The temperature dependence of the reflection intensities of anorthite (CaAl2Si2O8) and the corresponding formation of domains

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The Temperature Dependence of the Reflection Intensities of Anorthite (CaAl₂Si₂O₈) and the Corresponding Formation of Domains *)

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Zusammenfassung

Die Temperaturabhängigkeit der Reflexintensitäten von Anorthit wurde zwischen Zimmertemperatur und 1500° C gemessen. Die Intensitäten der sogenannten a- und b-Reflexe nehmen teilweise ab und teilweise zu. Die c-Reflexe zeigen eine kontinuierliche Intensitätsabnahme bis 240° C. Oberhalb dieser Temperatur ist ihre Intensität nahezu Null. Die Intensitätsänderungen werden durch die Entstehung von Domänen erklärt.

Abstract

The temperature dependence of the reflection intensities of anorthite has been measured between room temperature and 1500° C. The intensities of the so-called a- and b-reflections partly increase and decrease. The c-reflections show a continuous decrease of their intensity up to 240° C. Above this temperature their intensity is nearly equal to zero. The variation of intensity is explained by the formation of domains.

1. Introduction

The feldspar structures may be considered as TO_2-frameworks with relatively large voids occupied by the large cations. As details are concerned there are some features which still await satisfactory explanations.

TAYLOR, DARBYSHIRE and STRUNZ (1934) noticed that Ca-feldspar is distinguished from the alkali-feldspars by x-ray reflections that require doubling of the c-axis. It was assumed that some difference between the alkali ions on one side and the Ca ions on the other was responsible for such doubling.

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*) Dedicated to Sir Lawrence Bragg on his 80th birthday. The contents of this paper corresponds to a lecture given on the Bragg Symposium in London in April 1970.

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However, it was later shown (GOLDSMITH and LAVES, 1955) that this doubling is the consequence of Al/Si order on the T-sites. As experimental proof intensity changes of certain x-ray reflections were produced by the isomorphous replacement of Al by Ga, and Si by Ge. The structure determination of anorthite confirmed the crystal chemical reasoning (KEMPSTER, MEGAW and RADOSLOVICH, 1962; MEGAW, KEMPSTER and RADOSLOVICH, 1962).

It appeared practical to subdivide the anorthite reflections into three groups

    (a)   reflections,

    (b)   reflections, and

    (c)   reflections (designated by MEGAW as c- and d-reflections)

The structural meaning of these three reflection groups is illustrated in fig. 1. If we relate the feldspar structures to the same axes

$$a \cong 8 \text{ Å}; \quad b \cong 13 \text{ Å}; \quad c \cong 14 \text{ Å}$$

then the left side of fig. 1 represents the cell of the alkali feldspars. It is body-centered and c-edge centered. It shows reflections that we may call (a)-reflections. The middle cell is only body-centered; it shows in addition to the (a)-
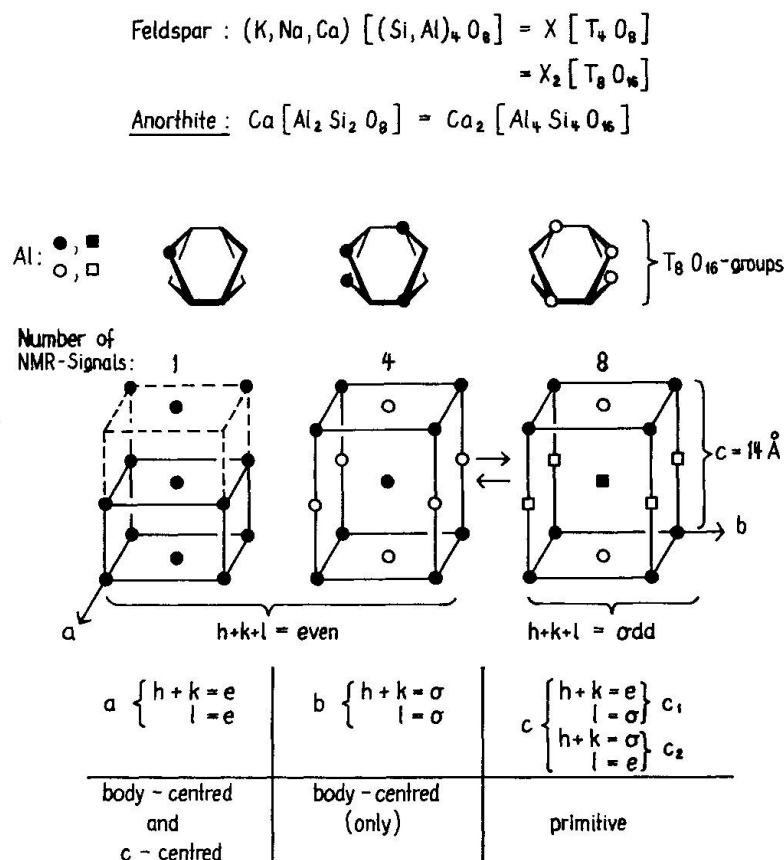

Fig. 1. Relations between superstructure reflections and corresponding elementary cells.

reflections the so-called (b)-reflections. As a consequence (a)-plus (b)-reflections lead to $h+k+l$ = even. If we add to $h+k+l$ = even-reflections the $h+k+l$ = odd-reflections then there is no condition, and we have a primitive cell as depicted on the right side of fig. 1. Thus the difference between the body-centered and the primitive lattice consists in the existence or non-existence of the $h+k+l$ = odd-reflections. They are called (c)-reflections.

There appears to be a continuous reversible nonquenchable variation of the stable states as a function of temperature (LAVES and GOLDSMITH, 1954). This variation becomes observable if one takes x-ray measurements at different temperatures (BROWN, HOFFMAN and LAVES, 1963) because even quick quenching does not preserve the equilibrium states of high temperatures.

The most interesting experimental facts reported up to now are the following:

The (a)-reflections are rather unaffected both by isomorphous replacement and by heat treatment.

The (b)-reflections are strongly affected by isomorphous replacement.

The (c)-reflections are strongly affected by heat treatment.

2. Experimental Results

We now deal with the temperature dependence of the reflection intensities. The measurements reported here are part of an investigation of the anorthite structure at different temperatures. The intensity measurements were carried out with an off line single crystal diffractometer using the θ-2θ-scan and filtered Mo-K_α-radiation. At each temperature the crystal was readjusted and the lattice constants were determined in order to measure the reflection intensities at the exact positions.

The crystal was mounted and heated in a hole at the top of a thermocouple. The latter was heated by an electric current in the first halfperiod of the alternating voltage, and its temperature was measured in the second halfperiod. The maximum deviation from the measured temperature is about $\pm 10°$ C.

Typical results are shown in figs. 2 to 4, which represent a selection of a large number of similar measurements. The marked errors given in the figures are equal to three times the standard deviation of the counting statistics. Some other results are reported and briefly discussed in CZANK, LAVES and SCHULZ (1970).

The (a)- and (b)-reflections remain sharp till the melting point (1540° C), whereas the (c)-reflections become weak and diffuse with increasing temperature.
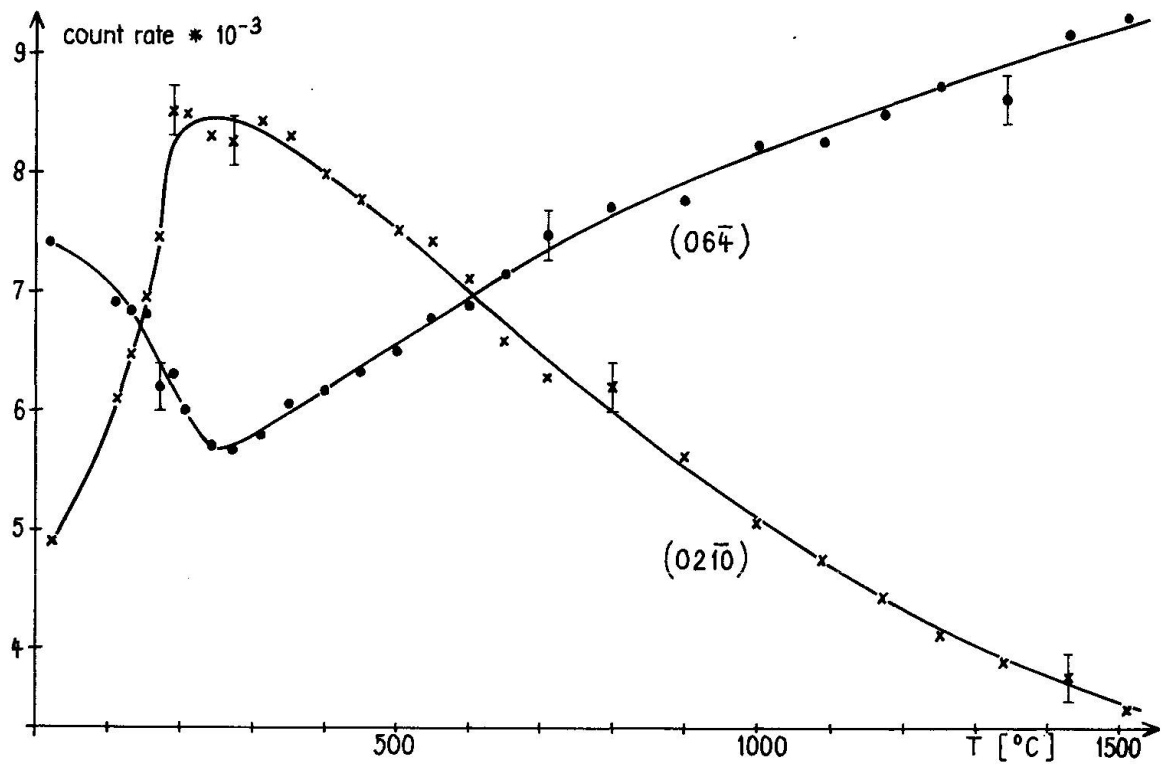
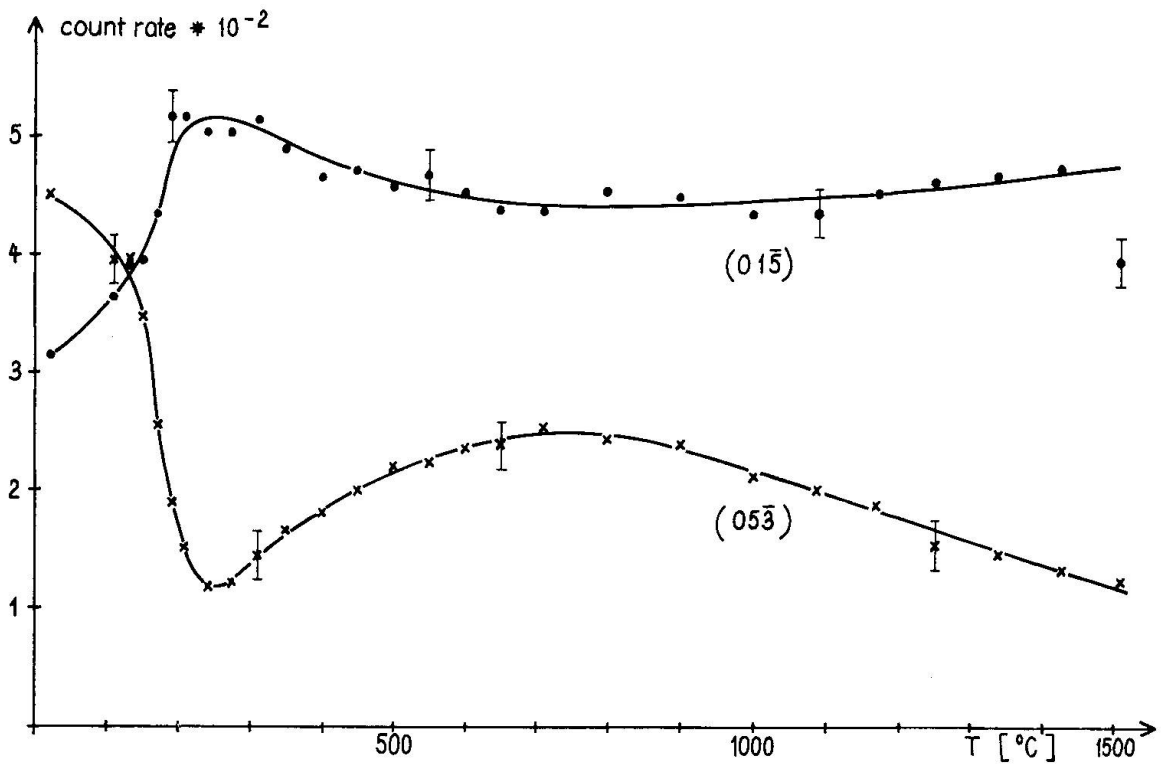Fig. 2. Temperature dependence of (a)-reflections.

Fig. 3. Temperature dependence of (b)-reflections.

Figs. 2 and 3 show that the (a)- and (b)-reflections change their intensity with temperature. There are reflections that lose intensity with rising temperature, and there are reflections that gain intensity with rising temperature. Thus a decreasing intensity is not only the consequence of a temperature factor (cf. GUBSER, HOFFMANN and NISSEN, 1964). The intensity behaviour of the a- and b-reflections between 200° C and 250° C point to strong structural alternations of the anorthite structure within this temperature range. The b-reflections often show weak intensity maxima or minima at about 700° C (cf. fig. 3).

The most obvious observation is that the c-reflections, which are sharp and rather strong at room temperature (under equilibrium condition), become increasingly diffuse and weaker with increasing temperature (fig. 4). At 400° C their intensity is practically nil, but still observable[1].
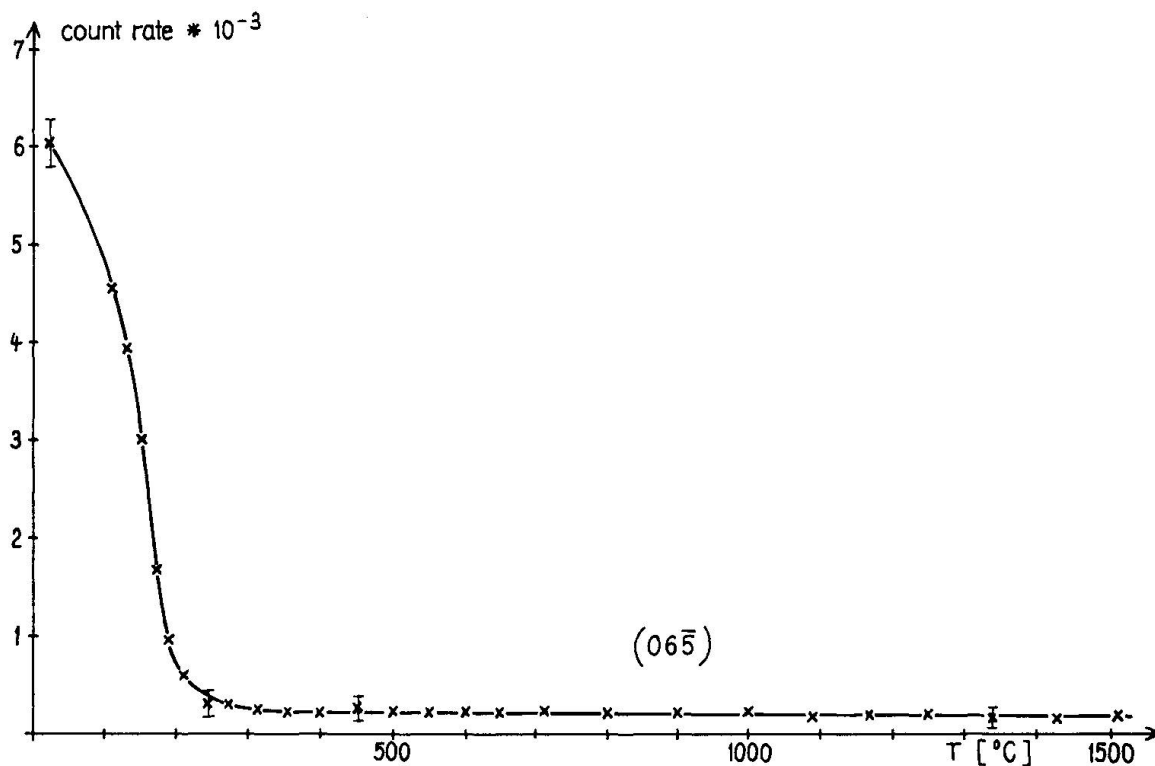

Fig. 4. Temperature dependence of (c)-reflections.

3. Discussion

For an explanation of the afore-mentioned observations a model is now discussed:

[1] In this connection a paper by FOIT and PEACOR, Z. Krist. _125_ (1967), 1–6, may be mentioned, who, however, found intensity kinks at about 130° C.

Any structure can be related to an arbitrarily chosen point as origin. We shall call the corresponding cell an "A-cell". If we choose the center of such an A-cell as origin, we shall call the corresponding cell a "B-cell". If we put A-cells together in a translational manner, so that the corners of the cells coincide, we shall call such an arrangement an "A-domain". Similarly we speak of a "B-domain", if B-cells are put together in the same fashion. Of course, the structures of A-domains and B-domains are identical. If a morphological unit consists either of A-cells or of B-cells, we call it a single crystal. If it consists of A-domains and of B-domains in such a way that all the corners of the cells coincide, we speak of an out-of-step-domain-texture.

One may expect that the size of the domains decreases with increasing temperature, i. e. the long-range order of the primitive structure becomes poorer with increasing temperature. In addition one might expect that the domains become so small that long-range-order effects are scarcely noticeable. Such material approaches a state that can be compared with a 50/50 mixed crystal (GREENHOLZ and KIDRON, 1970). The only difference is that a mixed crystal consists of different atoms A and B, nearly randomly distributed, whereas our material consists of the different cells A and B, which are chemically identical but are also randomly distributed.

Now, it is known that metallic compounds, which undergo order/disorder transformations, lose their long-range order at a critical temperature, but they still show some indication of order above the critical temperature. This sort of order is called short-range order (BRAGG and WILLIAMS, 1935).

In an analogous manner we think that the small intensity of the c-reflections, still observable near the melting point, is an indication for such a short-range order.

The main difference between the order/disorder transformations and the transformation described here lies in the meaning of the word "order". Both kinds of transformations have in common that they show disorder above, and order below the critical temperature. In the order/disorder transformations "order" means that the material has an ordered structure. In our case "order" means: below the critical temperature an out-of-step-texture is formed with A-domains and B-domains, large enough to be considered as having their own long-range-order. Thus our case corresponds more to the "unmixing behaviour" of a mixed crystal, where the size of the unmixed particles is a continuous function of temperature.

Consideration of the intensity curves in fig. 4 reveals that most pronounced changes $(d^3 I/dt^3 = 0)$ occur at approx. 230° C. Therefore, we propose 230° C as a critical temperature T_C. Below T_C the material behaves predominantly as primitive anorthite, and above T_C as body-centered anorthite.

This is also supported by NMR measurements (BRINKMANN and STÄHLI, 1968a; 1968b). Below 220° eight different Al-positions can be observed;

above 250°, only four (cf. fig. 1). – (Between 220° and 250° the measurements are inconclusive.)

In a way, this transformation can be called a displacive one, but not exactly in the sense defined by BUERGER (1961). It bears a strong similarity to Ferro-Magnetic and Ferro-Electric transformations. One might therefore call such a property "Ferro-Displacivity" or shorter "Ferro-Placivity".

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