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Structure and Volume Relations of the Alkali Feldspar Mixed Crystals

By *T. F. W. Barth* (Oslo)*)

With 2 figures and 1 table in the text

Abstract

The high-temperature solid solution series from albite to orthoclase (from $\text{NaAlSi}_3\text{O}_8$ to KAlSi_3O_8) exists at room temperature in a metastable state. The first third of the series shows triclinic symmetry, at 33 Or, 67 Ab there is a displacive transition into monoclinic symmetry.

The volumes of mixing show a non-linear and irregular change with composition. In the monoclinic part of the series the change is regular and high positive values are attained with a maximum of 6 \AA^3 at 63 Or, 37 Ab. In contrast, the triclinic part displays irregular changes and, in part, negative volume relations. At the transition point the volume itself is continuous, but shows a discontinuity in its first derivative. (See curve for ΔV in Fig. 1.)

These volume relations can be explained by assuming that all monoclinic mixed crystals are of similar structure with disordered Al-Si ions, but the triclinic mixed crystals exhibit structures that change with the composition: at the transition point they are disordered, but as Na increases some degree of order will develop. But the Al/Si pattern is here of a different kind, probably similar to that in plagioclase, and not corresponding to that in any of the modifications of K feldspar. See Fig. 2.

On the basis of known values for the heat of mixing, and for the change in volume the effect of pressure on the solvus has been calculated. See Fig. 1.

The molar heat, H_f , of the formation of solid solutions between high albite and orthoclase was measured by KRACEK and NEUVONEN (1952). The unit cell volumes of the mixed crystals were measured by DONNAY and DONNAY (1952).

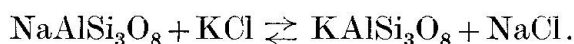
From these data ΔV is calculated, defined as the difference between the actual volumes and those corresponding to a linear relation between

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the components; ΔV is positive for most of the mixed crystals; see Table 1 which gives the pertinent data in units convenient for thermodynamic calculations.

The mixed crystals exist in a metastable state at room temperature, but are stable only at elevated temperatures; they will unmix upon slow cooling under equilibrium conditions. The shape of the solvus has been difficult to determine. The diagram of Fig. 1 shows three solvi:

1. The solvus determined by ORVILLE (1963) at 1 atmosphere by the reaction



2. The solvus determined by BARTH (1962, 1965) from the study of natural feldspars.

3. The solvus calculated for a pressure of 5000 bars v. i.

Experiments conducted by YODER, STEWART and SMITH (1957) show that the solvus is affected by pressure: the maximum on the solvus rises about $10^\circ/1000$ bars. Theoretically the rise may be calculated from the figures compiled in Table 1.

The solvus is the curve of the transition from a mixed crystal to two feldspar phases. If the unmixing were complete the equation of the transition would be



but the unmixing is not complete, and the phases of the right side of the equation are not the pure components but two mixed crystals, one enriched in Na, the other enriched in K. If the calculations are based on the assumption of complete rather than partial unmixing, the results will be inaccurate but useful as first approximations for the following reason: ΔV and H_f are approximately proportional to the degree of unmixing, and will both be reduced by a comparable relative amount if the unmixing is only partial, the ratio $\Delta V/H_f$ thereby remaining rather constant. Thus Clapeyron's equation may be used for any one point on the solvus:

$$\frac{dT}{dP} = \frac{T\Delta V}{H_f}.$$

T , ΔV , and H_f are given in Table 1; in the last column the results of the calculations are displayed. The agreement with the experiments of YODER et al. is good and indicates that the approximations in the calculations are permissible.

Table 1. *Thermodynamical Data for Alkali Feldspar Mixed Crystals*

Ab mole %	Or	ΔV cm ³ /mole	H_f cm ³ bar/mole	T degree K	dT/dP degrees/1000 bar
10	90	0.437	20 600	630	13
20	80	0.740	41 300	780	14
30	70	0.860	53 000	840	14
40	60	0.880	66 000	900	12
50	50	0.810	70 000	930	11
60	40	0.600	66 000	950	8.5
70	30	0.316	53 000	950	5.5
80	20	0.226	41 300	930	5
90	10	0.000	20 600	860	0
95	5	0.078	12 400	770	-5

ΔV = change of volume, H_f = heat of formation, T = absolute temperature refer to the reaction



and are recalculated from data of DONNAY et al., KRACEK et al., and ORVILLE, respectively.

An examination of Fig. 1 reveals several interesting facts.

1. The effect of high pressure — which as usual is similar to that of low temperature — is a general expansion of the field of exsolution. The maximum rise in the solvus with increasing pressure takes place rather close to the Or-side, whereas the solvus in the region 90—100 Ab is depressed. Thus the shape of the whole solvus is changed, the characteristic skewness of the low-pressure solvus is reduced and the high-pressure solvus becomes more symmetrical.

2. The curve for ΔV is shown in the middle part of Fig. 1. In various ways this curve reflects the fine-structure of the feldspars:

a) The high positive values (with a maximum at Ab 37, Or 63) are due to a small coefficient of thermal expansion of the monoclinic alkali feldspar structures; recent experiments of STEWART and VON LIMBACH (1964) show the triclinic (anorthoclase) structures to have a greater coefficient of expansion. At 600°C the transition monoclinic/triclinic is at approximately Ab 87, Or 13, which is close to the composition at which the pressure has no effect on the position of the solvus. See lower diagram.

b) At the transition point monoclinic/triclinic at Ab 67, Or 33 and room temperature the ΔV curve shows a discontinuity in its first deri-

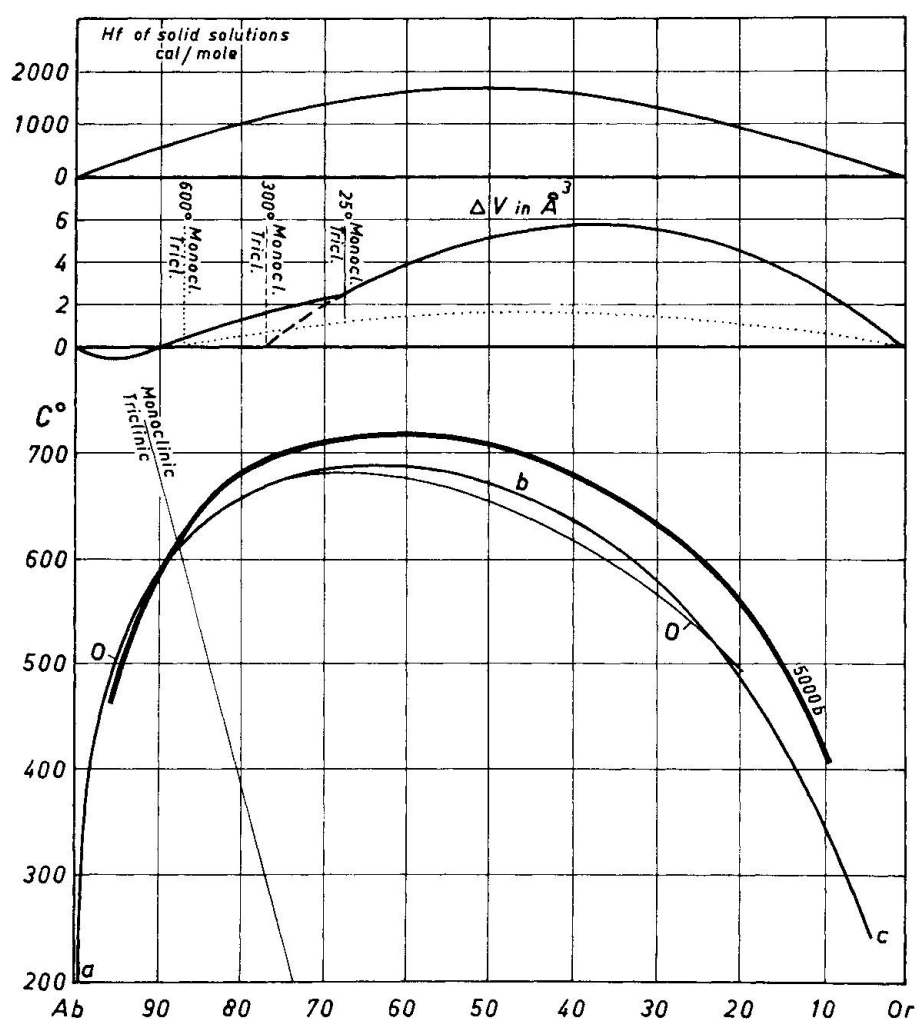


Fig. 1

Upper diagram: Molar heats of formation of solid solution for alkali feldspars from high albite and orthoclase.

H_f is based on very few experimental points, and is therefore just an average curve incapable of showing such details as exhibited by the ΔV curve (v. i.). It is probable that additional data would have revealed irregularities which would be connected with the difference in structure between the triclinic and monoclinic part of the solid solution series.

Middle diagram: The change in unit cell volumes due to the formation of solid solutions between high albite and orthoclase.

ΔV = change of volume in terms of the difference of the observed volumes from linearity. ΔV has a break at the monoclinic/triclinic inversion which divides the curve into two parts: a monoclinic part with a regular shape, and a triclinic part with an irregular shape. This suggests that the monoclinic solid solutions are crystallographically homogeneous, whereas the triclinic solid solutions exhibit variations in the crystal structure.

Lower diagram: Subsolidus equilibrium diagram for the alkali feldspars.

Heavy line: Solvus calculated for a pressure of 5000 bars

a-b-c: solvus as determined by analyses of natural feldspars.

O-O: solvus of synthetic feldspars at 1 atmosphere after Orville.

The thin and straight oblique line marks the displacive transition monoclinic \rightleftharpoons triclinic.

vative¹). Obviously the volume relations of the monoclinic part of the solid solution series contrast with those of the triclinic part. In the monoclinic part the ΔV curve has a regular shape indicating that all mixed crystals of this part are similar in structure. In the triclinic part, however, the irregular ΔV curve would seem to reflect a gradual change of the crystal structure from the completely disordered Al/Si pattern of the mixed crystals close to the transition point into the plagioclase-like pattern close to the Ab-side.

This transition is diffusive and affects the Al/Si distribution in the lattice; it throws some light on the structure of high albite.

Low albite with an ordered Al/Si distribution as in microcline is triclinic at all temperatures; it shows no displacive inversion and no irreversible effects until melting. However, low albite is not stable at elevated temperatures, but will on prolonged heating develop diffusional disorder in respect to Al-Si and gradually transform into *high albite*. The Al/Si distribution pattern in high albite is a function of temperature, and all stages of transition between high and low albite have been observed (experiments by MACKENZIE [1952, 1957] and others as well as a large number of observations in nature). The diffusional synthesis of high albite takes time, because the diffusion of Al and Si ions in the lattice is a slow process. BASKIN's (1956) experiments suggest that in the range 1000–1100° equilibrium will be attained within about 10 days. After this time no changes occurred in the interaxial angles of the crystals: γ first increased from 88°, passed 90°, and then became constant at about 90°20'; α^* remained at about 86°. In MACKENZIE's experiments the parameter $2\Theta_{131} - 2\Theta_{\bar{1}\bar{3}\bar{1}}$ which should be zero in a monoclinic crystal increased from about 1 to 2 by heating up to 1000° C. From these observations one point can be made: the crystal structure of albite does not approach monoclinic symmetry when heated. Consequently, the Al/Si

¹) This transition was investigated independently by LAVES (1952) and by DONNAY and DONNAY (1952). LAVES showed unequivocally that the transition is of the displacive type, such as in high \rightleftharpoons low quartz or high \rightleftharpoons low cristobalite.

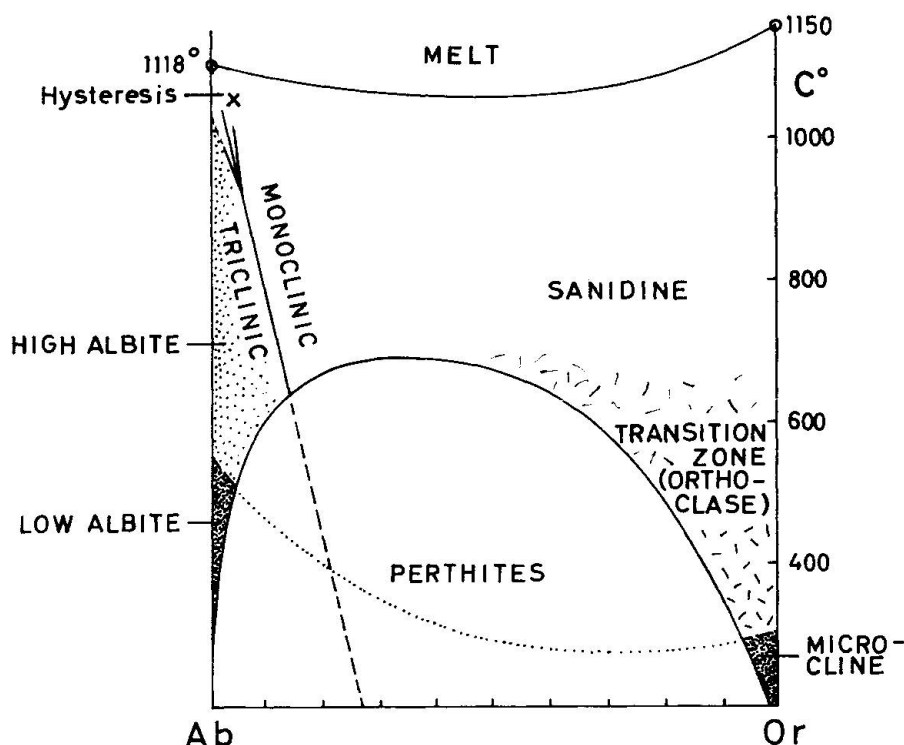


Fig. 2

The crystal structure of the solid solutions of the alkali feldspars in relation to temperature and composition.

Densely dotted areas: Microcline and low albite have the same crystal structure and an ordered distribution of Al and Si; Al occupies the points of one of the 4 structurally equivalent four-fold positions.

Stippled areas: Orthoclase derives from microcline by a diffusive transition; gradually a partial disorder develops. Al congregates in 2 of the four-fold positions.

Faintly dotted areas: High albite derives from low albite by a diffusive transition; a partial disorder develops, but the kind of disorder is different from that in orthoclase.

White area above the solvus: Sanidine develops from orthoclase by a further diffusive transition; the partial disorder passes into full disorder: Al is distributed with equal probability over the 4 four-fold positions.

No change in disorder takes place at the monoclinic/triclinic line of displacive transition, but if the line is crossed from right to left a further increase in Na will change the sanidine disorder pattern into that of high albite.

If a monoclinic mixed crystal, x, at 1050° C containing 5 Or is quenched, it will at about 1000° invert into triclinic symmetry although the Al/Si distribution pattern remains as before. By further cooling this structure becomes unstable even above the solvus (at, say, 700° C); by a diffusive transition it then passes into a structure of the high-albite type. If this is true, one should expect to find Na-rich anorthoclases of different structural states.

distribution in high albite does not aim at ideal disorder, as is the case in high potassium feldspar (= sanidine).

How does this harmonize with the fact that albites with very small amounts of K in the lattice do become monoclinic with a truly ideally disordered structure at temperatures in the range 1000° — 1100° C? STEWART and VON LIMBACH (1964) showed that synthetic albite (possibly containing traces of K) became monoclinic at 1044° on heating: it remained monoclinic on cooling to 970° , when it again became triclinic. Thus a hysteresis loop of about 80° was established, a fact which excludes a displacive transformation. The explanation favoured by me is indicated in Fig. 2.

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