Electron-diffraction study of subsidiary maxima of scattered intensity in nepheline.

(With Plate III.)

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Summary. A detailed electron and X-ray diffraction study of a suite of nephelines from a wide range of paragenetic environments indicates that, in all cases studied, additional weak maxima of scattered intensity are present. Similar intensity maxima have previously been observed and described in an isolated case by Sahama. Thermal treatment at temperatures as low as 200° C causes these maxima to become noticeably diffuse, implying a structural transformation.

THE present paper deals with certain anomalous diffraction effects observed in natural nephelines representative of a wide range of both chemical composition and paragenetic environment. The observations have been made using both single-crystal X-ray and electron-diffraction techniques. The paper also includes the results of a preliminary study of these diffraction effects in specimens heat-treated over a wide range of temperature (150 950° C) under both dry and hydrothermal conditions.

The anomalous diffraction effects observed comprise additional intensity maxima,[1] which in certain specimens are sharp. In the latter case the positions of the additional maxima may be defined in reciprocal space in terms of the normal reciprocal cell for nepheline by coordinates $\pm(\frac{1}{3}, \frac{1}{3}, \pm z)$. Electron-diffraction study of the maxima shows that the c^* coordinate z is in general irrational and varies with the composition of the nepheline concerned.

The presence of these maxima, which have been observed for all the nephelines studied, indicates that the structure of nepheline at low temperatures cannot adequately be described in terms of the Buerger unit cell (Hahn and Buerger, 1955), which must accordingly be regarded as an average over the true structure involved. The additional inten-

[1] Similar maxima in nepheline have been described by Sahama (1958) for a nepheline from Iivaara.

sity maxima may be interpreted quite generally as implying a statistical antisymmetrical distribution involving a unit cell of three times the volume of this average cell with $a' = a\sqrt{3}$ and $c' = c$. Direct evidence for this antisymmetrical distribution exists in the published structural analysis and is indicated, for example, by the threefold degeneracy of oxygen O_1. In that the additional intensity maxima in nepheline become diffuse at temperatures above 200° C on thermal treatment, the low-temperature structural state characterized by sharp maxima can be stable only below this temperature. Further, in that the maxima cannot be completely removed by extended thermal treatment at high temperature (1000° C) the possibility of Al–Si ordering in the antisymmetrical state must be considered.

Natural nepheline specimens studied. The nepheline specimens studied in the present investigation were kindly provided by Prof. C. E. Tilley. As already noted, they were chosen in order to illustrate a wide range of compositions and modes of origin. Certain analytical data for these nephelines, where available, have been set down in table I, which also contains some information on their petrological associations. Data from two new analyses of nepheline (specimens 2 and 3 of table I) were provided by Prof. Tilley. Both in table I and in fig. 1 the composition of the individual nepheline samples has been presented in terms of the atomic percentage of Ca, Na, K, and vacancies (□) on large cation sites (Smith and Sahama, 1954). In terms of composition the nephelines chosen range from 81 at. % Na to 54 at. % Na. In respect of origin they range from a typical phonolite to a nepheline–biotite–scapolite gneiss and include representative nephelines from both igneous and metasomatic alkali syenites.

Preliminary X-ray study. A preliminary single-crystal X-ray study of a number of nephelines showed that maxima similar to those observed by Sahama (1958) were invariably present. The maxima were in most cases readily visible on single-crystal photographs taken with normal exposure times. In oscillation photographs with oscillation axis [0001] the maxima occurred on additional layer lines distant approximately $\pm 2/9$ of the true repeat from the main layer lines.

Examination of single crystal photographs of different nepheline specimens (these have been indicated in table I) showed that whereas the maxima were invariably present in the same positions[1] different specimens varied quite widely in the sharpness of the maxima observed.

[1] The precise positions of the maxima were determined at a later stage by electron diffraction technique for all the nephelines that showed sharp additional maxima.

TABLE I. Data on the nepheline specimens studied. The asterisks in the last two columns indicate whether the specimen was examined by electron diffraction, or by X-ray diffraction, or by both.

Serial number.	*Locality and rock type.*	*Section number.*	Ca.	Na.	K.	□	*Examined by electron*	*X-ray.*
1	*Phonolite* Abbot's Hill, Dunedin, New Zealand	63197	1·8	80·3	11·2	6·6	*s	*
2	*Intrusive aplite* Snipe River, Tambani, Nyasaland	65984	0·7	81·0	13·4	4·9	*vs	*
3	*Nepheline pegmatite* Goulding Keene Quarry, Egan Chute, York River, Ontario	61894	1·3	75·5	16·6	6·7	*d	*
4	*Nepheline pegmatite* Gooderham, Ontario	62066	1·9	73·4	16·7	7·9		*
5	*Theralitic canadite* Trooper Lake, Glamorgan Township, Haliburton Co., Ontario	64872	0·9	79·6	11·3	8·3	*d	
6	*Lardalite* Laagendal, South Norway	65936	1·3	76·6	13·3	8·9	*d	
7	*Tinguaite* Cargill's Castle, Sea View, Dunedin, New Zealand	63361		unanalysed			*ms	*
8	*Phonolite* Wolf Rock, Cornwall	65842		,,				*
9	*Nepheline, scapolite, biotite gneiss* Egan Chute, York River, Ontario	62015	4·9	70·7	16·4	8·0	*vs	
10	*Potassic lava* East Africa	FEAE 92	2·3	54·3	38·7	4·7	*vd	
	Morozewicz composition		—	76·1	19·1	4·8		

The character of the additional maxima as observed by electron diffraction have been indicated thus: vs very sharp; s sharp; ms moderately sharp, d diffuse; and vd very diffuse.

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4. H. S. Yoder and C. E. Weir, Amer. Journ. Sci., 1951, vol. 249, p. 687.
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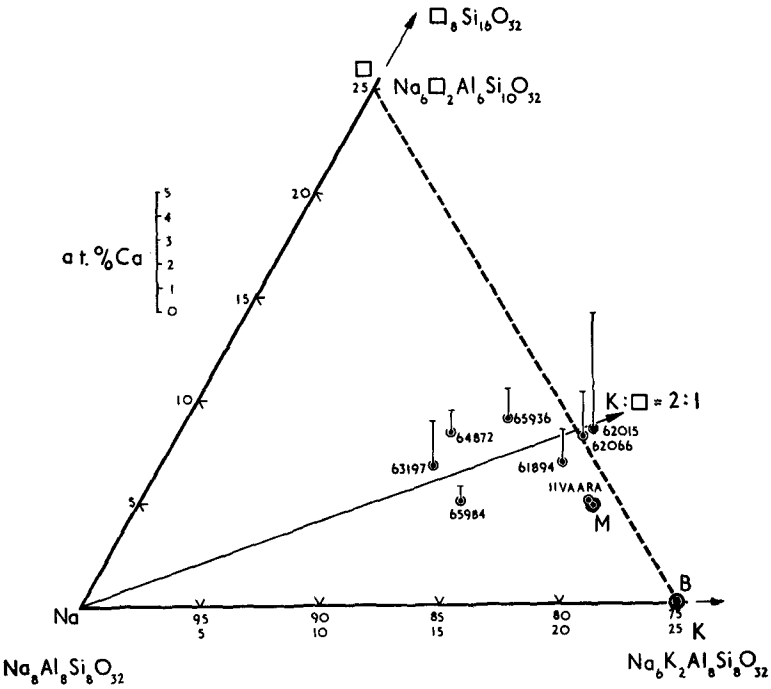

FIG. 1. Plot showing the compositions of the nephelines studied in terms of the atomic percentage of Ca, Na, K, and vacancies. The individual points have been projected on the Na–K–□ face of the tetrahedron and the Ca content has been illustrated.

Only in one specimen examined by X-ray technique were the maxima really sharp. This was the case for the Nyasaland nepheline, 65984.

Electron-diffraction study of the additional intensity maxima in low-temperature nepheline.

In view of the relatively high intensity shown by the additional intensity maxima on X-ray single crystal diffraction photographs their observation was attempted by electron-diffraction technique. The instrument used was an Elmskop I which was operated throughout the experiments at 100 kV. In order to avoid undue heating effects in the nepheline samples examined, beam currents in the range 5–10 μA were used and extensive use was made of defocused illumination.[1]

[1] An account of the behaviour of the additional maxima during thermal treatment is presented below (p. 120). The experimental results obtained during laboratory

Crushed nepheline samples were found to yield a wide range of reciprocal lattice sections on diffraction, implying that there was little if any tendency to preferred orientation on the carbon mounting film. The anomalous diffraction effects were observed in all the nepheline specimens studied but, as anticipated from the single crystal X-ray study, the maxima for different specimens showed a wide range of character in respect of intensity and sharpness. In only three of the specimens studied were the maxima sufficiently sharp to allow of accurate measurement of their positions in reciprocal space, and in the case of the potassic nepheline FEAE 92 they were extremely diffuse. In that the results of the measurements on the sharp maxima were particularly interesting it will be convenient at this point to summarize the main advantages achieved by using electron-diffraction technique in this context. Suitable diffraction plates were obtained in times of the order of one-minute exposure using a defocused condensing lens system and a selected-area diffraction aperture subtending a specimen diameter of one micron. The additional maxima were not visible directly on the fluorescent screen. In the first place the radiation used was rigorously monochromatic.[1] Further in that a series of effectively undistorted and 'stationary' reciprocal lattice plots were obtained it was possible to define the shape and size of the additional maxima, their precise positions when sharp, and the nature of weak associated diffraction effects, from a limited number of diffraction plates.

These points are well illustrated by the two photographs presented in plate III, which, when taken together, serve to define the position and character of the additional maxima for nepheline 65984. In fig. A of this plate the additional maxima constitute a Laue zone that enters the reflecting sphere from the left, due to tilt of the c^* axis. It shows clearly the spacing of the additional maxima along c^* rows and indicates that the maxima are slightly disk-shaped, being broader in dimension normal to c^*. The photograph indicates that the additional maxima approach but do not equal the primary Bragg maxima in sharpness.[2]

Pl. III, fig. B, illustrates the occurrence of the additional maxima in

heating suggest that the crystals were not heated to temperatures exceeding 200° C by the electron beam during the observations.

[1] High-tension stability over a period of one minute is quoted as being better than one part in 50 000.

[2] Care must be taken in assessing the true half-peak width of the Bragg maxima since the photograph is over-exposed. An indication of the sharpness of the Bragg maxima can best be obtained by studying the maxima at some distance from the main reflecting position.

the plane ac^*. It also shows the presence of weak Bragg maxima of type $000l$ with l odd. Such maxima are forbidden in space group $P6_3$ to which nepheline has been assigned. In that they are invariably very weak the presence of symmetry operator 6_3 must be considered a very good approximation.

In the three nepheline specimens that yielded sharp additional maxima, measurement of their positions showed that they could be defined in terms of the reciprocal unit cell for nepheline by vector coordinates $\pm(\frac{1}{3}, \frac{1}{3}, \pm z)$. The measurements showed that the c^* coordinate was in all cases irrational and varied quite appreciably for the two nepheline specimens with the sharpest maxima. The determined values of this coordinate are:

Ne 65984	z 0·2068±0·0010
Ne 63197	0·2058±0·0025
Ne 62015	0·2134±0·0010

The measurements involved were made on the diffraction plates using a travelling microscope. The positions of the additional maxima in reciprocal space have been illustrated schematically in fig. 2. Fig. 2*b* illustrates the measurements used to determine the z coordinates, and fig. 2*c* illustrates the distribution of the additional maxima about a single reciprocal lattice point.

The following observations were made on the general distribution of the additional maxima in reciprocal space. No systematic absences were observed but it was noted that additional maxima about the Bragg maxima $000l$ with l even were considerably stronger than all others. It was also noted that the additional maxima, though weak, were also present about reciprocal lattice points $000l$ with l odd. The maxima were also observed about the direct beam 0000 but in this case they were of average intensity only. Attempts to use them in conjunction with the primary beam in direct electron optical resolution experiments were unsuccessful (for the details of this technique see, for example, McConnell and Faria, 1961).

With the exception of the three nephelines dealt with above, all the nephelines studied by electron-diffraction technique showed diffuse additional maxima. In all cases these maxima were particularly broad in the direction normal to c^*. It was possible only to define their positions as being consistent with the measurements made on the sharp maxima. The general character of the diffuse maxima has been illustrated in fig. 2*d*. In most cases weak streaks of approximately uniform intensity joined the diffuse maxima to adjacent Bragg maxima, as illustrated. As

in the case of the sharp maxima the diffuse maxima were strongest about Bragg maxima $000l$ with l even.

Thermal treatment of natural nephelines.

Heating experiments were carried out on nephelines 61894 and 65984 in order to determine the minimum temperature at which appreciable

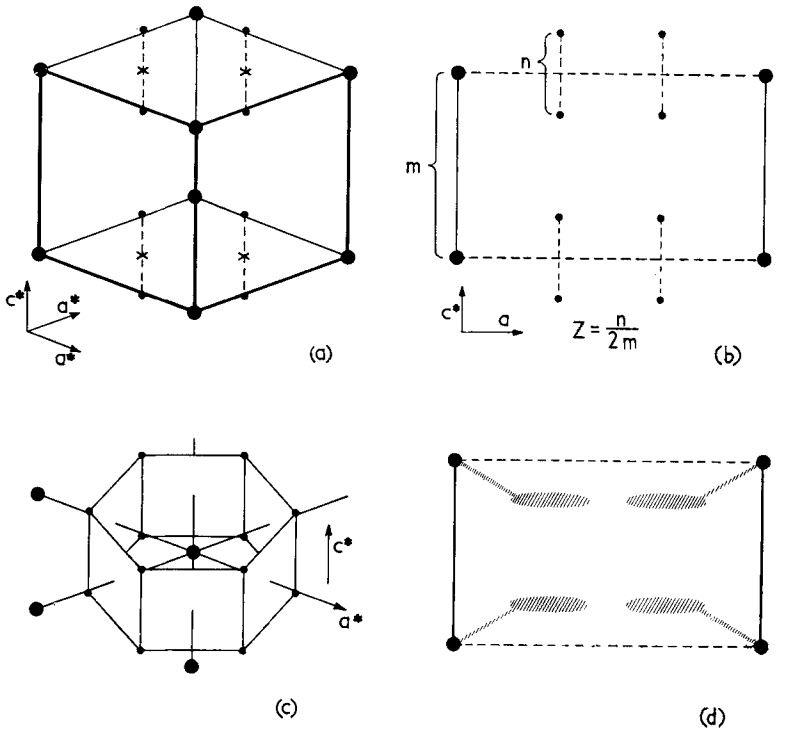

FIG. 2. Schematic plots showing the positions and character of the additional maxima in reciprocal space. Fig. *b* illustrates measurement of the c^* coordinate of the maxima, fig. *c* illustrates the positions of the maxima in respect of a single Bragg maximum, and fig. *d* shows the character of the maxima when diffuse.

change in the character of the additional maxima could be observed and the extent to which the maxima could be diminished in intensity by treatment at high temperatures. The details of these heating experiments are presented in table II. The single crystals were examined by X-ray technique since a sequence of isothermal treatments were accorded to the same single crystal in several cases.

At all temperatures above 200° C heat treatment produced a noticeable change in the character of the sharp maxima of Ne 65984 in a short time. At 250° C, where an extended sequence of observations were made, it was noted that an initial period of heating for 10 minutes produced a diffuse halo around the additional maximum, which at the same time remained sharp and intense. Little change in the intensity and diffuseness occurred during the succeeding treatment at 250° C, which

TABLE II. Data on the thermal treatment of nephelines studied by single crystal X-ray technique.

Specimen.	*Temperature* (° C).	*Pressure* (*atm.*).	*Time* (*hours*).	*Nature of the additional maxima present.*
2	950	dry	24	very weak and diffuse
2	900	dry	24	very weak and diffuse
3	600	dry	24	weak and diffuse
3	500	dry	26	weak and diffuse
3	750	1000	138	weak and diffuse
3	600	1000	89	weak and diffuse
2	500	dry	2	weak and diffuse
2	400	dry	2	weak and diffuse
2	250	dry	0·17	sharp maxima on a diffuse background
			0·5, 1·0, 2·0, 6·0, 32·5	very slight increase in diffuse character, maxima remained intense
2	200	dry	4·0	maxima slightly diffuse
2	150	dry	5·0, 29·0	no observable change in the maxima

continued for a total time of 32½ hours. No detectable change in the additional maxima was observed in a single crystal specimen after heating at 150° C for 29 hours, but a specimen heated at 200° C for a short time did show appreciable change.

In the temperature range 400° to 500° C the maxima became quite weak and diffuse after several hours heating. A sample of Ne 65984 heat-treated in the dry at 550° C was examined by electron-diffraction technique. The maxima observed were very diffuse and particularly broadened normal to c^*. The diffuse maxima were also connected to adjacent Bragg maxima in the manner illustrated in fig. 2*d*.

Extended thermal treatment of single crystals at temperatures in the range 600° to 950° C using both dry and hydrothermal techniques showed that while the maxima were considerably reduced in intensity, and had become very diffuse, they were still present.

A series of experiments were also carried out on powdered specimens, thermally treated under both wet and dry conditions, in order to detect, if possible, any change in lattice parameters associated with the reduction in intensity of the additional maxima. These experiments were carried out on Ne 65984 and are detailed in table III. The quenched powders were examined by X-ray diffractometer technique in the range appropriate to the Bragg maxima $21\bar{3}0$ and $20\bar{2}2$ using an internal silicon standard (Smith and Sahama, 1954). The results of measurements of peak positions on comparison with those of the untreated

TABLE III. Data on the thermal treatment of the Nyasaland nepheline 65984; X-ray diffractometer study. All except the last run under 1000 atmospheres water-vapour pressure; run 125 dry.

Run.	*Temperature* (° C).	*Time* (*hours*).	*Run.*	*Temperature* (° C).	*Time* (*hours*).
121	500	136	124	650	89
123	550	89	120	700	138
122	600	89	125	1050	15

material showed that there was no appreciable change in the lattice constants of the heat-treated specimens, the results of all measurements lying within permissible observational limits of $\pm 0{\cdot}005°$ of θ.

In summary the results of the heating experiments indicate that whereas noticeable change in the character of the additional maxima occurs at temperatures as low as 200° C, the maxima are still present after experiments of considerable duration at high temperatures.

General conclusions.

The present investigation suggests that additional intensity maxima are characteristic of nephelines from all types of paragenetic environment, and are shown by nephelines of widely varying composition. The structural implications of these maxima, when they are intense and sharp, are important in that they imply that the structure of nepheline at low temperatures cannot be adequately described in terms of the unit cell defined by Hahn and Buerger, 1955. This unit cell must be regarded as an average in respect of the true structure. The irrational character of the c^* coordinate of the additional maxima, as defined from the electron-diffraction study, also implies that it would not be correct to define the low-temperature structural state in terms of a superlattice in the normally accepted sense.

In that the additional maxima occur in pairs about reciprocal lattice

points defining a cell of three times the volume of the Buerger unit cell, i.e. with $a' = a\sqrt{3}$ and $c' = c$, it is convenient at this stage to suppose that the true structure in the low-temperature state involves a statistical antisymmetrical array in respect of this large cell. The sharpness of the additional maxima in certain cases suggests that the probability rules defining this antisymmetrical array are quite precise in character.

It is of interest at this stage to examine the Buerger structure in the light of this suggestion. Certain details of the structure, as recorded, point directly to the correctness of the hypothesis suggested. This is particularly obvious, for example, in respect of the oxygen labelled O_1, which in the averaged cell occupies a threefold degenerate position just off the triad axis. Similar effects are also observed in respect of the other oxygen atoms present. A further point concerns the possibility of Al–Si ordering in the low-temperature structural state. In that the additional maxima remain after prolonged thermal treatment at high temperatures it may be anticipated that they are concerned with the effects of Al–Si ordering in the structure. The Buerger structure indicates that, in respect of the average cell defined, only the tetrahedral sites on the triad axis have an ordered Al–Si distribution. The possibility of ordering of all the tetrahedra, in a manner consistent with the antisymmetrical distribution proposed, must therefore be admitted.

Further comments on the structure of low-temperature nepheline must await more detailed structural investigation based on the intensities of the additional maxima. This work is currently in progress.

The wide range in character shown by the additional maxima of intensity in nepheline allows of no simple correlation being made with natural equilibration rates as is the case, for example, for similar diffraction effects in the plagioclase feldspars. It would appear that the additional maxima present in the nepheline from a phonolite may be sharper and more intense than those observed in a nepheline of low-temperature origin. Apart from suggesting that the maxima almost certainly reflect on the whole equilibration cycle of the specimen, down to quite low temperatures, and may be affected by later reheating, this anomaly cannot at present be explained.

A kinetic study of the thermal behaviour of the additional maxima and further work on their structural and thermodynamic implications are in hand.

Acknowledgement. The author wishes to express his sincere thanks to Prof. C. E. Tilley whose advice, help, and interest have been invaluable in the present investigation.

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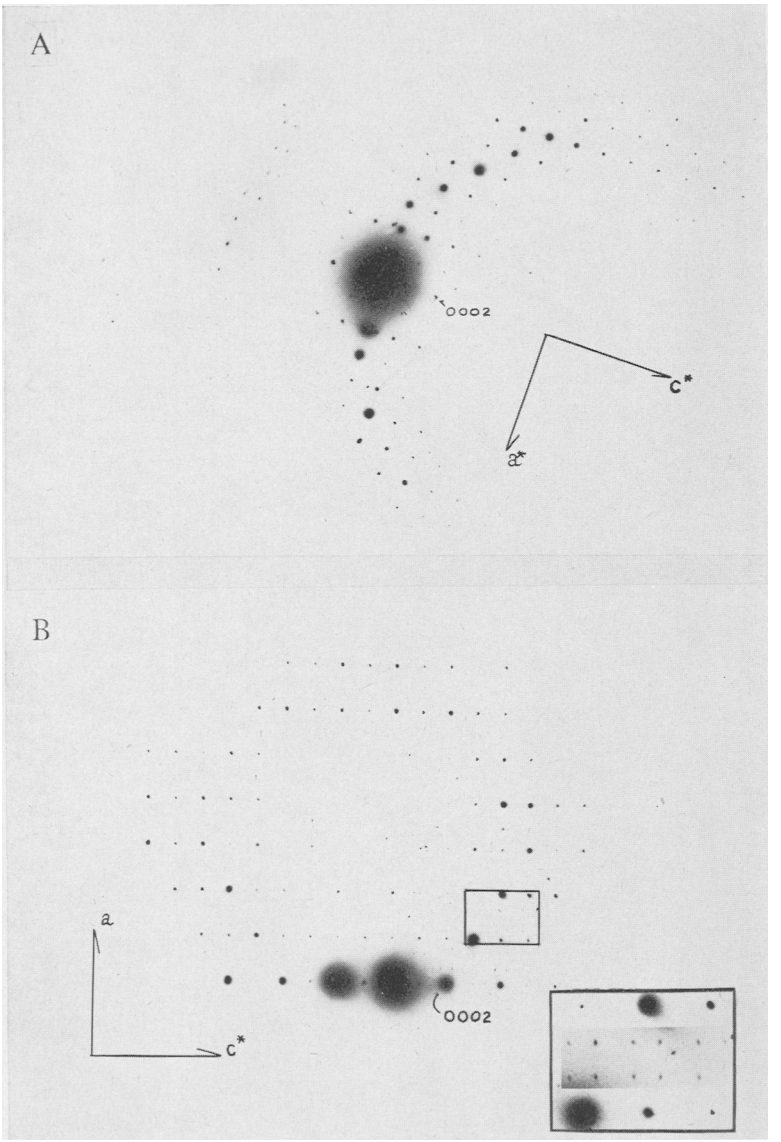
EXPLANATION OF PLATE III.

FIG. A illustrates the occurrence of the additional maxima lying on c^* rows on the left of the photograph.

FIG. B illustrates the position of the additional maxima in the plane ac^*. A small area of the photograph is shown enlarged in the bottom right-hand corner. A masking technique was used during enlargement in order to show clearly the positions of the additional maxima with respect to the Bragg maxima which on the original plate were very considerably over-exposed.



J. D. C. MCCONNELL: ELECTRON-DIFFRACTION STUDY OF SUBSIDIARY MAXIMA OF SCATTERED INTENSITY IN NEPHELINE