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A high temperature single crystal diffractometer study of leucite, $(K,Na)AlSi_2O_6$*

By **Donald R. Peacor**

Department of Geology and Mineralogy
The University of Michigan, Ann Arbor, Michigan

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Auszug

Es wurden die Intensitäten einiger ausgewählter Interferenzen natürlich verzwillingter Leucitkristalle in Abhängigkeit von der Temperatur bestimmt. Diese Funktionen sind ebenso wie der Verlauf des Achsenverhältnisses $c:a$ im Einklang mit einer einzigen Umwandlung bei $605 \pm 5\,°C$, mit dem direkten Übergang von der Raumgruppe $I4_1/a$ in die Raumgruppe $Ia3d$ und mit dem Verschwinden der Verzwillingung bei derselben Temperatur. Die Kristallstruktur der Hochtemperatur-Modifikation wurde verfeinert auf Grund der bei $635 \pm 5\,°C$ gemessenen Intensitäten.

Abstract

The intensity vs. temperature functions of several selected reflections from originally twinned leucite crystals have been determined. These, together with the change in axial ratio c/a, are consistent with a single transformation at $605 \pm 5\,°C$ with a direct change in space group from $I4_1/a$ to $Ia3d$, and with a disappearance of twinning at the same temperature. The crystal structure of the cubic high-temperature polymorph has been refined with intensity data measured at $635 \pm 5\,°C$.

Introduction

Faust (1963) has reviewed the literature concerning the transformation of low-temperature tetragonal leucite to a high-temperature cubic polymorph. The variety of methods used for studying the transformations indicate that it appears to occur either at a single temperature, over a temperature range, or at two temperatures, separated by a temperature interval. Although estimates of tem-

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* Contribution No. 293, from the Mineralogical Laboratory, Department of Geology and Mineralogy, The University of Michigan.

perature of transformation vary, all values are in the approximate range 600 ± 50 °C.

In a detailed study of the inversion using the D.T.A. method, FAUST confirmed the apparent compound nature of the transformation as shown by two endotherms separated by an interval of 20 to 40 °C, the first appearing at about 610 to 640 °C. The values vary with the sample studied, but confirm the complete reversibility in the transformation, which in this sense resembles a displacive one. FAUST suggests that the D.T.A. results may indicate "the existence of either a transient polymorphic phase or an Al—Si order-disorder relationship".

WYART (1938, 1940) did a rather complete study of leucite in which he showed that leucite is mimetically twinned "par rotation de 120° autour de l'axe pseudo-ternaire du trapézoèdre 122". He showed that the low-temperature form has space group $P4_1/a$ and the high-temperature form space group $Ia3d$, with Al and Si ordered with respect to one another in the low-temperature form. He suggested that an ordered high-temperature form D_{4h}^{20} would have space group $I4/acd$, a subgroup of $Ia3d$ (which requires Al,Si disorder over a single equipoint), and a supergroup of $I4_1/a$. Of importance was his determination of the changes in a and c as a function of temperature. A curve of $c-a$ vs. temperature shows that the change in cell geometry to that of the cubic system is a continuous one, being complete at about 625 °C. These results yielded no evidence for a compound transformation, but the number of data points were small and temperature intervals large.

This study was undertaken to better define the apparent complexity of the transformation and to further relate it to the twinning mechanism. The occurrence of a structure of space group intermediate to those of the low and high forms should be detectable through the determination of accurate intensity values as a function of temperature using a proportional counter. In addition, the nature of the structure of the high-temperature polymorph should be better defined with a refinement using three-dimensional data.

Variable temperature functions

Specimens of leucite were obtained from the University of Michigan mineralogical collection. Two single crystals from Ariccia, Rome, Italy were examined for changes as a function of temperature, while a third from Vesuvius was examined in this way, and in addition used as a source for measurement of three-dimensional intensity values. Cleavage prisms elongated along [100] were carefully selected for mounting in a silica capillary so that [100] was parallel to the capillary axis for convenient orientation with respect to the high-temperature furnace axis. These were examined using Weissenberg and precession instrumentation to define relative orientations of twin-related reflections, and subsequently mounted on a single-crystal diffractometer fitted with a resistance furnace (Foit and Peacor, 1967). Intensity values were recorded on a strip chart recorder, Cu$K\alpha$ radiation being used with pulse-height analysis and a proportional counter. Temperature values were determined using a thermocouple placed close to the crystal and through comparison with calibrated curves of power input to the furnace vs. temperature.

The first crystal examined was from Ariccia, Rome and was a quadruply twinned crystal, the twin law being such as to yield *h0h* reflections occurring with equal values of Υ (*b*-axis mounting) with registry of two of the four twin-related reflections. Since these reflections were well resolved but had small differences in φ, any set could be observed with a single short scan at constant Υ and variable φ. The reflections 404, 303, 202 and 101 were selected for examination as a function of temperature for these reasons, and because 303 and 101 should become extinct above the inversion temperature if the space group of the high-temperature polymorph is $Ia3d$. The reflection 020 (doublet as a result of twinning) was selected for the same reason. The 080 and 008 doublets were selected because, although their values of Υ and φ were all similar, they should coalesce at the inversion temperature if there is a single inversion temperature involving space groups $I4_1/a$ and $Ia3d$.

Temperature change was achieved at a rate of about 1 to 3 °/min. For temperatures up to about 500 °C the intensity values were measured from 1 to 12 hours following change in temperature. As a check on the achievement of equilibrium, values were obtained both while temperature was varied, and after intervals of up to 12 hours with constant temperature. The results confirmed that all intensity changes were immediate with respect to change in temperature. The more closely spaced points of Figs. 1 to 3 at higher temperatures include measurements made both while temperature was changing and those made while holding at a constant temperature for a varying number of hours.

As temperature was increased the intensities of reflections changed continuously, as did the separation, $\Delta\varphi$, of twin-related reflections. The axial ratio, c/a, is directly related to the separation. Figure 1 is a plot of c/a vs. temperature as obtained in this way, and is similar to a less complete plot obtained by Wyart. It verifies the continuous decrease in c/a to a value of 1.0, where the lattice is at least geometrically cubic. The temperature corresponding to this change in geometry is 605 ± 5 °C.

Figure 2 is an intensity variation plot for 303 and is typical for those reflections which were predicted to become extinct with inversion to the cubic polymorph. Since those twin-related reflections which were resolvable in a changing φ scan at room temperature became unresolvable at high temperatures due to the decreasing c/a ratio, the sum of the intensities of the twin-related intensity values is shown for all temperature values. The curve shows that the sum of the 303 intensity values decreases continuously as temperature is increased, changing rapidly as the inversion temperature is reached. The rate of change roughly parallels the corresponding rate in c/a. In addition, the temperature corresponding to an intensity value of zero is that where the axial ratio becomes equal to 1.0.

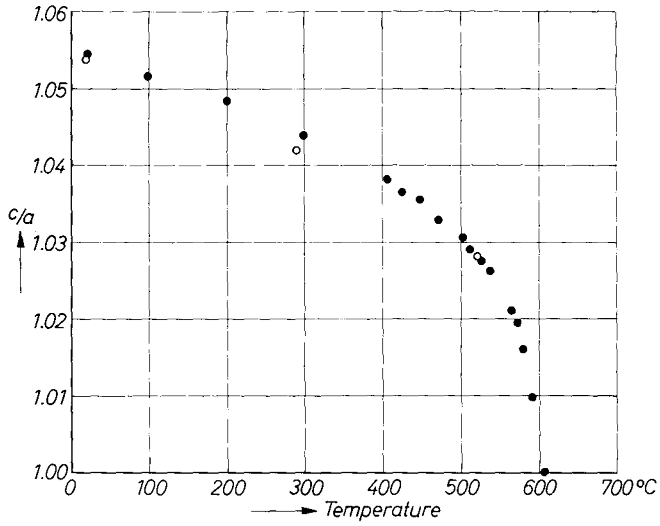

Fig. 1. Axial ratio, c/a, as a function of temperature. Open circles correspond to data obtained by Wyart (1938)

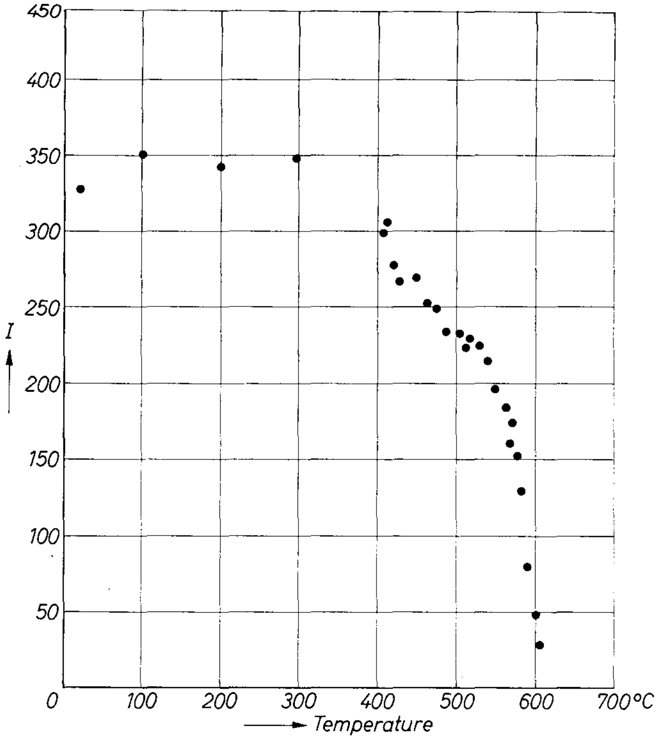

Fig. 2. Sum of the integrated intensity values for three twin-related 303 reflections as a function of temperature. The reflections coalesce as they become "extinct"

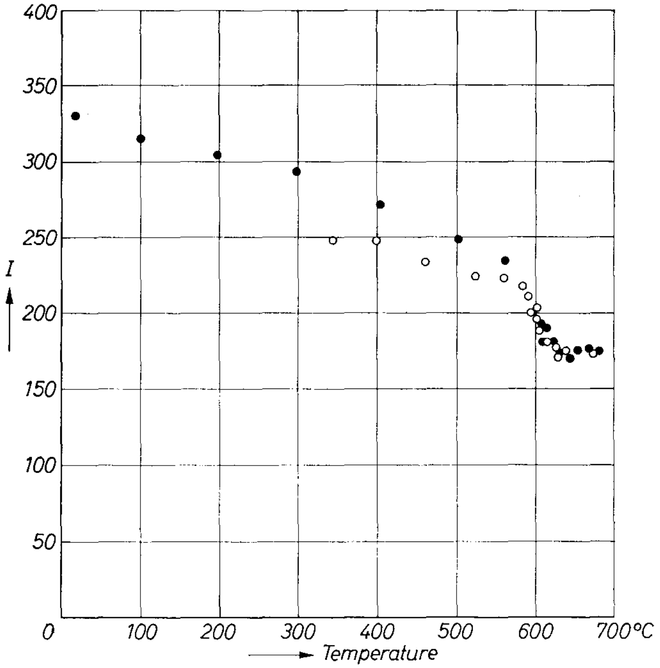

Fig. 3. Sum of the integrated intensity values for three twin-related 404 reflections as a function of temperature. Twin components are resolvable below about 605 °C. Above this temperature leucite is cubic and the three twin components are replaced by a single reflection

Figure 3 is an intensity variation plot for 404 and is typical of those which should not become extinct. The sum of twin related intensity values is again plotted. The blackened circles were obtained with increasing temperature and the open circles with a decreasing temperature. The form of the curve for intensity change is again similar to that for change in c/a, with accelerating decrease in intensity as the inversion temperature is approached. There is a rather sharp inflection point slightly above 600 °C, however, above which the intensity of the then single reflection remains approximately constant. Temperature was increased to about 80 °C beyond the indicated temperature of inversion in order to detect possible changes in structure as indicated by FAUST's (1963) D.T.A. data. The change in intensity values with temperature is accompanied by an increasing diffuseness of reflections. However, at the inversion temperature where all twin-related intensity values finally completely coalesce there is a pronounced increase in sharpness of reflections. With decrease in temperature, intensity values and the axial ratio c/a show significant changes in the same way as with rise in temperature, although the intensity values change. Twin-related reflections reappear immediately as predicted as the temperature is dropped, and the crystal may be cycled back and forth through the inversion. After the crystal had been cooled to room temperature a Weissenberg photograph was taken. This duplicated the one taken before heat treatment, except that significant lineage structure had developed. This readily explains the lack of precise duplication of the intensity variation shown in Fig. 3 for temperature increase and decrease.

The experiment was duplicated for a second crystal from Ariccia, Rome, which was a twin consisting of only two types of domains, rather than four. The results confirmed those for the first crystal. The Weissenberg photographs taken after heating again nearly duplicated the preliminary ones. In the cases of both crystals, then, the relative volumes of different twin domains following inversion and re-inversion were approximately the same, but different from each other. This confirms WYART's (1938) observation that the crystals have a "memory" in this regard.

These data are consistent with only a single polymorphic change, such that there is a continuous adjustment in atom coordinates as temperature is decreased below that where symmetry changes. These diffraction data give no indication of the meaning of the second peak exhibited on D.T.A. records. The transformation is displacive in nature due to the rapidity with which it occurs with change in temperature, and clearly cannot involve an Al—Si order-disorder relationship.

Structure refinement for cubic polymorph

Because of the very small size of twin domains, we were unable to obtain an untwinned crystal of the tetragonal polymorph. No attempt could be made to obtain intensity data for the refinement of this structure, although refinements with data obtained at a number of temperatures would be useful for complete definition of the transformation and twinning mechanisms. A structure refinement of the cubic polymorph was therefore carried out in the hope that it might shed light on these relations.

A silica capillary-mounted cleavage fragment ($.15 \times .12 \times .40\,\mathrm{mm}^3$) from Vesuvius was mounted within the diffractometer furnace and the temperature raised in steps to 635 ± 5 °C. Measurement of selected intensity values and twin-related reflection resolution during temperature increase duplicated the general relations obtained with the crystals from Ariccia, the transformation being complete at about 595 °C. With settings computed for an *a*-axis crystal mounting, data were measured such that $k \geqslant l \geqslant h$, consistent with cubic symmetry. Reflection scans were recorded and peak profiles measured with a planimeter. Scans were made for all reflections predicted to be extinct through glide-plane operations, consistent with the above index relation, as a check on the validity of the assumption that the space group is *Ia*3*d*. A total of 45 such reflections were extinct as predicted, with no exceptions. A total of 149 reflections not required to be extinct were measured. Due to a high background coupled with low intensity values at high values of theta, caused in part by high thermal motion, about 25% of these were unobservable. These data were assigned values of $\frac{1}{2}F_{\min}$ with the latter value being a function of theta. The intensity data were corrected for Lorentz, polarization and absorption factors using modified versions of C. T. PREWITT's program DFSET and C. W. BURNHAM's program ABSRP.

Full matrix least-squares refinement of the structure was carried out based on the following conditions: 1. trial coordinates as determined by WYART (1940). 2. Weighting scheme that of unit weighting in initial stages, that of CRUICKSHANK (1965) in final cycles. 3. The degree of Na substitution for K was assumed to be about 15%, the diagnostic average for Vesuvius leucite. The refinement converged rapidly with cycles of varying coordinates alternated with cycles in which isotropic temperature factors were varied. At this stage the functions $\varrho(xyz)$ and $\Delta\varrho(xyz)$ were calculated. Both of these functions showed no unusual features. In particular, the space-group symmetry and lack of twinning in the crystal used as a data source were further confirmed since there was no indication of other than normal electron-density functions which might appear, for example, through the occurrence of "split-atom peaks". Final convergence was readily achieved

Table 1. *Refined coordinates and temperature factors*
(Standard errors in parentheses)

	K	O	Si
x	1/8	.1033 (10)	1/8
y	1/8	.1322 (10)	.6622 (2)
z	1/8	.7200 (7)	$.5878^2$
β_{11}	.0210 (10)	.0137 (11)	.0035 (2)
β_{22}	$.0210^1$	.0113 (9)	.0039 (1)
β_{33}	$.0210^1$	.0051 (6)	$.0039^2$
β_{12}	.0022 (13)	.0041 (9)	.0005 (1)
β_{13}	$.0022^1$	.0032 (7)	$.0005^2$
β_{23}	$.0022^1$	.0005 (7)	.0000 (2)

[1] $\beta_{33} = \beta_{22} = \beta_{11}$; $\beta_{23} = \beta_{13} = \beta_{12}$.
[2] $z = 1/8 - y$; $\beta_{33} = \beta_{22}$; $\beta_{13} = \beta_{12}$.

Table 2. *Observed and calculated structure factors*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	4	0	222.32	-260.46	1	5	2	21.18	- 21.02	2	13	3	7.46	- 6.53	3	12	5	8.83	3.80
	8		72.15	68.73		3		16.56	- 13.81		11		4.79	3.07		14		3.79	- 3.33
	12		5.54	1.81	1	4	3	33.94	- 34.98		9		36.57	37.34	3	13	6	9.83	- 10.01
	16		9.20	- 12.11		6		5.46	- 5.31		7		71.62	- 65.92		11		4.80	2.57
0	2	2	23.13	- 24.06		8		36.88	33.14		5		19.83	15.53		9		34.57	33.41
	4		33.22	35.43		10		33.86	35.88		3		88.25	86.52		7		35.65	37.44
	6		27.79	25.49		12		4.79	- 7.17	2	6	4	20.90	- 22.03	3	12	7	4.39	2.42
	8		38.52	- 34.56		14		17.34	- 16.94		8		16.95	- 15.27		10		5.07	- 9.65
	10		4.63	- 9.01	1	15	4	11.75	11.09		10		8.79	7.73		8		21.03	- 16.25
	12		19.78	22.02		13		14.18	14.51		12		14.99	13.52	3	9	8	5.29	3.71
	14		4.32	0.34		11		22.26	- 21.44		14		4.09	0.43	4	4	4	3.28	- 2.83
	16		10.38	- 11.83		9		16.38	- 12.84	2	13	5	4.41	- 0.53		8		4.66	- 3.70
0	4	4	87.57	84.53		7		41.55	37.38		11		4.87	- 3.45		12		10.72	11.72
	6		44.27	45.03		5		11.86	10.74		9		13.74	- 9.12	4	13	5	11.03	12.27
	8		23.12	- 18.24	1	6	5	16.03	17.64		7		9.58	7.07		11		17.76	17.97
	10		17.56	- 19.06		8		4.79	5.00	2	8	6	17.42	14.09		9		4.97	- 7.56
	12		9.97	- 10.99		10		34.90	34.05		10		5.04	- 0.21		7		26.62	- 27.56
	14		4.20	3.57		12		4.76	- 1.28		12		10.74	- 9.34	4	6	6	28.68	29.98
0	6	6	35.64	- 33.23		14		13.63	- 13.88		14		3.77	0.16		8		22.86	- 21.87
	8		51.16	49.99	1	15	6	3.18	5.54	2	13	7	4.07	- 5.08		10		12.71	- 12.34
	10		14.55	14.91		13		4.35	6.24		11		14.85	- 14.25		12		22.46	21.77
	12		33.62	- 35.56		11		4.92	- 7.01		9		11.84	- 13.77	4	13	7	3.65	- 1.49
	14		3.90	- 1.32		9		28.26	- 26.35		7		56.12	55.04		11		4.59	- 1.66
0	8	8	5.26	- 2.82		7		11.53	- 9.79	2	10	8	8.36	- 5.22		9		15.81	12.86
	10		21.30	22.24	1	8	7	41.45	- 40.04		12		4.33	- 4.01	4	8	8	5.15	1.45
	12		14.94	12.78		10		10.28	- 11.17	2	11	9	10.48	10.16		10		9.34	- 9.02
	14		3.31	- 1.55		12		7.97	8.36		9		12.72	- 15.91	5	6	5	7.52	- 9.89
0	12	10	11.64	16.98		14		6.58	4.96	3	6	3	46.06	- 47.81		10		32.93	- 33.69
	10		12.39	- 9.54	1	13	8	14.22	- 13.85		10		31.93	33.77	5	11	6	4.47	- 2.78
1	2	1	57.94	56.99		11		24.03	23.27		14		14.86	- 15.25		9		5.03	2.15
	6		30.27	- 28.17		9		11.61	10.54	3	13	4	6.69	- 5.38		7		4.63	- 1.91
	10		51.23	- 48.11	1	10	9	7.72	- 5.09		11		8.73	8.15	5	8	7	32.04	29.52
	14		22.78	22.93		12		4.13	0.89		9		4.77	- 3.94		10		4.78	0.77
1	15	2	6.93	- 8.66	1	11	10	4.22	3.67		7		13.92	- 14.85	5	9	8	8.20	- 6.46
	13		11.07	- 10.13	2	4	2	17.88	18.68		5		13.16	18.26	5	10	9	17.36	19.18
	11		12.91	11.85		8		13.01	- 9.96	3	6	5	7.81	5.02					
	9		42.19	41.68		12		4.76	5.75		8		22.32	- 20.39					
	7		13.83	16.28	2	15	3	3.62	5.42		10		12.92	15.55					

with cycles in which anisotropic temperature factors, coordinates, and the single scale factor were refined. The final R value, including all data, is 11.5%. Table 1 contains a listing of the refined structure parameters and their standard errors. The observed and calculated structure factors are given in Table 2. Interatomic distances, angles and thermal ellipsoid parameters, as calculated using ORFFE, written by BUSING and LEVY, are tabulated in Tables 3 and 4. Standard errors of all structure parameters were calculated using the variance-covariance matrix of the final cycle of refinement, and estimated errors of lattice parameters.

Table 3. *Interatomic distances and angles*
(Standard errors in parentheses)

	no thermal component	averaged over independent thermal motion
(Si,Al)—2O	1.611 (11) Å	1.721 (12) Å
2O′	1.627 (12)	1.706 (11)
O—2O′	2.70 (2)	2.77 (2)
O″	2.59 (2)	2.68 (2)
2O″	2.66 (2)	2.74 (2)
O′—O″	2.56 (2)	2.64 (2)
K—6O	3.54 (2)	3.57 (2)
6O′	3.35 (2)	3.37 (2)
Si—O—Si′	145.4° (8)	

Table 4. *Magnitudes and orientations of principal axes of thermal ellipsoids*
(standard errors in parentheses)

Atom	Principal axis	r.m.s. displacement	angle to $+a$	angle to $+b$	angle to $+c$
K	1	.418 (18) Å	114 (19)°	114 (19)°	35 (29)°
	2	.418 (12)	114 (99)	114 (99)	36 (99)
	3	.486 (30)	55 (0)	55 (0)	55 (0)
O	1	.191 (14)	111 (4)	81 (6)	23 (6)
	2	.284 (14)	62 (5)	145 (6)	72 (7)
	3	.402 (16)	37 (5)	56 (5)	76 (3)
Si	1	.165 (8)	42 (3)	125 (3)	110 (7)
	2	.184 (6)	105 (10)	136 (4)	50 (9)
	3	.199 (6)	52 (6)	68 (9)	47 (10)

The refinement results confirm the complete disorder of Al and Si over tetrahedrally coordinated sites, as required by their distribution on a single equipoint of *Ia3d*. Such ordering results in coordinate differences which, because intensity data were measured only for the asymmetric unit of this space group, would result in "split" atoms in the Fourier functions calculated following isotropic temperature-factor refinement. As noted above, no such features were present.

The average (Si,Al)—O bond distance (1.62 Å) is approximately 0.04 Å less than the value predicted from the data of SMITH and BAILEY (1963) for a tektosilicate of this composition. The average for this structure is close to that expected for sites containing no Al. This appears to be more unusual since there is an overall relative expansion in volume of about $5^0/_0$ from room temperature to 635 °C. Thus the average distance was expected to be even greater than that predicted from room temperature data. Because the standard error in (Si,Al)—O distances is about 0.01 Å, the difference between observed and expected values appears to be real. The relatively small (Si,Al)—O distances are reflected in the average value of 2.64 Å for O—O distances.

YOUNG (1962) has determined the structure of α and β quartz as a function of temperature with data obtained at several temperatures. His results detail structure changes particularly as regards the transformation at 573 °C. The average Si—O distance of this structure decreases about 0.01 Å from room temperature to 570 °C, with an apparent additional small decrease through the inversion. The apparent decrease in distance with temperature, as YOUNG suggests, is unrealistic. Interatomic distances were therefore calculated for leucite such that they are averaged over thermal motion and assumed to move independently. The two Si—O distances are 1.706 and 1.721, these values being about 0.1 Å greater than those calculated without taking thermal vibration into account. Data for other silicates at high temperature must be made available before trends in parameter changes with temperature can be reliably assessed however.

Values of temperature factors also show major departures from values expected at the outset of refinement. The values of root-mean-square vibration amplitudes (Table 4) are a factor of three or four times greater than those typically obtained from room-temperature data. This is reflected in values of equivalent isotropic temperature factors (15.4 for K, 7.3 for O, 2.7 for Si). By comparison, YOUNG obtained values for equivalent isotropic temperature factors for

O and Si of about 4.0 and 1.7, respectively, from data measured at 600 °C for β quartz. Values similar to those of YOUNG's were expected, since they are consistent with the approximate predicted change in vibration amplitude with temperature.

Only oxygen has a markedly anisotropic vibration ellipsoid. As expected, the largest axis is directed approximately normal to the plane of the Si—O—Si bonds, and the smallest axis approximately parallel to the corresponding Si—Si bond. The relative values of the principal axes of the (Si,Al) ellipsoid are approximately equivalent to those normally obtained from room-temperature data. The 12-fold coordination of K with six K—O distances of 3.54 Å and six of 3.35 Å is consistent with the more nearly isotropic character of its vibration ellipsoid.

Although the relatively high magnitudes for temperature factors may be at least partially rationalized with respect to experimental errors, a more likely cause is apparent in the mechanism of the polymorphic change. Intensity data were measured only about 30 °C above the inversion temperature. Data obtained by other investigators on the nature of the structure change, and data reported here relative to intensity variation as a function of temperature, suggest that the transformation involves a gradual change in coordinates in direct response to changes in thermal energy. Above about 605 °C atom coordinates are symmetrically consistent with space group *Ia*3*d*. Immediately below this temperature, displacements occur which are the same for all unit cells within an individual twin domain, but related to those of other domains by symmetry elements of *Ia*3*d*. As temperature decreases toward the inversion temperature, increasing positional disorder, as expressed in increasing thermal motion, should occur. The large temperature factors are in part an expression of the broadening of potential minima about the sites of *Ia*3*d* as the inversion is approached.

These results confirm the relations described by WYART as regards the general nature of the change in structure as a function of temperature. There is no evidence for more than a single transformation involving structure parameters as determined by x-ray diffraction. The distribution of Al and Si must be one of complete relative disorder in both the high- and low-temperature polymorphs. The cause of the second D.T.A. peak occurring near the one corresponding to the structure inversion must in large part be determined with other instrumental methods of analysis.

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