The powder patterns and lattice parameters of plagioclase felspars. II.

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[Read 28 March 1957.]

Summary. The angular separations (2θ (131)$+2\theta$ (220)-4θ ($1\bar{3}1$)) and (2θ ($1\bar{1}1$)-2θ ($\bar{2}01$)) for 111 analysed plagioclase felspars have been determined from diffractometer records. From An_0 to An_{70} the petrological environment has a strong influence on these separations, and if the An-content is independently known an accurate estimate of the structural state can be made from the first of these angular separations. From An_{70} to An_{100} there are only small variations in both separations with An-content and structural state. From An_{85} to An_{100} inconsistencies in the data suggest that other factors can influence any interpretation so seriously that only qualitative or semi-quantitative deductions may be made. Consideration of the angular separations and subsidiary reflections of sodic plagioclases from a wide range of geological environments has led to the novel hypothesis that in this composition region even plutonic specimens are in a metastable state with slightly disordered structures.

The value to the petrographer of the available methods for the estimation of An-content and structural state is critically discussed. Although it is thought that the standard optical curves in present use are in need of some revision, the determination of optical orientation by universal-stage methods is probably adequate for routine studies. For more detailed investigations, this may be supplemented by X-ray powder data and refractive index measurements, whilst a complete description of the felspar requires the addition both of chemical analysis and single-crystal X-ray work. In particular, the efficacy of the various X-ray methods that have been proposed is discussed, and recommendations of the most suitable method for various composition ranges are made.

IN paper I (Smith, 1956) the variation of lattice parameters of sodic plagioclases with chemical composition and thermal history was presented, and on the basis of these changes simple X-ray powder methods for the estimation of structural state[2] and chemical composition were given. The variation of the cell dimensions with the An-content of the natural plagioclases from pegmatites and granites is continuous. Upon heating just under the solidus, the cell dimensions changed towards the

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[2] This term is now preferred to 'thermal state', which was used in earlier papers on the plagioclase felspars.

values given by the synthetic plagioclases, most of the specimens giving final values nearly identical with those for the synthetic specimens of the same composition. These and other results provide justification for defining high and low series of soda-rich plagioclases. Natural specimens from volcanic rocks exist in structural states intermediate between these two series. In sodic plagioclases, the effects on the lattice parameters of drastic heating and of increasing lime-content are so similar that, in practice, one of the two variables, An-content and structural state, must be known before the other can be estimated by X-ray powder methods.

This paper records the results obtained by an extension of the X-ray powder studies through the remaining composition range. The angular displacements between certain adjacent reflections have been correlated with both the An-content and the geological and thermal history of natural and synthetic specimens, but further clarification of the phase relations is thought to be advisable before the determination of the cell dimensions is begun.

It is necessary in assessing the results of the powder work to take into account the structural variations in the plagioclase series revealed by single-crystal X-ray studies (Cole, Sörum, and Taylor, 1951; Gay, 1953, 1954, 1956; Gay and Taylor, 1953; Gay and Smith, 1955; Gay and Bown, 1956; Laves, 1954; Laves and Goldsmith, 1951, 1954; Sörum, 1951), and a brief résumé of the results of this work would be appropriate at this point. Most natural plagioclases from low-temperature environments (plutonic, metamorphic, pegmatitic, &c.) give complex single-crystal patterns. The low-albite structure (with $c \approx 7$ Å. for a face-centred lattice) tolerates only a little lime-felspar in solid solution, for specimens from An_3 to An_{17} were found to consist of a submicroscopic parallel intergrowth, a peristeritic texture of low-albite and a lime-rich phase (An_{20-25}). More basic specimens gave patterns with extra weak reflections in addition to the main reflections of the albite pattern; the variations in these weak reflections distinguish one structure type from another. For lime-rich specimens from An_{70-75} to An_{80-85} (the limits are imperfectly known as yet) these additional weak reflections show that if the conventional orientation of the felspar cell is retained it has a doubled c-axis and is effectively body-centred. With increasing lime content, this structure is gradually replaced by the transitional anorthite structure (An_{80-85}—An_{90-95}) and finally by the primitive anorthite arrangement (An_{90-95}—An_{100}), both of which have a doubled c-axis. Over the range An_{20-25} to An_{70-75} the single-crystal patterns reveal pairs of weak reflections symmetrically disposed about the positions that would be

occupied by the extra reflections of body-centred anorthite; the patterns are remarkable, for the separations of these pairs are variable and apparently a linear function of composition. This intermediate structure is thought to be caused by a special kind of unmixing into lime-rich and soda-rich regions, which have been tentatively identified with body-centred anorthite and the calcium-rich component of unmixed albite-oligoclases. Recent unpublished results on specimens close to the boundaries of the intermediate composition range suggest further structural complexities.

In the high-temperature series, from An_0 to An_{90} there is only one structure type, high albite, which has a face-centred cell with c-axis $\approx$ 7 Å.; it differs from low albite in that the Si–Al arrangement is disordered. Quenched synthetic anorthite (An_{100}), however, shows the transitional anorthite structure with $c \approx 14$ Å. All natural specimens may be converted into their high-temperature counterparts by prolonged heating; most natural specimens from volcanic and hypabyssal rocks are already in states part way between the low and high forms. Apart from the region of peristeritic unmixing, the effects of heat treatment upon the diffraction patterns are known. For the intermediate specimens, the pairs of subsidiary spots gradually become weaker and finally diffuse without change of position; their complete disappearance results in the attainment of the high-albite structure. Anorthites with the primitive structure undergo a rapid and reversible inversion to the transitional anorthite structure if heated above a given temperature; this critical temperature is strongly dependent on the albite content. Calcic bytownites with the transitional structure invert less readily to the body-centred structure and then to the high-albite structure. For the more basic specimens, the reaction rates are so fast that only the most rapidly cooled natural specimens retain the high-temperature structure. Over the remaining composition range, the inversion occurs slowly and has so far proved irreversible in laboratory times.

The weak reflections that distinguish these structure types are rarely apparent on powder records, and in powder work it is convenient to use the face-centred cell with 7 Å. c-axis for the indexing of reflections.

In addition to paper I of this series, X-ray powder studies have been reported by Claisse (1950), Goodyear and Duffin (1954, 1955), and Smith (J. R.) and Yoder (1956). Claisse's work was based on a photographic study of only eight natural specimens. Goodyear and Duffin extended the work to cover a wider range of natural specimens and were also able to use synthetic specimens; they found that the synthetic and

natural specimens fell into two separate groups. In their later paper, they describe the production, by the heating of natural specimens, of felspars with reflection angles between the two groups. Unfortunately, the range of geological environments covered by Goodyear and Duffin's specimens was small and only one unheated specimen gave reflection angles indicating a transitional state. Smith (J. R.) and Yoder have examined specimens from a much wider range of environments, covering the whole composition range except the anorthite field. They found that different thermal histories cause large variations in the reflection angles, with the volcanic and hypabyssal specimens generally lying between the plutonic and synthetic ones. They concluded that 'composition determinations cannot be made by the use of the available curves based on the variation of reflection separations, because there is no *a priori* way of knowing how closely a given plagioclase is represented by a particular curve. However, given the composition of a plagioclase, the curves are useful for making an estimate of its degree of inversion towards some undefined low-temperature state.'

All the separations used by Smith (J. R.) and Yoder, and all but one of those used by Goodyear and Duffin, are effectively dependent on the angle γ^*. The values of these angular separations in the composition range An_{80} to An_{100} are almost independent of structural state and Goodyear and Duffin suggested that the composition could be determined from them. The other separation used by Goodyear and Duffin (between the peaks labelled *F* and *G*) was proposed as an indicator of structural state for this composition range. Unfortunately peak *F* is complex and Goodyear and Duffin state that 'while the *F* peak is reasonably resolved from neighbouring reflections for all the natural specimens, difficulties arise in its interpretation in the patterns of some of the synthetic materials'. In our opinion, peak *F* is not suitable for routine investigation. Fortunately, the angular separation between the well-resolved $(1\bar{1}1)$ and $(\bar{2}01)$ reflections has proved to give a similar variation for basic specimens and is to be preferred to the *F*–*G* separation. It is thought that the effectiveness of both these separations depends largely on the angle β^*.

Measurements. Of the reflections that depend on γ^*, the ones most suitable for measurement in intermediate and basic specimens are 220, $1\bar{3}1$, and 131. The 220 and $1\bar{3}1$ reflections from many low albites and acid oligoclases are unsuitable because of the peristeritic unmixing and because γ^* passes through 90° with the consequent interchange in position of 220 and $2\bar{2}0$: in this composition range, the methods developed

in paper I are to be recommended. In the remaining composition range a more valuable variable is the angle $2\theta\,(131)+2\theta\,(220)-4\theta\,(1\bar{3}1)$, to be called Γ (capital gamma). As the $1\bar{3}1$ reflection lies between the other two, systematic errors in the X-ray diffractometer records are cancelled. The other separation used in the present work is the angle $2\theta\,(1\bar{1}1)-2\theta\,(20\bar{1})$, to be called B (capital beta); these two reflections are adjacent (at $2\theta_{Cu} \approx 23°$ and $\approx 22°$, respectively) and no appreciable systematic errors can occur if the diffractometer is correctly aligned. Smith (J. R.) and Yoder have measured the separate quantities $2\theta\,(1\bar{3}1)$–$2\theta\,(131)$ and $2\theta\,(220)$–$2\theta\,(1\bar{3}1)$ and Γ may be obtained by subtracting the first quantity from the second. (Unfortunately they have used the wrong sign and all their quantities should be reversed.) Many specimens used by Smith (J.R.) and Yoder have also been measured by us and an estimate of the reliability of measurement may be readily obtained. The average discrepancy in Γ, 0·015° in 2θ, is astonishingly good. Comparison of independent measurements of B indicates that an accuracy of 0·01° in 2θ has been obtained.

About half of the powder records were taken by the first author on a Norelco diffractometer at the Geophysical Laboratory; the remainder were taken on a Berthold diffractometer whose design has been severely modified by the authors and which was rebuilt by Mr. A. N. Lanham. Filtered Cu-$K\alpha$ radiation has been used for all the records. Portions of the powder pattern that contain the 131, $1\bar{3}1$, and 220 peaks have been figured by Smith (J. R.) and Yoder.

Discussion. The values of Γ for 78 natural, 16 synthetic, and 17 heated plagioclases together with the values of B for 62 natural, 9 synthetic, and 17 heated plagioclases are given in table I and plotted against An-content in figs. 1 and 2. Thirty-four values of Γ have been obtained from the data of Smith (J. R.) and Yoder, whilst 41 specimens have been measured by both sets of workers.

An attempt has been made to arrange the specimens into groups whose probable thermal histories have offered comparable opportunities for the development of an ordered structure. The groups are: synthetic; heated natural; volcanic; hypabyssal, including anorthositic specimens from the upper parts of gabbroic sills; plutonic and pegmatitic; metamorphic and charnockitic. Smith (J. R.) and Yoder separated the specimens from the stratiform layered intrusions from the other plutonic specimens and this segregation has also been retained in order to facilitate discussion. Most of the specimens can be readily assigned to one of these groups; the doubtful classification of others does not affect the validity

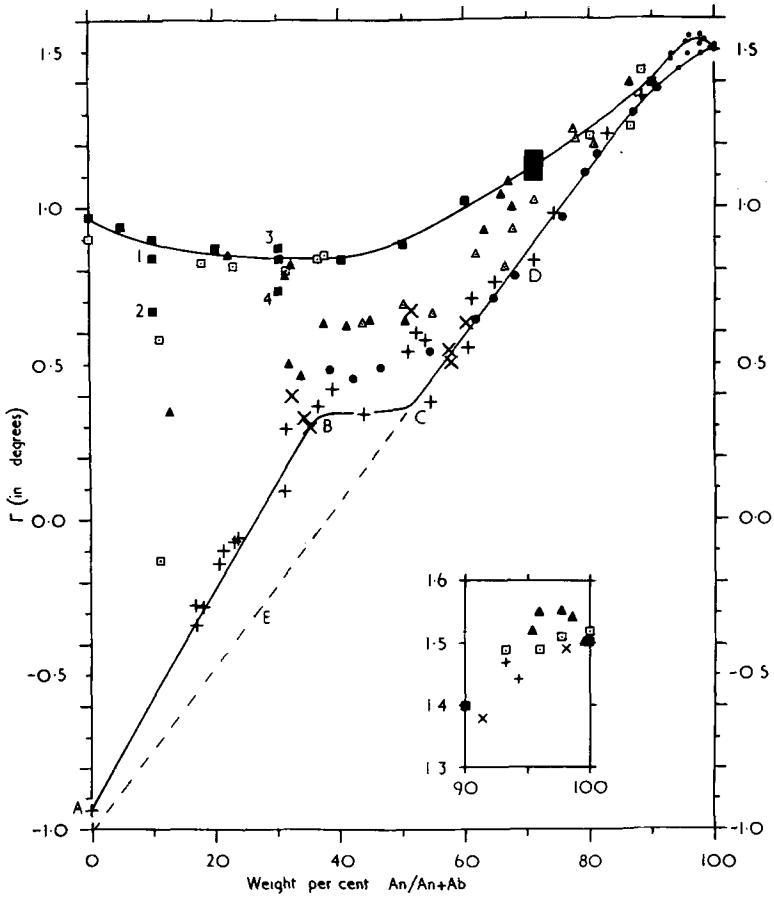

FIG. 1. The variation of $\Gamma(2\theta(131)+2\theta(220)-4\theta(1\bar{3}1))$ with wt. % An/(An+Ab). The specimens have been allocated into six groups on the basis of their origin and heat treatment, with the following symbols: ■ synthetic; □ heated natural; ▲ volcanic; △ hypabyssal; + plutonic and pegmatitic; X metamorphic and charnockitic; ● Skaergaard, Stillwater, and Bushveld igneous complexes. Specimens labelled 1, 2, 3, and 4 were synthesized hydrothermally by Smith (J. R.) and Yoder. The significance of the curves is explained in the text. Many values fall too close for individual reproduction especially those for six specimens of compositions An_{70}–An_{72}, which have been replaced by a rectangle elongated vertically in such a way as to approximately represent the spread of the values. Similar confusion in the region An_{90} to An_{100} has been avoided by representing all values by dots. An enlarged portion of this region using the proper symbols is given in the inset diagram.

of the interpretations to be put forward. It will be convenient to discuss the composition ranges An_0 to An_{70} and An_{70} to An_{100} separately.

TABLE I. B and Γ values for plagioclase felspars* (for definition of B and Γ see text, p. 572).

Ref.	Specimen label	% An and Class.	B.	Γ.	Γsy.
Natural specimens					
7	KN 12	0·0—N	1·014°	(−0·94)°	
3	BM 1940, 27	11·2—N	0·988		
1	E 2 (10)	11·6—N	1·00		
10	Larsen 9	12·5—L			+0·35°
1	E 3 (73)	16·6—N	0·99		−0·27
1	E 4 (156)	16·9—N	0·98		−0·34
7	KN 8	17·9—N	0·968		−0·28
11	SLR 596	18·9—N	0·957		
1	E 5 (94)	20·4—N	0·97		−0·14
1	E 32 (0–761–4)	21·2—N			−0·10
15	24335	21·8—L	0·898	+0·848	
7	KN 9	22·9—N	0·958		−0·07
7	KN 10	23·6—N	0·969	−0·04	−0·06
7	KN 11	31·0—N	0·935		+0·09
15	11277	31·0—L	0·892	+0·785	
1	E 28 (D—638)	31·3—N			+0·29
10	Larsen 8	31·8—L			+0·50
15	15472	32·1—L	0·872	+0·822	
5	S—347	32·2—P	0·903	+0·42	+0·39
10	Larsen 4	33·9—L			+0·46
5	6436	34·1—P	0·917	+0·33	+0·33
5	2270	35·1—P	0·907	+0·32	+0·29
1	E 6 (152)	36·4—N	0·915	+0·37	+0·36
1	E 7 (64)	37·3—L	0·875	+0·63	+0·63
20	4145	38·4—Q	0·906	+0·48	+0·48
1	E 8 (144)	38·8—N	0·880	+0·41	+0·43
10	Larsen 7	41·0—L			+0·62
20	2580	42·1—Q	0·900	+0·45	+0·45
11	EL 38–28	43·8—N	0·897	+0·34	
13	M 3174	44·1—M	0·880	+0·63	
Natural specimens					
1	E 12 (97)	57·3—P	0·880°	+0·55°	+0·55°
1	E 13 (92)	57·7—P	0·880	+0·52	+0·51
5	2941	60·2—P	0·860	+0·66	+0·63
1	E 14 (167)	60·6—N			+0·55
1	E 16 (132)	61·1—N	0·870	+0·70	+0·71
17	BV 63	61·8—Q			+0·64
1	E 15 (53)	61·8—M	0·86	+0·87	+0·85
10	Larsen 2	63·2—L			+0·93
17	EB 41	64·3—Q			+0·71
11	SLRM 334	64·7—N	0·847	+0·76	
7	KN 7	65·9—L	0·800	+1·08	+1·04
1	E 17 (52)	66·3—M	0·850	+0·81	+0·81
6		66·9—L	0·800	+1·08	
10	Larsen 1	67·6—L			+1·00
1	E 18 (134)	67·8—M	0·850	+0·89	+0·91
17	EB 42	68·2—Q			+0·78
1	E 19 (61)	70·7—L	0·795	+1·13	+1·10
1	E 20 (22)	71·1—N	0·850	+0·82	+0·84
7	KN 5	71·3—M	0·805	+1·14	+1·15
1	E 22 (54)	71·3—M	0·820	+1·11	+1·09
1	E 21 (51)	71·7—M	0·820	+1·02	+1·03
1	E 23 (165)	74·5—N	0·825	+0·98	+0·98
17	EB 43	75·8—Q			+0·97
1	E 24 (1 B)	77·4—M			+1·24
1	E 25 (1 A)	77·8—M	0·800	+1·20	+1·23
1	E 26 (109)	79·3—Q	0·815	+1·12	+1·11
2	15	80·9—M	0·815	+1·20	
17	EB 38	81·3—Q	0·800	+1·18	+1·16
1	E 27 (166)	83·0—N	0·790	+1·24	+1·23
4	Juvinas	86·2—L	0·747	+1·40	

TABLE I (*contd.*)

Ref.	Specimen label	% An and Class.	B.	Γ.	Γsy.
10	Larsen 5	44·6—L			+0·64°
20	1963	46·6—Q			+0·49
13	EH 20	50·3—M	0·863°	+0·69°	
10	Larsen 3	50·3—L			+0·64
1	E 9 (24)	50·9—N	0·895	+0·54	+0·54
17	C 41	51·5—P			+0·67
1	E 10 (132)	52·2—N	0·890	+0·59	+0·60
1	E 11 (151)	53·6—N	0·900	+0·58	+0·58
17	GD 29	54·3—Q			+0·54
7	KN 6	54·6—N	0·890	+0·36	+0·39
13	EH 201	55·1—M	0·863	+0·66	
Synthetic specimens					
	0	0·0—H	0·88	+0·97	
	5	5·0—D			+0·94
	10	10·0—D	0·85	+0·90	+0·90
18	S 2—1	10·0—H			+0·67
18	S 2—2	10·0—H			+0·84
	20	20·0—D			+0·87
	30	30·0—D	0·83	+0·82	+0·83
18	S 2—3	30·0—H			+0·73
Heated specimens					*Treatment.*
7	KN 12	0·0	0·915	+0·89	60°—23
3	BM 1940, 27	11·2	0·950	−0·13	60°—12
3	BM 1940, 27	11·2	0·908	+0·58	60°—24
7	KN 8	17·9	0·865	+0·82	90°—42
7	KN 9	22·9	0·895	+0·81	90°—42
7	KN 11	31·0	0·865	+0·80	90°—42
1	E 6 (152)	36·4	0·880	+0·84	90°—28
1	E 7 (64)	37·3	0·860	+0·84	90°—14
1	E 20 (22)	71·1	0·760	+1·13	300°—3

Ref.	Specimen label.	% An and Class.	B.	Γ.	Γsy.
17	EB 18	86·7—Q	0·791°	+1·30°	+1·31°
14	Rhum	88·4—N	0·780	+1·35	
18	HGIF-An-53	91·3—P			+1·38
7	KN 1	93·3—N	0·757	+1·47	
12	SLR 354	94·3—N	0·730	+1·44	+1·44
16	Tarumaé	95·5—L	0·711	+1·52	
8	†	96·0—L	0·720	+1·55	
8	HK 33010901 e	97·8—L	0·710	+1·55	
19	C 50	98·1—P	0·733		+1·49
9	‡HK 350826046	98·6—L	0·707	+1·54	
2	§	99·7—L	0·700	+1·50	
Synthetic specimens					
18	S 2–4	30·0—H			+0·87
	40	40·0—D			+0·80
	50	50·0—D	0·785	+0·88	+0·86
	60	60·0—D	0·770	+1·02	+1·01
	70	70·0—D	0·740	+1·10	+1·11
	80	80·0—D	0·730	+1·24	+1·21
	90	90·0—D	0·687	+1·40	+1·40
	100	100·0—D	0·670	+1·50	+1·50
Heated specimens					*Treatment.*
7	KN 5	71·3	0·780	+1·13	100°—4
7	KN 5	71·3	0·773	n.d.	300°—4
17	EB 18	86·7	0·740	+1·36	300°—3
4	Rhum	88·4	0·713	+1·44	100°—3
7	KN 1	93·3	0·693	+1·49	180°—3
8	Hatiszyô-zima	96·0	0·713	+1·49	‖
8	HK 33010901 e	97·8	0·737	+1·51	¶
	100	100·0	0·723	+1·52	**

† Phenocrysts from olivine basalt occurring as beach sand. Hatiszyô-zima volcano, Seven-Izu Islands, Japan.
‡ Ejected block of allivalite in tuff, Hakoné, Japan.
§ Crystal lapilli (?), Mikyinna, Japan.
‖ 'Annealed' 8 days at 750° C.
¶ 'Annealed' 8 days at 850° C.
** 'Annealed' 1 day at 1100° C.

In the first composition range, Γ varies much more widely than B and may be expected to give a more reliable indication of structural change, for it should be affected proportionately less by such possible factors as solid solution of potassium and iron. Within the limits of experimental error the plagioclases synthesized in the dry way form a continuous series. The natural specimens fall in a broad band with those from

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* *Notes*: Values of B and Γ quoted in degrees. The column headed Γsy under natural and synthetic specimens contains data derived from the measurements of Smith (J. R.) and Yoder (1956). The An-content is given as An/(An + Ab), wt. %. The natural specimens have been classified into five groups on the basis of their occurrence: L, volcanic; M, hypabyssal including anorthosites from the upper levels of gabbroic sills; N, plutonic and pegmatitic; P, metamorphic and charnockitic; Q, Skaergaard, Stillwater, and Bushveld specimens.

Under the synthetic specimens, H (in the class column) indicates a hydrothermal synthesis, D a dry synthesis. The details of hydrothermal treatments may be found in the appropriate reference, except for specimen O which was crystallized at 800° C., under 1000 Kg./cm.^{2} pressure for 5 days. The dry synthetic specimens were all prepared by Dr. J. F. Schairer (Geophysical Laboratory, Washington).

The column headed 'Treatment', under heated specimens, gives the temperature in degrees above 1000° C. and the time of heating in days, e.g. 300°—3 indicates heating at 1300° C. for 3 days, and 90°—42 indicates 1090° C. for 42 days.

plutonic rocks usually the farthest displaced from the dry synthetic series. The volcanic and hypabyssal specimens fall into intermediate positions, whilst there is some tendency for the values for hypabyssal specimens to plot between the plutonic and volcanic ones. It is not surprising that the spread of values for each group is quite large, for each group must embrace a wide range of conditions. Some of these specimens have been examined by single-crystal methods and the displacements of the values of Γ are in accordance with the estimates of structural disorder inferred from the single-crystal photographs. Thus it seems reasonable to correlate Γ with the state of order.

For igneous specimens, the nature of occurrence is clearly of prime importance in controlling the degree of order attained by a particular felspar. It is natural to assign a leading role to the rate of cooling in view of the known effect of heating on the state of order, but other factors such as pressure and the volatile content of the magma undoubtedly have important effects although their relative importance cannot as yet be assessed.

When plagioclases are strongly heated, any structural order is destroyed and the completely disordered state may be approached in an apparently continuous manner. After the severest heat treatments, the values of Γ and more especially B do not quite reach those recorded for corresponding dry synthetic plagioclases, and it seems likely that the differences are significant. The reason for this is unknown, although the known solid solution of potash-felspar in natural plagioclases provides a possible explanation. The broken-line curve in fig. 2 probably represents the limit towards which B for natural plagioclases tends as they are heated until no further change occurs. A further complexity has been introduced by the work of MacKenzie (1952) who found slight spacing differences in the powder patterns of albite synthesized in various ways. Smith (J. R.) and Yoder have also reported variations for synthetic plagioclases crystallized hydrothermally at high pressure and moderate temperature (points 1, 2, 3, and 4 in fig. 1). Again the significance of these observations is not clear, though the latter may represent some slight order introduced into the structure by the conditions of crystallization.

Apart from these small variations, the powder and single crystal X-ray studies and the optical work provide justification for the definition of two limiting series of plagioclase felspars. Ideally the series are defined in terms of the structural arrangement, the 'high' series corresponding to the most disordered structure, the 'low' series to the structures with the

highest degree of order. In practice some more easily determinable function must be used. It is suggested that over the composition range An_{20} to An_{70} Γ is most suitable, for it is easily determined and provides a more sensitive criterion for the detection of deviations from the limiting series than any other so far suggested by X-ray and optical work. Other functions are more suitable for the ranges An_0 to An_{20} (one or more of the

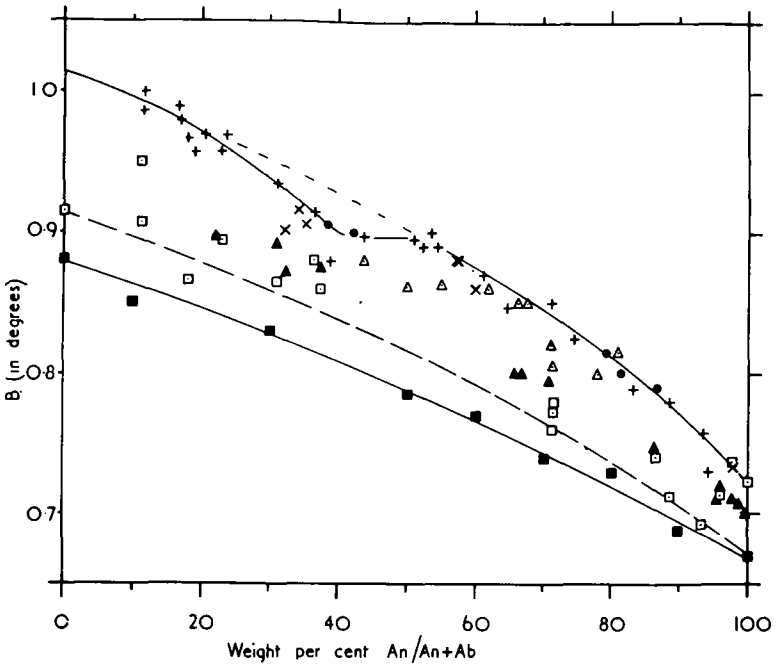

FIG. 2. The variation of B $(2\theta\,(1\bar{1}1)-2\theta\,(\bar{2}01))$ with wt. % An/(An + Ab). The symbols are the same as those in fig. 1. The significance of the curves is explained in the text.

angles given in part I) and An_{70} to An_{100} (to be discussed in detail later). The high series is characterized by the values for quenched synthetic plagioclases and the low series by the curve *ABCD* in fig. 1 which passes through those values of Γ with the greatest deviation from corresponding points on the high curve. (Obviously the discovery of plagioclase specimens showing greater displacements than those plotted in fig. 1 would result in a modification of the shape of the low curve.)

The high curve has the form of a gentle bow. The low curve has a curious shape, consisting of two linear portions of slightly different slope

joined by a short horizontal portion. The B curve for low specimens has similar characteristics, the central portion occurring in both cases at the same composition range, An_{40} to An_{50}. If the portion *CD* in fig. 1 is extrapolated to An_0, it coincides within experimental error with the point *A* for low albite. This and two other arguments to be considered in the next few paragraphs lead to the suggestion that the low series as previously defined may be metastable over the region An_0 to An_{50} and that plagioclases stable at low temperatures in the strict thermodynamic sense would give Γ values along the line *AECD*.

The first argument is based on the single-crystal studies of Gay. The intermediate structure was found to extend from An_{20} to An_{70} (Gay, 1956) and it would not be unreasonable to expect a linear or near linear relation for the Γ and B values of fully ordered plagioclases. Gay and Bown (1956) found that the plutonic specimens from An_{45} to An_{70} gave sharp subsidiary reflections which under drastic heat treatment became diffuse and gradually disappeared. Volcanic and most hypabyssal specimens yielded either no subsidiary reflections or only weak diffuse ones. In the composition range An_{20} to An_{41} even the plutonic specimens gave diffuse subsidiary reflections.

The correlation between the deviations from linearity of Γ and the diffuseness of the reflections from plutonic specimens is surely not fortuitous. The diffuseness might result from one or both of two causes: the structure might be partly disordered, for it has been shown that transition to the disordered high-albite type of structure results in a fading and spreading of the subsidiary reflections; or the crystals might consist of separate fully ordered regions that are too small to give sharp X-ray reflections. It is known that the first possibility gives a change in Γ: it is probable that the second possibility would not, though a reliable assessment must await a full interpretation of the structural changes that occur in the intermediate region.

The second argument is based on the variation of Γ with the petrological environment. If equilibrium were easily attained, the ordered structure would be formed even under hypabyssal and most volcanic conditions: only plagioclases from glassy rocks would give intermediate values. Around An_{40}, a fairly continuous spread of values is found; in particular, two specimens from the Southern Californian batholith deviate rather more from the high curve than do plagioclases of similar composition from the Skaergaard intrusion. Consequently it would not be surprising if equilibrium had not been reached even in such a slowly cooled complex as the Californian batholith. Smith (J. R.) and Yoder

grouped the plagioclases from the Skaergaard intrusion with those from the Bushveld and Stillwater igneous complexes and focused attention on them because, 'All these plagioclases probably have similar thermal histories, inasmuch as they all crystallized at basaltic magma temperatures, and, as a result of the tremendous thickness of the intrusions, cooled very slowly during and after crystallization. . . . Since these plagioclases are the most slowly cooled of all magmatic plagioclases in the composition range which they cover (An_{36} to An_{86}) and since they make up a well-defined series by the criterion of reflection separations. . . . While the present authors agree that the Bushveld, Stillwater, and Skaergaard bodies are of tremendous thickness, they nevertheless believe that plagioclases from bodies such as the Southern California and the Nevada batholiths may well have had a better chance of approaching equilibrium. In addition, X-ray and optical evidence has been obtained by Gay and Muir (to be published) that shows that many plagioclases from the Skaergaard intrusion have disordered structures. Consequently the present authors see no reason for attaching especial importance to specimens from the Bushveld, Stillwater, and Skaergaard bodies as indicators of the low structural state.

Nevertheless, it is apparent that there is no conclusive evidence in favour of the hypothesis. Conclusive evidence might arise from either of two sources. Either plagioclases that have undergone even longer 'annealing' periods may be found, or a theoretical proof might emerge when the nature of the ionic movements involved in the high–low inversion has been fully elucidated. The small difference in Γ between the Skaergaard and other plutonic specimens indicates that very long periods at moderate to low temperatures will be required to produce the 'hypothetical-low' specimens. The necessary conditions might be found in some metamorphic rocks but the situation might be complicated by the opportunity for mineralogical reconstitution with ensuing change of composition. For the present, however, such speculation must be discarded and the low series of plagioclases be regarded as defined by the curve *ABCD* (fig. 1) from An_{20} to An_{70}, and by the angles defined in paper I from An_0 to An_{20}.

Over the remaining composition range, An_{70} to An_{100}, there are many complex features. The difference in Γ values between synthetic and natural specimens decreases from 0·25° at An_{70} to about 0·06° for anorthites. Values of B occupy a band whose width ranges from 0·10° at An_{70} to 0·05° at An_{100}. The variation of both B and Γ with structural state is rather small and anomalies arise when attempts are made to

correlate the values of these quantities with the probable thermal history. Goodyear and Duffin found that from An_{80} to An_{100} there was little variation with thermal state of those angular separations dependent mainly on γ^*, and hence proposed that the An-content might be deduced from measurements of such angles. The present results, which are based on many more specimens, lead to more pessimistic results. Specimens differing in composition by as much as 7 % An give indistinguishable values of Γ; a determinative method of such low accuracy is of little practical application. The Γ values of quenched dry synthetic plagioclases give a more consistent variation with An-content than natural plagioclases and for this type of specimen the An-content from An_{80} to An_{100} can probably be estimated with an accuracy of 2–4 %.

There are striking anomalies in the values of Γ produced by heating. Before heating, Γ for a plutonic specimen of composition An_{88} lay on the curve that represents the average position for plutonic specimens; after heating Γ had increased by 0·09° and then lay 0·05° on the wrong side of the synthetic curve. Before heating, Γ for another plutonic specimen of composition An_{87} lay on the best curve for plutonic specimens but after heating Γ had decreased by 0·04°.

At first sight the values of B appear more promising. The quenched synthetic specimens give a continuous curve within experimental error. All the plutonic specimens except one give B values that lie on a continuous curve passing through the value for annealed synthetic anorthite. Volcanic specimens lie about midway between the two curves and the hypabyssal specimens lie close to the plutonic curve. Upon heating at elevated temperatures, the B values of the natural specimens from An_{70} to An_{96} move towards the synthetic curve. One volcanic specimen, of composition An_{98}, was annealed into the low-temperature state and it gives a B value on the plutonic curve. There is an excellent correlation between B and the structural state determined from single-crystal studies or deduced from the petrological environment except for the single plutonic specimen mentioned above. This specimen (SLR 354, An_{94}) comes from a calcic gabbro in the Southern California batholith and would be expected to give a B value on the plutonic curve; the deviation from the curve is only 0·02° but sufficient extra measurements were made to lower the random error of measurement to 0·005°. It would be surprising if this specimen were not in a fully ordered structural state; yet the B value indicates a state of inversion one-third of the way from that of other plutonic specimens.

The single-crystal studies of Gay and of Laves and Goldsmith have

shown that the structural changes in bytownites and anorthites are very involved and further unpublished work upon sodic bytownites has revealed additional complexities. In the intermediate plagioclases only one structural change occurs and a smooth variation of Γ is to be expected and indeed seems to exist. In the bytownites and anorthites there may be two interrelated structural changes between the low and the high forms. The transition between primitive and body-centred anorthite is dependent on the Na and Ca ions, and the change from body-centred anorthite to the high-albite-type structure depends on Al–Si order-disorder. As the velocity of the first structural transition is probably strongly dependent on the Al–Si order the structural arrangement in natural basic plagioclases may depend critically upon the cooling history of the felspar, and the simple classification that has been adopted here may not be valid.

From the present evidence, it is clear that in the composition range An_{70} to An_{100}, values of Γ are of little significance for the deduction of either structural state or composition. Apart from the single anomalous specimen, the values of B suggest that a good estimate of structural state may be made although the total variation is only five to ten times the experimental error. Although the anomalous specimen may have crystallized under singular conditions, the effect of factors other than structural state (iron or potassium atoms within the plagioclase lattice) may be important. The interpretation of structural state from values of B must be regarded, therefore, with some uncertainty, and its use is suggested only because optical measurements are particularly insensitive in this region and because it avoids the laborious techniques of single-crystal methods. It is to be noted that the peaks *F* and *G* of Goodyear and Duffin are thought to be dependent on the same dimensional variables that the B plot employed; apart from any difficulty in the accurate location of peak *F* mentioned before, the separation *F*–*G* must be regarded as subject to all the limitations described above for the B plot.

Practical applications of the powder methods.

The authors feel that the non-specialist, faced with the large volume of original work that has appeared in recent years, may find it laborious to decide how the various techniques are to be most efficiently applied, so in this section they attempt to assess the relative merits of the various techniques in the estimation of An-content and structural state.

The An-content may be determined most reliably by the standard analytical methods or may be estimated by spectroscopic methods; both

are destructive and give no information about the structural state of the plagioclase. In routine petrographic studies, optical methods are in general use. The An-content may be estimated by comparing the refractive indices with the standard curves that have been obtained by averaging over numerous analysed plagioclases. The variation of refractive indices with structural state has not been systematically studied, although Kano (1955) and Schwarzmann (1956) have recently shown that the standard curves of Chayes (1952), while applicable to low plagioclases, may lead to serious error (5 % An) for those sodic plagioclases that have a disordered structure. The structural state appears to have little effect on the refractive indices of calcic plagioclases. The optic axial angle varies considerably with structural state for albites and oligoclases, though the variation over the remaining composition range is small.

The relative orientation of the crystallographic and optical axes is of considerable value, for under favourable conditions it provides an estimate of both the An-content and the structural state. A large body of data has been obtained by universal-stage methods (see van der Kaaden, 1951, for example) and from this the An-content may be estimated with a theoretical precision of about 2 % if the experimental error is 2°. The data on the effect of structural state are less complete, but indicate that eight stages in the transition from low- to high-albite might be distinguished: for intermediate specimens, the separable stages fall to three, whilst for basic specimens (for which few observations are available) the determination of structural state appears to be impracticable.

Although a great wealth of experimental information on the optical properties of plagioclase felspars has been obtained in the past, there has been little correlation between the results of one worker and another: comprehensive studies of the effects of strong heating and of the petrological environment have not so far been attempted. The results of many workers have shown a wide spread of optical parameters for crystals taken from the same hand specimen. While some of the spread is undoubtedly caused by variable An-content and structural state, other factors such as poor definition of crystallographic elements and solid-solution of impurity atoms may well be of importance. The authors have found from their X-ray work that the more comprehensive the study, the greater the number of exceptions and variations that are found, and they would expect a similar situation for optical studies. Consequently, while they believe that the broad outlines of plagioclase optics have been established, they would urge that detailed interpretation

be made with some caution until the optical variations have been authoritatively established by wide-ranging complete studies. Subject to this limitation, the present value of optical methods may be summarized: They are rapid and non-destructive. The composition and structural state of albites and oligoclases may be reliably estimated from the optical orientation with confirmation, if desired, from the refractive indices and optic axial angle. For andesines and labradorites, the An-content may be reliably estimated from the refractive indices or from the optical orientation; the structural state can only be estimated in a crude manner from the optical orientation. For bytownites and anorthites, although the An-content may be determined either from the refractive indices or the optical orientation, there is little hope of deducing the structural state from the optical properties.

Turning to the X-ray powder methods, the reflection angles are governed by six fundamental variables, the three lattice angles and the three lattice repeats. Unfortunately in sodic plagioclases b^*, c^*, α^*, and γ^* vary in a similar manner (but γ^* much more than the others); a^* appears to be unreliable, probably because of solid-solution of potash felspar, whilst β^*, although showing an independent form of variation, changes so little that it is not of practical value. Hence there is effectively only one useful form of variation, so that either the structural state or An-content must be known before the other can be estimated. In practice, the cell dimensions themselves are not used as variables and some simple angular relationship between the X-ray reflections is measured. As discussed earlier, the Γ function is most useful from An_{20} to An_{70}, whilst the three angles in part I are to be preferred from An_0 to An_{20}. The method permits the detection of as many as fifty steps between high- and low-albite. The sensitivity falls rapidly to An_{30} and then more slowly to An_{70} where several stages of structural variation may still be recognized. From An_{70} to An_{100}, two variable parameters may be detected in the angular positions of the powder diagrams, but their variations are small, and factors other than An-content and structural state appear to have significant effects. However, an estimate of structural state may be made from the B variation, and appears to be reliable for the majority of specimens. Since the completion of the present study, Laves and Goldsmith (1956) have demonstrated that the powder pattern of anorthite contains a reflection whose intensity provides a measure of the transition from the primitive to the body-centred structure. It is hoped that further study of the variation of this reflection with An-content and structural state will lead to an accurate deter-

minative method—especially as the other methods are so ineffective in this composition range.

Single-crystal X-ray methods can yield an unambiguous estimate of structural state for intermediate and basic plagioclases from An_{40} to An_{100}. An elegant method for the independent determination of An-content in the intermediate region (An_{40}–An_{70}) has been described. Nevertheless, it is unlikely that routine determinative methods can be developed; for apart from the inherent technical difficulties, most of the methods of estimating structural state involve the observation of the intensity, and perhaps diffuse character, of certain weak reflections. Thus, for plagioclase felspars, the chief value of single-crystal methods will be in the provision of a rigorous standard against which the simpler routine methods may be checked.

Finally, suggestions will be presented for the application of these methods to mineralogical and petrological studies. First, for routine survey work, optical measurements obtained from thin sections would appear to be sufficient for the characterization of plagioclase felspars. Secondly, in petrogenetic studies, where greater reliability is required, universal-stage measurements could be supplemented by powder X-ray measurements and the determination of refractive indices. The region An_{70} to An_{100} is particularly difficult, for the estimates of structural state, obtained from the powder X-ray measurements, are not definitive. Thirdly, if a complete description of the plagioclase felspar is required, all the methods may be employed with advantage. The An-content may be obtained from chemical analysis and checked by the refractive indices. The structural state may be determined by both powder and single-crystal X-ray methods, the former being more valuable for sodic specimens and the latter for calcic ones. The An-content and structural state can then be checked by a determination of the optical orientation.

Although this threefold scheme is of wide application, the peculiarities of the various methods may be advantageously employed to suit the special requirements of a particular problem. Many uncertainties still remain, particularly in the knowledge of the optical properties, but it is hoped, and indeed expected, that their clarification will not enforce serious modification of these conclusions.

Acknowledgements. We are particularly indebted to Drs. J. R. Smith and H. S. Yoder for friendly co-operation and to the following for the supply of specimens: Profs. R. C. Emmons, H. Kuno, and L. R. Wager; Drs. P. Game, R. A. Howie, F. C. Kracek, E. S. Larsen, I. D. Muir, K. J. Neuvonen, S. Schwarzmann, and A. P. Subramanian. Prof. C. E. Tilley and Dr. W. H. Taylor have further increased our debt to them by their continued advice.

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