	0·007
Acmite$_{20}$Diopside$_{80}$	0·510	0·003	0·231	0·004
Acmite$_{10}$Diopside$_{90}$	0·537	0·004	0·170	0·004
Diopside	0·545*	—	0·136*	—

* Lack of resolution of the 002 and 221 peaks.

TABLE V. A comparison of the cell parameters of the three main components of natural alkali pyroxenes. Hedenbergite data from H. Kuno and H. H. Hess, 1953, for material from Herault, California

	Synthetic acmite $NaFeSi_2O_6$	Synthetic diopside $CaMgSi_2O_6$	Hedenbergite $Ca_{48}Mg_3Fe_{49}$
a	9·658 Å	9·748	9·854
b	8·795 Å	8·924	9·024
c	5·294 Å	5·251	5·263
β	107·42°	105·79	104·33

there is also complete solid solution between hedenbergite and acmite, these data indicate that the effect of solid solution of hedenbergite in acmite alters the acmite parameters in the same way as does diopside but to a much greater degree; the values a and b increase while c and β decrease from acmite to diopside to hedenbergite.

This study was undertaken as part of a broader investigation being carried out by the present authors of the effect of the addition of $CaMgSi_2O_6$ (diopside) and $NaFeSi_2O_6$ (acmite) to compositions in 'petrogeny's residua system'. The data should be of value to others working in related systems although their application to natural pyroxenes is clearly very limited.

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