Time–temperature study of the intensity of satellite reflections in nepheline

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Abstract

This paper describes the use of a new precision heating device, mounted on a Philips PW1100 single crystal diffractometer, in following the intensity changes in the satellite reflections of nepheline on heating. This time–temperature study of the satellite intensities indicates that two kinetically distinguishable structural changes are involved. Spontaneous and reversible changes in intensity, on heating and cooling, are attributed to a displacive component in the transformatioon behavior. Irreversible intensity changes, associated with an activation energy of 19 kcal/g ion, are attributed to the process of disordering K ions and vacancies in the large channels of the nepheline structure, by analogy with the behavior described for the self diffusion of K ions, in similar circumstances, in K-substituted analcime.

Introduction

This paper is concerned specifically with the study of the time–temperature behavior of the intensity of satellite maxima in nepheline. These satellites were first described by Sahama (1958) and were observed in a large number of nephelines by McConnell (1962). The present heating experiments were done on a new, precision heating device which was designed to be totally compatible with the Philips PW1100 single crystal diffractometer. A description of the new heating device has been included in the present paper.

The heating experiments on nepheline were initiated because it appeared likely that nepheline, with its incommensurate fine structure, was likely to be a further example of the type of resonance structure first described by McConnell (1978) for intermediate plagioclase feldspars. In order to test this hypothesis, it was necessary to study the temperature dependence of the satellite maxima to determine whether or not two kinetically-distinguishable structural events could be defined in relation to the postulated resonance structure.[1] Prior to the heating experiments

there was no clear indication of the likely nature of the postulated resonance components, except that it was reasonable to suppose that one of them was concerned with displacements in the tetrahedral framework of the nepheline structure.

The possibility of using the kinetics of intensity change to study the components of the transformation behavior of nepheline was initially envisaged in the context of the analysis of similar kinetic data on the resonance structure in the intermediate plagioclase feldspars (McConnell, 1978). In this case the reversible changes observed for the satellites on heating were associated with ordering on the basis of the Ca/Na component of the structural resonance, whereas the irreversible loss of the satellites at high temperature was associated with the loss of Al/Si order (Foit and Peacor, 1967; Bown and Gay, 1969).

In order to apply a similar experimental technique to the satellite intensities in nepheline it was anticipated that measurements of intensity change, on a total time scale of the order of tens of minutes, would be necessary (McConnell, 1962). It was for this reason that a single crystal, computer-controlled, diffractometer was employed, and a precision heating

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[1] The threefold displacement of the oxygen atom O_1 in nepheline, which is observed in the average structure at all temperatures (Foreman and Peacor, 1970), constitutes evidence for an independent displacement mode associated with the tetrahedral framework in nepheline. In the original definition of the concept of a structural resonance (McConnell, 1978) it was

demonstrated that independent transformation modes which are forbidden by symmetry from interaction at a symmetry point in K-space may do so off the symmetry point if their reduced symmetry is then the same. In general this favorable interaction is responsible for the appearance of satellite reflections symmetrically disposed about the symmetry point in question.

device with very low thermal inertia was designed and built.

Previous work

The earliest experiments on the thermal behavior of the satellite intensity maxima in nepheline are recorded by McConnell (1962). In these experiments the single crystal X-ray studies were done at room temperature after heating experiments in a conventional laboratory furnace. The experiments showed that, on heating to temperatures in excess of 200°C for a short time, an irreversible loss of intensity occurred. Similar studies in which a heating device (Rickson et al., 1963) was mounted on a single crystal X-ray oscillation camera, were later carried out by Parker (1970), and the results of these experiments are recorded in his thesis and by Parker and McConnell (1971). These experiments indicated that intensity is partially recovered on cooling the nepheline single crystal, but that the time scale utilized in the photographic recording method used was such that it was impossible to monitor the short term changes in intensity involved. These latter data collected by Parker are entirely consistent with the present results, obtained on the single crystal diffractometer, and will not be referred to further in the present paper.

Experimental details

Methods

In the present study of nepheline Parker's data were used to select some of the strongest satellite maxima for the heating experiments on the single crystal diffractometer. In using this instrument it was convenient to index the satellite maxima in terms of a large cell with $a' = a\sqrt{3}$, and $c' = 5c$, where a and c are the standard cell dimensions of the Buerger unit cell for nepheline (Hahn and Buerger, 1955). The c^* coordinate for the satellites in the nepheline specimen used in these experiments, HC65984, was actually 0.2068, as measured on electron diffraction photographs (McConnell, 1962).

On the basis of the indexing system defined above, the strongest satellite maximum observed by Parker was 1 0 29. The related member of the pair, 1 0 31, had an observed intensity of only one third of that of 1 0 29. These two satellites were symmetrically disposed about the absent true superlattice point (1 0 30), which may be referred to as a point in the set {⅓ ⅓ 0 } (McConnell, in prep.). The strong satellite maximum, 1 0 29, was used throughout the present series of heating experiments on the single crystal dif-

fractometer. Its intensity during the course of the experiments was monitored by observing, at frequent intervals, the intensity of the adjacent strong Bragg reflection 0 0 30, (0 0 6). The intensity ratio (0 0 30) : (1 0 29) was determined as 1.0:0.0055 at room temperature. By using this Bragg reflection as a reference it was possible to ensure that the observed satellite intensity changes were real, and not due to misorientation effects resulting from the movement of the single crystal on its ceramic support during heating.

Intensity measurements on the satellite maximum 1 0 29 during the heating experiment were made in two ways. A conventional $\theta/2\theta$ scan was used to obtain a digital record of the integrated peak intensity and the relevant background counts. At the same time, and in all the experiments, an analogue record of peak shape and position within the scan window was obtained using a conventional x–y recorder. The scan width chosen was 1.8°, and the collecting slits were 2.0° and 1.5°, in horizontal width, and in height, respectively. A scan speed of 0.005° per second represented the best compromise, in relation to total counts and the time scale for observed changes in intensity, in preliminary experiments. Monochromatic CuK_α radiation was employed, and a count rate in the range 400 cps was observed initially for the strong satellite 1 0 29. With an observed background count rate of 8 cps there was an adequate peak to background ratio of counts even when substantial loss of peak intensity occurred at higher temperature. Six single crystals of nepheline, all prepared as spheres with diameters in the range 200–300 microns, were used in the experiment.

The heating device

Two objectives were defined in designing a heating device for the Philips PW1100 single crystal diffractometer. The first was simply that the heating facility should be entirely compatible with all possible operations and movements of the diffractometer. The second objective, especially important for the study of rapid and transient intensity changes, was to achieve a high degree of precision and stability in temperature control in a device with very low thermal inertia.

The central component of the heating device is a block of duralumin with cylindrical recesses into which a pair of windows were fitted (Fig. 1). This block was drilled vertically at both ends to take a pair of carefully balanced heater elements with a maximum power consumption of twelve watts. The
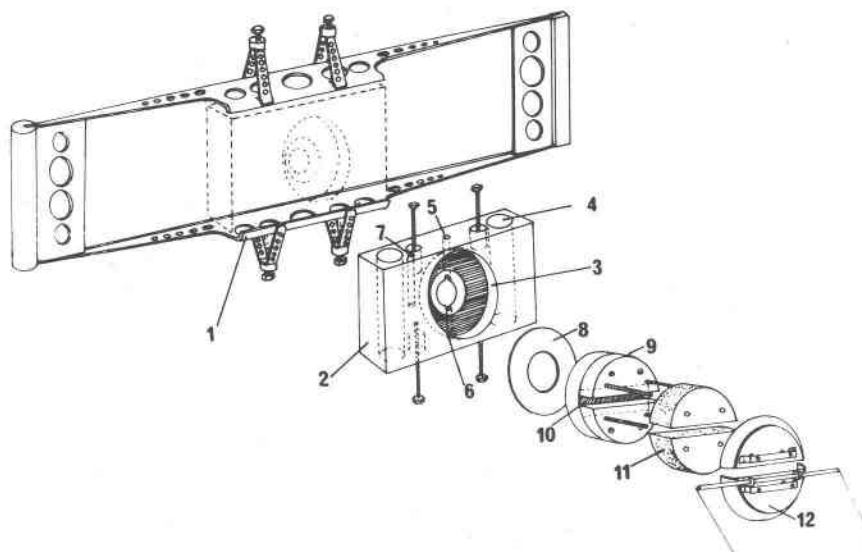
Fig. 1. Details of the heater block, the windows and the support frame. 1. Stainless steel support frame; 2. Heater block; 3. Recess for the window; 4. Heater element; 5. Record thermocouple well; 6. Crystal entrance hole; 7. Control thermocouple well; 8. Tungsten friction washer; 9. Window disc; 10. Trapped 1 micron thick aluminum foil window; 11. Insulation; and 12. Radiation caps, with lower cap carrying the ceramic support tube for the spring loaded support system.

block was also drilled to hold control and recording thermocouples and to provide access for the single crystal mounting system, which was used on the goniometer provided with the instrument.

The heater block, its heating elements, and thermocouples were supported within a light, stainless steel frame by four long thin stainless steel screws (Fig. 1). These screw supports had the effect of reducing the heat loss from the block by conduction to very low values. The frame, in which the block was rigidly held, was set on slides to provide for a vertical movement of approximately two centimeters, which was necessary in mounting the single crystal. The slides were also adjustable to allow for movement of the frame, both within and normal to the plane of the CHI circle. With these facilities it was a simple matter to set the heating block with the crystal entrance hole exactly aligned on the vertical axis of the diffractometer. The adjustable slides were, in turn, built into a cylindrical ring which was bolted into the CHI circle of the diffractometer.

Because the entry hole in the heated block for the single crystal mounting was made as narrow as possible, it was necessary to devise a system of mounting the single crystal on the goniometer so that it was precisely centered along the vertical axis of the diffractometer. This was achieved by mounting the crystal with ceramic cement on a length of 100 micron silica glass fiber. This fiber was then cemented into a length of 0.5 mm, stainless steel, hypodermic

tubing which was a push fit in an axially-drilled steel cylinder. This small cylinder fitted exactly the existing socket on the Philips goniometer head. Although the total free length of the hypodermic tubing and the silica glass fiber was approximately 16 mm, this method of mounting ensured that misalignment of the crystal did not exceed 50 microns in the horizontal plane.

The construction of the windows, which fit into the heater block, is illustrated in Figure 1. The part of the window assembly that is heated is composed of discs which were separated from the bearing surface in the block itself by a thin tungsten washer. This washer also helped to reduce friction during operation. The two duralumin discs were slotted horizontally and screwed together, trapping between them a 1 micron thick Al foil. This foil sealed off the small cavity in the block occupied by the single crystal and, at the same time, permitted the passage of both incident and diffracted X-ray beams. During experiments the window discs were heated very effectively to the temperature of the heater block itself by direct, spring-loaded contact. The window disc assembly was heavily insulated externally, and this insulation was held in position by a pair of polished radiation caps, which were secured to the disc assembly by four long thin stainless steel screws to reduce heat transfer. The lower of the two caps held a fine ceramic tube into which were inserted the spring steel support wires for the complete window assembly

(Fig. 1). The window support wires were held in an adjustable frame which was bolted directly to the base of the CHI circle, and rotated with it on the OME axis of the diffractometer.

This design for the windows, and their support system, ensured that loss of heat by radiation and conduction from the window discs was extremely low. The mounting also allowed some flexibility and permitted the windows to adjust naturally within the recesses in the heater block.

In operation the heater block, in its support frame, was free to rotate to ±180° with the CHI circle, whereas the windows, with their horizontal slits, remained stationary. The obvious advantages of this design were that the single crystal was effectively contained in a highly-conducting metal thermostat, and that it was practicable to change temperature reliably at rates up to 100°C per minute because the system had very low thermal inertia. In practice it was found that control and record thermocouples, which were made of copper-constantan, never differed by more than 2°C and that, for discrete changes in control temperature of the order of ten degrees, the time lag at the record couple was only a few seconds. A Eurotherm, 2μV step, fast-switching controller was used to control the temperature of the heater block, with a control copper-constantan thermocouple as sensor. In isothermal experiments the heating device was capable of temperature control to ±0.02°C. The maximum temperature to which the heater was tested was 300°C.

In spite of the fact that the whole heater assembly, apart from the windows, was uninsulated, it was possible to operate reliably in an open room, providing that one took elementary precautions to avoid draughts. In the final system all parts of the furnace and the wiring system were designed to stay within the available 30° obscuration angle of the diffractometer in all permissible instrumental configurations.

Experimental results

In a preliminary study of the satellite intensities using the single crystal diffractometer it was important to establish initially that sets of satellite reflections related by the sixfold axis in nepheline were really equal in intensity, and that the mineral showed no discernible departure from hexagonal symmetry in the context of the additional maxima. Such measurements were made at room temperature on reflections of the set containing 1 0 29 for each of the six different nepheline single crystals used in the com-

plete series of experiments. The intensity data indicated that there was no reason for suspecting that nepheline lacked a sixfold axis.

Although a large number of experiments on the nepheline single crystals were done at elevated temperatures, we report here only the details on the final sequence of experiments which were designed to provide a continuous time–temperature record of the satellite intensity behavior in the temperature range 100–150°C. Preliminary experiments demonstrated clearly that, in this temperature range, it is possible to observe change in intensity of the satellites as a function of time in isothermal experiments. In addition, once the single crystal of nepheline had been held for sufficient time at any chosen temperature in this range, a perfectly reversible, and apparently spontaneous decrease and increase in intensity occurred on heating and cooling the specimen, up to this limiting temperature. Subsequent heat treatment, over a time period, at some higher temperature resulted in further, irreversible loss in intensity but, apart from this loss, the crystal again behaved quite reversibly with regard to intensity change within the new temperature limits. In the final, definitive series of experiments it did not appear necessary to return to room temperature between each of the isothermal runs because the behavior could be anticipated from the preliminary experiments.

In the final sequence of experiments a single crystal of nepheline was heated, in less than three minutes, from room temperature to 100°C. The intensity of the satellite 1 0 29 was then monitored continuously over a period of six hours, and until there was no evidence of further loss in intensity. The behavior in this run, plotted in terms of total integrated peak counts, is illustrated in Figure 2. The single crystal
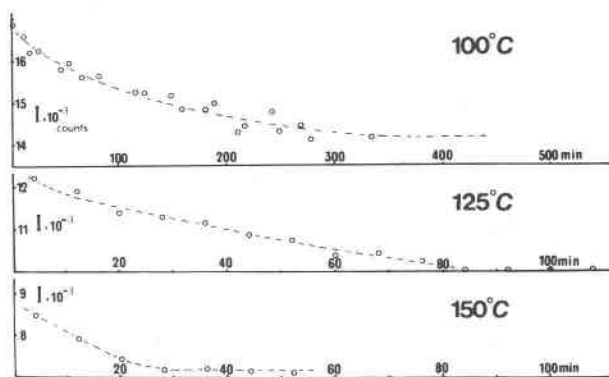

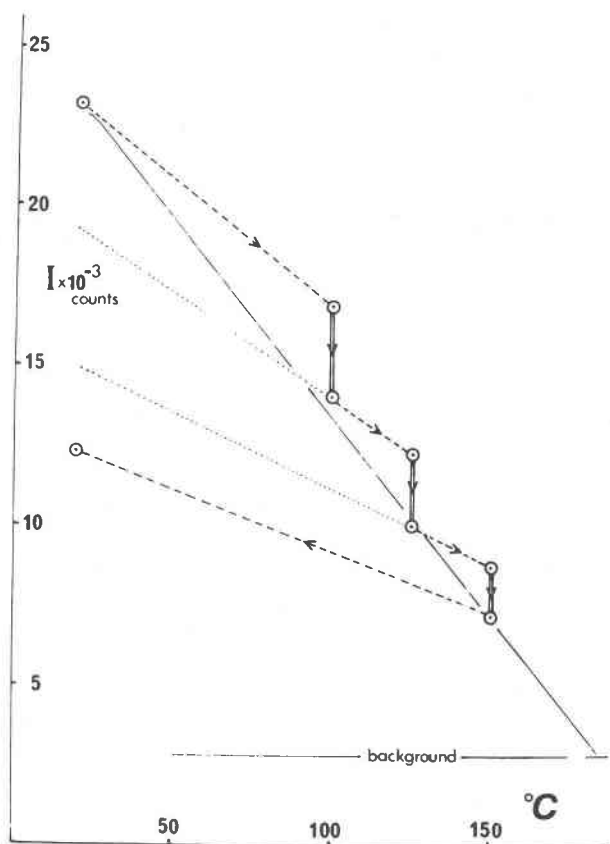Fig. 2. Intensity plots, as a function of time, for the satellite peak 1 0 29 at three different temperatures.

Fig. 3. Composite diagram showing the overall intensity changes of peak 1 0 29 with both time and temperature. The dashed lines indicate spontaneous change in intensity on rapid heating and cooling. The double full lines indicate the irreversible change in intensity in isothermal runs, and the dotted lines indicate the inferred changes in intensity on heating and cooling between the isothermal runs, as observed in prior experiments on other crystals.

was then heated within approximately one minute from 100°C to 125°C, and the intensity change recorded is shown in Figure 2. In the final experiment of the series, the temperature was raised in approximately one minute from 125 to 150°C and the isothermal loss of intensity took place in approximately half an hour as shown in Figure 2. Throughout these experiments both the intensity and position of the Bragg reflection 0 0 30 (0 0 6) were monitored at frequent intervals. This reflection showed a slight decrease in peak intensity on heating to the temperature of the experiments.

The results of this series of experiments are summarized in Figure 3 where the spontaneous change in intensity, on heating, is shown by dashed lines. The isothermal change in intensity is represented by double, full lines, and the extrapolated behavior of

the specimen, if it had been cooled to room temperature between each isothermal run, is shown with dotted lines.

From the recorded data on the three isothermal runs at 100, 125 and 150°C it was possible to extract data on the kinetics of the process associated with the irreversible loss of intensity at these temperatures. Because the intensity loss over a greater part of the time scale was approximately linear, it was possible to use the slope (dI/dt) at $t = \frac{1}{2}$ as a measure of the rate constant for the process. In using this parameter it was advisable to renormalize in terms of the total intensity change in each isothermal run, on the simple assumption that the rate data must depend linearly on the total change in intensity. Having plotted ln k, the rate constant, against T^{-1} (K) an activation energy of 19.3 kcal/g ion was established. This value is probably correct to ± 15%, an accuracy which is adequate for the purposes of interpreting the present data. It was not considered wise to attempt a more sophisticated analysis. The Arrhenius plot for the data is shown in Figure 4.

Discussion

The interpretation of the experimental data obtained from the single crystal heating experiments is reasonably straightforward. The spontaneous and reversible change in intensity observed on heating and
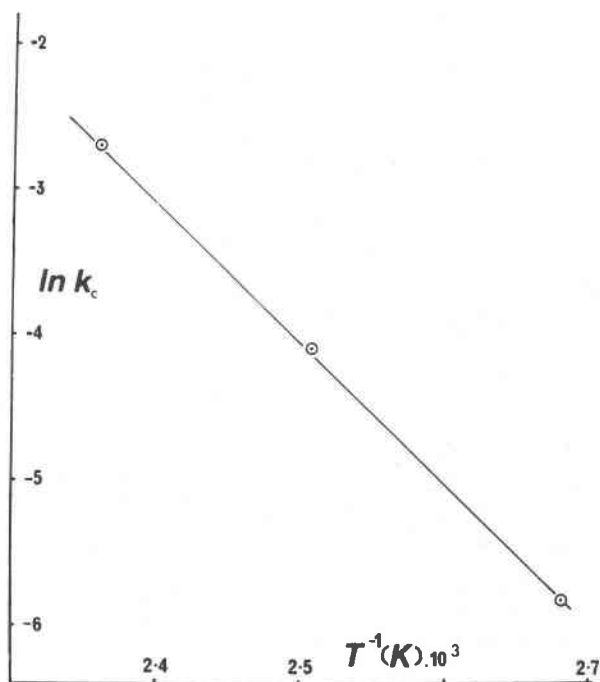

Fig. 4. Arrhenius plot of the rate data for the loss of intensity in isothermal runs at 100, 125 and 150°C.

cooling must clearly be associated with a displacive structural event in the overall transformation behavior of nepheline at low temperatures. The additional irreversible changes in intensity observed in the isothermal experiments merit further discussion. There is no serious reason for suspecting that change in the degree of Al/Si order is involved because the activation energy observed, 19 kcal/g ion, is much too small, and also the recent structural refinements on natural low temperature nephelines indicate that Al and Si are effectively completely ordered on the basis of the Hahn and Buerger unit cell (Foreman and Peacor, 1970; Dollase, 1970; Parker, 1970).

The only additional possible cation movements within the structure comprise the migration of either Na or K ions within the framework. Because the Na ion sites are fully occupied in the nepheline structure, they can only be directly involved if exchange occurs with the K ions in the channels. Because the Na and K sites remain distinct up to high temperatures (Foreman and Peacor, 1970), this suggestion carries little weight. Thus it is necessary to consider finally the possibility that the observed activation energy is associated with migration of the K ions in the large channels of the nepheline structure. Here there are strong *a priori* reasons for considering that such movements may occur because both the data available on compositions (McConnell, 1962) and data from all the recent structural analyses imply that approximately one-third of the K ion sites, $00z$, in the nepheline structure are normally vacant. Therefore there is a good case for suggesting that the irreversible loss of satellite intensity in nepheline must be associated with a process of disordering of the K ion and vacancies on the large channel sites.

Data available in the literature on the self diffusion of K ions in the related structure of analcime provide further confirmatory evidence for this hypothesis. In a series of experiments on the diffusion of tracer isotopes ^{134}Cs, ^{86}Rb, ^{42}K and ^{24}Na in the analcime structure, Barrer and Rees (1960) determined both the activation energy for self diffusion and the relevant self diffusion coefficients for all of these ions. In the analcime structure the Al/Si tetrahedral framework contains both eightfold and sixfold oxygen rings through which the large cations must pass in the course of the diffusion process. Whereas the configuration of the sixfold rings of oxygen ions in the analcime structure is comparable to that in the open channels of the nepheline structure, the existence of additional eightfold rings in the analcime structure implies that there need not be a very

close analogy between the mechanism of diffusion for large cations in the two structures. However, a general comparison of the kinetic data for the diffusion of large cations in the two structures is permissible.

Barrer and Rees (1960) obtained values for the activation energy for the diffusion of Na and K ions in analcime of 11.5 and 16.4 kcal/g ion respectively. Their data also indicate values of 1×10^{-11} and 1×10^{-14} cm^2 s^{-1} for the self diffusion coefficients of Na and K, respectively, at 100°C. These data imply that it is reasonable to associate the activation energy observed in the heating experiments on nepheline with the diffusion of K ions in the open channels of the structure, while noting that in nepheline the K ion is likely to be more tightly bound than the K ion in the more open analcime structure. A value for the diffusion coefficient associated with disordering K ions in the nepheline structure at 100°C may be obtained by using the period of the incommensurate structure, 41.8Å, and the time for half disordering at 100°C, 6 $\times 10^3$s. This gives an effective diffusion coefficient of the order of 3×10^{-17} cm^2 s^{-1}, which compares reasonably with the self-diffusion coefficient observed for the K ion in the analcime structure. However, the process of disordering of K ions and vacancies in the channels of the nepheline structure is a one-dimensional diffusion process, and must include an unfavorable entropy-of-activation term.

Conclusions

The results of these heating experiments on nepheline suggest strongly that the loss of satellite intensity is the result of two different, but intimately-related structural events. The spontaneous changes in intensity observed may be explained in terms of a simple displacive process in the nepheline framework. An additional, kinetically-hindered, structural event is present and can be studied in isothermal experiments. The kinetic analysis of this second transformation component accords well with the migration of the large K ion in the sixfold channels of the nepheline structure. This diffusion process causes a change in the satellite intensity pattern because it is related to the disordering of K ions and vacancies. The present experiments provide the first and only available direct experimental evidence which implies that in the fine structure of nepheline the ordering of K ions and vacancies forms an intrinsic component of the low temperature transformation behavior.

The existence of satellite intensity maxima in nepheline, when taken with the new evidence for a

second, ordering transformation mode involving potassium atoms and vacancies, provides a strong *prima facie* case for the existence of a structural resonance between ordering and displacement modes in nepheline. A full analysis of the nature of this structural resonance has already been made using Patterson data prepared from the nepheline satellite intensities. This analysis will be reported on in detail in a later paper.

Acknowledgment

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