

A high-temperature study of the low-high leucite phase transition using the transmission electron microscope

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ABSTRACT

That leucite transforms from a tetragonal to a cubic polymorph with increasing temperature has been accepted for nearly a century, but the precise nature of this transition has provoked some disagreement. X-ray diffraction experiments suggest that leucite inverts directly from space group $I4_1/a$ to $Ia3d$; however, two distinct absorption events appear in most calorimetric experiments, raising the possibility that leucite passes through an intermediate phase with space group $I4_1/acd$. In this paper, the evidence for both hypotheses is reviewed in detail.

Further, the transition between low and high leucite was examined in situ during heating experiments with a transmission electron microscope. Dark-field imaging with the 420 diffracted beam revealed pseudomerohedral and merohedral twin types in the low-temperature polymorph, and with increasing temperature the contrast among both sets of twins steadily diminished. The transition temperature T_c was deduced from the merging of split spots in selected area electron-diffraction patterns, indicating an equivalence in the lengths of a and c . Merohedral twins could not be discerned above T_c , whereas the pseudomerohedral twin boundaries definitely could be distinguished above the transition temperature.

We conclude that leucite can indeed occur as a distinct intermediate phase with space group $I4_1/acd$ that is metrically but not symmetrically cubic within the error of our measurements. The failure of leucite to transform directly to a cubic structure may be related to Al/Si ordering. Further, the observation that leucite remains tetragonal above the nominal transition temperature explains the memory effect long associated with leucite.

INTRODUCTION

Leucite ($KAlSi_2O_6$) is not commonly found in nature. As a feldspathoid, it is restricted to rocks that are deficient in silica but enriched in alkalis, and its tolerance for Na decreases markedly with increases in P_{H_2O} ; even slightly sodic crystals will revert upon cooling to pseudo-leucite, a mixture of nepheline and orthoclase. Consequently, leucites occur either in sodium-poor phonolites and trachytes or in mafic extrusives quenched from high temperatures. Nevertheless, leucite localities are scattered across the world, and most rocks composed of nepheline and orthoclase contained leucite at some point during their cooling histories (Fudali, 1963). Despite leucite's scarcity, then, a full understanding of its crystal chemistry can be helpful in extracting the complete crystallization chronology of many alkalic rocks. Furthermore, the intricacies of the phase transformation experienced by leucite may provide important insights into the general transition behavior of rock-forming silicates.

The compositional simplicity of leucite belies its real structural complexity. Its formula notwithstanding, leu-

cite is a derivative of no known silica polymorph, and, like all other feldspathoids, its affinity with feldspars is not structural but chemical. Efforts to discern the crystal system of the low-temperature phase date to the early 19th century, but it was not until 1890 that Charles and Georges Friedel, using optical evidence, identified it as tetragonal (see Wyart, 1938, for details). The first rigorous X-ray structure refinement of low leucite was carried out as recently as 1976 by Mazzi et al.

Attempts to refine low leucite are complicated by its two distinct twin types, which are pervasive and occur on a submicrometer scale. To circumvent this problem, crystallographers initially focused on the higher-temperature cubic phase, which seemed free of twin domains. In so doing, however, new questions emerged regarding the transformation from one phase to the other. Several observers, for example, noted that upon cycling leucite crystals about the critical temperature, a memory of the positions of the twin boundaries and twin volumes was somehow retained (Wyart, 1938; Peacor, 1968). Furthermore, although the transition originally was thought to involve only tetrahedral tilting, some researchers have invoked Al/Si ordering (Grögel et al., 1984), intertunnel migration of K^+ cations (Rüscher et al., 1987), and even a separate intermediate phase (Faust, 1963; Lange et al.,

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1986) to explain the inversion from cubic to tetragonal symmetry.

Inasmuch as any of these processes might bear on the formation and location of the two types of twin domains, it seemed probable that direct observation of the domains themselves would reveal the operative mechanisms. Since these domains are so small and since one twin type is visible only under special imaging conditions, the transmission electron microscope (TEM) was deemed the ideal instrument for observing this phase transition (Heaney and Veblen, 1988).

EXPERIMENTAL

The specimens employed in this study were kindly supplied by the U.S. National Museum (samples B18711, B18734, 96430) and by the Harvard Mineralogical Museum (sample 15126). All leucite crystals occurred as phenocrysts in phonolitic lavas in Italy. Samples B18711 and B18734 are from Lake Latium; sample 96430 is from Villa Senni near Grotta Ferrat in the Alban Hills; and sample 15126 is from Mt. Vesuvius. Each specimen displayed to various degrees the trapezohedral morphology that is pseudomorphic after the high-temperature phase. The crystals were translucent and averaged about 1 cm in diameter.

Specimens were prepared from petrographic thin sections cut normal to one of the pseudocubic *a* axes; they were thinned further by argon-ion milling and coated lightly with amorphous carbon. Electron microscopy was performed with a Philips 420 microscope equipped with T or ST objective lenses and operated at 120 keV. A 50- μ m objective aperture was used for HRTEM experiments. Heating experiments were carried out with a Gatan Model 628 single-tilt heating holder. Unsupported foils of 3-mm diameter were heated by an annular-tantalum furnace, which warmed in response to increases in electrical current through a molybdenum-strip heater. Specimen temperatures could not be measured directly, but furnace temperatures were registered by a platinum-13% rhodium thermocouple spot welded to the furnace body. The furnace was heated to the leucite transition temperature at a rate of about 5° per min and allowed to stabilize for 1 h before observations were begun.

PREVIOUS WORK

Crystallography

Using X-ray diffraction techniques, Wyart (1938; 1940) first proposed that the inversion from high to low leucite entails a change in space group from *Ia3d* to *I4₁/a*. With the aid of an earlier structure determination of the topologically identical mineral analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) by Taylor in 1930, Wyart also determined unit-cell parameters and atomic coordinates for high leucite, and he suggested values for the low-temperature polymorph.

Subsequent refinements generally have been consistent with Wyart's model. (See N ray-Szab , 1942, and Mazzi et al., 1976, regarding low leucite; and Peacor, 1968, re-

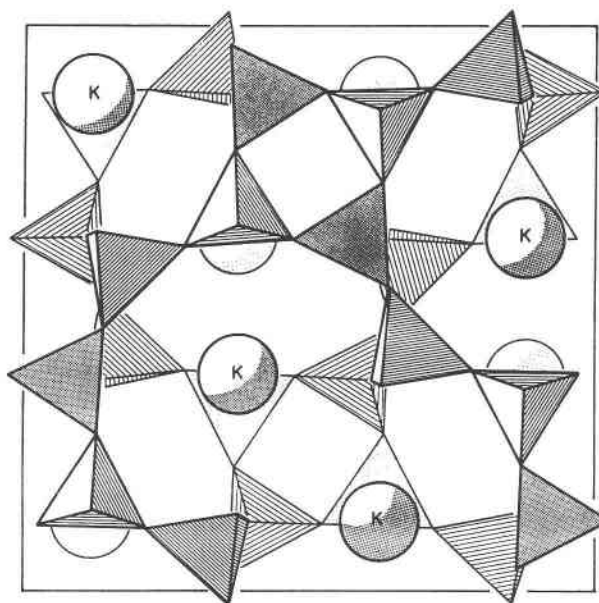


Fig. 1. The lower half of the unit cell of low leucite viewed down the *c* axis. (Reprinted from Papike, 1988.)

garding high leucite.) The unit-cell parameters of tetragonal leucite (after Mazzi et al.) are $a = 13.09(1)$ Å and $c = 13.75(1)$ Å at room temperature, whereas in cubic leucite *a* lengthens and *c* shortens to 13.536 Å at 690 °C (after Taylor and Henderson, 1968). The structure itself (Fig. 1) consists of corner-sharing tetrahedra that reticulate into four-membered rings normal to the *c* axis and six-membered rings normal to [111]. These rings in turn frame large cavities that contain K cations in 12-fold coordination; cavities are interconnected by tunnels through the six-membered rings along [111].

Al/Si order in leucite

The distribution of Al and Si among the tetrahedral sites in leucite is somewhat uncertain. The high-temperature space group *Ia3d* requires that all tetrahedral sites correspond to the same equipoint; thus, Al and Si must be completely disordered if those sites are to be symmetrically equivalent and high leucite is to be strictly cubic. On the other hand, the low-temperature space groups *I4₁/a* and *I4₁/acd* allow for three distinct tetrahedral sites, so Al/Si order is possible but not necessary.

X-ray diffraction experiments have not demonstrated tetrahedral order in either the high- or the low-temperature phase. Wyart (1938) and Peacor (1968) detected no Al/Si order in high leucite, and Mazzi et al. (1976) discerned no order in low leucite. Likewise, two magic-angle-spinning nuclear magnetic resonance (MAS/NMR) studies based on ^{27}Al failed to distinguish intensity differences among the spectral peaks corresponding to the three tetrahedral sites in low leucite, suggesting complete disorder over those sites (Phillips and Kirkpatrick, 1986; Brown et al., 1987).

Other analytical techniques, however, contradict these results. Neutron powder-diffraction studies and a Rietveld refinement "clearly revealed a partial Si-Al ordering of the starting material at room temperature, which becomes complete after heat treatment at higher temperatures and totally disordered again in the cubic phase" (Grögel et al., 1984). In addition, two MAS/NMR experiments using ^{29}Si detected short-range order among the three sites of low leucite (Brown et al., 1987; Murdoch et al., 1988), though the Si-Al distributions proposed by the two studies are different. Brown et al. determined the values $g_1 = 0.56$, $g_2 = 0.36$, and $g_3 = 0.08$, whereas Murdoch et al. obtained the values $g_1 = 0.39$, $g_2 = 0.16$, and $g_3 = 0.42$, where g_i represents the fraction of the i^{th} tetrahedral site occupied by Al. In perfectly disordered stoichiometric leucite, $g_1 = g_2 = g_3 = 0.33$.

Therefore, a review of the literature suggests that high leucite is disordered with respect to Al and Si, whereas order in low leucite remains unresolved. It should be noted, however, that ordering in leucite depends upon the nature of the transformation between the tetragonal and the cubic phases. If, for example, this transition is rapid and displacive, then it is unreasonable by analogy with feldspars (Yund and Tullis, 1980) to expect the tetrahedral cations to transform instantaneously from partial or complete order to total disorder, especially given the relatively low temperature of the leucite transition.

The transition between low and high leucite

Polyhedral tilting. At some temperature between 600 °C and 750 °C, depending upon the sample, high leucite inverts to a lower-symmetry polymorph. Taylor and Henderson (1968) describe the transformation as one induced primarily by the gradual collapse of the tetrahedral framework about the cavity containing the K cation; at the transition itself some critical symmetry-breaking point is reached. The distortion of this cavity is marked indeed; in high leucite, K is coordinated to six O at 3.35 Å and six O at 3.54 Å (Peacor, 1968), whereas in low leucite these bond lengths change to 3.0 Å and 3.5–3.8 Å (Mazzi et al., 1976).

Propping open the tetrahedral framework by artificial means therefore should increase the stability field of the cubic phase, and in fact substitution of larger alkali ions in the cavity sites lowers the transition temperature (Taylor and Henderson, 1968; Martin and Lagache, 1975; Hirao et al., 1976). The inversion for $\text{RbAlSi}_2\text{O}_6$ occurs at 310 °C, and synthetic $\text{CsAlSi}_2\text{O}_6$ is cubic at room temperature (Taylor and Henderson, 1968). Henderson (1981) also observes that shrinkage of the tetrahedral framework is analogous to substitutions of larger alkali cations. Excess Si in the tetrahedral sites of leucite results in a contraction of the framework and a decrease in the transition temperature, since Si^{4+} is smaller than Al^{3+} . In leucites with an Si/Al ratio of 2.35, the critical point is lowered by 80 ° (Henderson, 1981).

Twin formation. The transformation from the cubic space group $Ia3d$ to the tetragonal $I4_1/a$ involves the loss

of two distinct sets of symmetry elements: a threefold rotation axis along [111]; and a d -glide plane along (110). With the loss of the threefold rotation the crystal system inverts from cubic to tetragonal, and the space group $Ia3d$ degenerates to the subgroup $I4_1/acd$. When the (110) glide plane vanishes, $I4_1/acd$ degenerates in turn to its subgroup $I4_1/a$. Thus, the existence of an intermediate phase in leucite with space group $I4_1/acd$ would require that the threefold rotation axis be lost at a separate, higher temperature than the temperature at which the d -glide plane disappears. Conversely, the absence of an intermediate phase implies a simultaneous disappearance of the two symmetry elements.

The loss of each symmetry element produces twins. The twin domains associated with the loss of the threefold rotation share one a axis, but the other a axis and the c axis are interchanged. Because the lengths of a and c are nearly identical in low leucite, these twins approximate merohedrism and are denoted as pseudomerohedral (Mazzi et al., 1976). On the other hand, the twins produced by the loss of the (110) d -glide plane are truly merohedral, since the positions of the a_1 and a_2 axes are interchanged while the c axis is unmoved.

Experiments involving the transformation

Much effort has been expended to determine whether or not the leucite transition is rigorously displacive, as defined by Buerger (1951). Does the high-temperature structure with symmetry $Ia3d$ invert to the $I4_1/a$ polymorph at a single temperature through a process that is rapid, reversible, and thermodynamically second-order?

Single crystal X-ray experiments by Wyart (1938), Peacor (1968), and Sadanaga and Ozawa (1968) reveal no hysteresis about the critical temperature and no temperature at which the cubic and tetragonal phases coexist. These researchers also found that the approach towards equivalence in the lengths of a and c as leucite is heated (such that the ratio c/a approaches unity) is gradual and continuous. The point at which $c/a = 1$ coincides exactly with the appearance of a diamond glide, as denoted by the disappearance of the $hk0$ diffractions in which either h or k is odd. In addition, Peacor plotted the variation of intensity of the 404 reflection with temperature and observed no discontinuities up to 80 °C above the transition temperature. Measurements of enthalpy (Pankratz, 1968) and of unit-cell volume (Taylor and Henderson, 1968) also suggest that the transition is second-order.

Nevertheless, other experiments support the interpretation that an intermediate phase is stable between the low and high polymorphs. Faust (1963) examined nine natural and four synthetic leucites by differential thermal analysis (DTA), and he observed two absorption events associated with the transition, the first slightly more intense than the second. These events are separated by about 25 °C and also occur on cooling with no hysteresis. Similarly, Lange et al. (1986) measured heat capacities of synthetic and natural leucite by differential scanning calorimetry (DSC) and detected two peaks around the tran-

sition temperature. Unlike Faust, however, Lange et al. observed a window of 82 °C to 176 °C over which the transition takes place, and they also perceived a hysteresis of about 10 °C between heating and cooling cycles. Both Faust and Lange et al. noted that the behavior of the iron analogue of leucite (KFeSi_2O_6) directly contrasts with that of the aluminum end-member and exhibits a single absorption peak at the transition.

Taylor and Henderson (1968) studied the thermal expansion of leucite and its alkali derivatives and found that changes in unit-cell volume with respect to temperature in synthetic Rb- and Cs-substituted equivalents of leucite occur in three distinct stages. These researchers suggest that the inversion to cubic symmetry takes place at the end of the first stage and that full expansion of the tetrahedral framework is attained by the end of the second. However, the occurrence of an intermediate expansion rate in synthetic potassium leucite was questionable and clearly was absent in natural leucite. These results and interpretations generally were confirmed by Hirao et al. (1976), who extended the study to potassium, rubidium, and cesium-ferrileucite, which also exhibit three stages of thermal expansion.

In addition, Martin and Lagache (1975) measured the change in unit-cell parameters with increasing temperature in the alkali leucite system via X-ray powder diffraction, and they observed an actual coexistence of cubic and tetragonal phases near the transition points of phases in the solid solution series $(\text{K,Cs})\text{AlSi}_2\text{O}_6$ and $(\text{Rb,Cs})\text{AlSi}_2\text{O}_6$. Similarly, Henderson (1981) examined a suite of synthetic and natural silica-rich leucite by X-ray powder diffraction methods, and he detected the appearance of a faint peak between the 400 and 004 reflections, 120 °C below the transition temperature. As T_c was approached, the faint peak grew more intense at the expense of its neighbors, which became less intense and merged into this central peak at 600 °C. Like Martin and Lagache in their work with the alkali leucites, Henderson noted a slight volume discontinuity of about 1% between the coexisting phases; therefore the transitions in these systems technically are first-order. It should be noted, however, that Henderson also investigated K end-member leucite and observed no coexistence of phases and no hysteresis in the inversion temperature.

Lastly, the dc-conductivity of leucite was studied by Rüscher et al. (1987) and revealed three distinct stages. During heating, the activation energy was nearly constant until the transition temperature was reached, at which point a steep increase in conductivity was registered. A much lower activation energy was exhibited after transformation to the cubic phase.

Interpretations of the transition mechanism

Many hypotheses have been proposed to explain the peculiarities that attend the leucite transition. Sadanaga and Ozawa (1968) view the transition as classically displacive; they assert that the second trough in the DTA spectra arises merely from "certain minute changes [that

need to be] introduced to complete the high-temperature structure, such as migration of ions or vacancies from domain boundaries." Faust (1963) favored an order-disorder relationship involving Al and Si, as occurs in alkali feldspars, and he rationalized the DTA data in terms of the sluggishness of diffusion among tetrahedral cations. Grögel et al. (1984) also state that Al-Si ordering controls the transition and that an intermediate phase with space group $I4_1/acd$ occurs. Rüscher et al. (1987) take the presence of an $I4_1/acd$ polymorph for granted and argue that diffusion of K^+ cations plays a prominent role.

Henderson (1981) concludes that, for silica-rich leucites at least, both the tetragonal and the cubic phases participate in an intermediate structure through a martensitic-like process. According to this model, as leucite approaches the transition temperature, emerging nuclei of cubic leucite are enveloped by the parent tetragonal leucite, and a quasi-equilibrium in the strain energy between the two lattices stabilizes the two-phase structure. Such nuclei enlarge with increasing temperature until eventually the entire crystal is transformed. Lange et al. (1986) present arguments for both a martensitic transition and for an intermediate phase with space group $I4_1/acd$; however, it would seem difficult to reconcile these two possibilities if the martensitic transition involves the coexistence of tetragonal and cubic phases with space groups $I4_1/a$ and $Ia3d$.

Finally, Martin and Lagache (1975) suggest that for leucite solid solutions, two phases of slightly different compositions may exist over the transformation interval. One phase would be cubic and the other tetragonal, but both solids would be stable, generating a two-phase loop in a T - X diagram of the binary system. Supporting this contention is the probability that alkali cations will not be partitioned equally between tetragonal and cubic unit cells having different volumes and that analogies exist in the nepheline-kalsilite system. Thus, it would seem from this model that only stoichiometric end-member leucite will transform in a purely displacive manner.

The memory effect

The transformation between high and low leucite also is characterized by the occurrence of a memory with regard to the positions of the pseudomorph twin boundaries after a heating and cooling cycle. Wyart (1938) observed this phenomenon optically when he mounted a specimen in a petrographic microscope and heated it above the transition temperature. Differences in birefringence between the two twin orientations disappeared, but upon quenching the specimen the twin lamellae returned to their original locations. Similarly, Lee and Peacor (personal communication, 1983) observed that, after heating leucite specimens above T_c outside the electron microscope, the pseudomorph twin domains returned to their original orientations and the boundary positions were approximately repeated.

Peacor (1968) likewise observed a memory effect using X-ray diffraction. Weissenberg photographs were taken

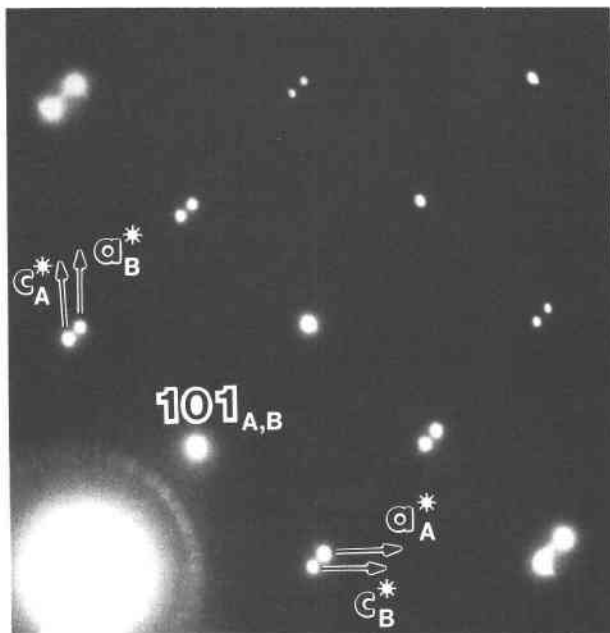


Fig. 2. A selected-area electron-diffraction pattern taken of adjacent pseudomerohedral twin domains, here labeled A and B. Spot splitting results from the unequal lengths of a and c , and the reciprocal space direction of the unsplit row $[101]^*$ reveals the twin plane as $\{101\}$.

before and after two leucite crystals were heated to 80°C above the transition temperature and then quenched. In each case, the second photograph duplicated the first. Peacor inferred from these results that the relative volumes of each twin type remained the same. Further, Sadanaga and Ozawa (1968) observed no change in the orientation of the crystallographic axes during their heating experiments. Lastly, Mazzi et al. (1976) studied a set of diffractions arising from the three pseudomerohedral twin orientations in crystals subjected to several different heat treatments; in each case, they detected no variation in intensities among the diffractions recorded before and after heating.

THIS WORK

In light of the questions surrounding the transformation in leucite, we concluded that direct observation of the pseudomerohedral and the merohedral twins at the transition point might provide some critical insights into the reaction mechanism. To this end we imaged the two twin types in specimens cut from single crystals of leucite with the transmission electron microscope and heated the samples in situ.

Imaging the twin domains

Adjacent pseudomerohedral twins in low leucite share one a axis, and the other a axis and c are interchanged. Because the lengths of a and c in low leucite are not exactly identical, the lattices of adjacent domains are rotated slightly with respect to each other. As a result, pseu-

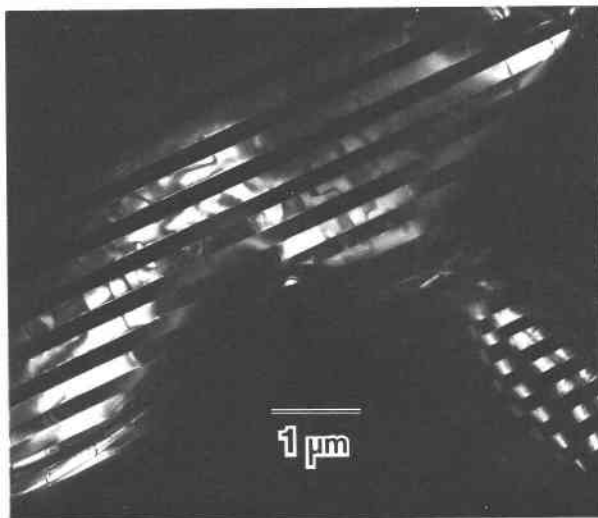


Fig. 3. A dark-field electron micrograph using one diffracted beam from a split pair, $g = 400$. Pseudomerohedral twins appear as alternating light and dark bands.

domerohedral twins can be distinguished with the optical microscope, since neighboring domains will not go to extinction simultaneously. Further, the juxtaposition of these tilted lattices is manifested in X-ray and electron diffraction photographs by the splitting of diffractions (Fig. 2).

Although pseudomerohedral twins can be imaged with the TEM via bright-field electron microscopy (Amelinckx and Van Landuyt, 1976), dark-field microscopy reveals the pseudomerohedral domain structure somewhat more clearly. By forming an image with only one of the diffracted beams from a split pair, the two orientations appear as light and dark regions. From Figure 3 it can be seen that these twins occur as broad sheets less than $0.5\ \mu\text{m}$ thick. The boundaries appear as planar, parallel surfaces, and the alternation of domains can be remarkably periodic. Using X-ray precession methods, Sadanaga and Ozawa (1968) suggested that the twin boundaries lie along the $\{101\}$ planes, and their conclusion is confirmed by the direction of the unsplit row in the electron diffraction photograph of Figure 2 and by the orientation observed in TEM images.

Merohedral twins, however, cannot be observed with a petrographic microscope, but they can be imaged with an electron microscope. In fact, merohedral twin boundaries can be seen in the micrographs of Amelinckx and Van Landuyt (1976) but were called antiphase boundaries. The proper imaging technique is outlined in an abstract by Rüscher et al. (1987). In a selected-area electron-diffraction pattern taken across merohedral twin boundaries, the hkl diffracted spot of one twin orientation will be superimposed on khl of the other. By forming a dark-field image from a diffracted beam with structure factors $F(hkl)$ and $F(khl)$ that differ markedly, adjacent merohedral twin domains will contrast strongly.

It can be seen from Table 1 that distinct contrast can be obtained from the 420 diffractions when the merohe-

TABLE 1. Selected structure factors for low leucite

(hkl)	$ F_o $
420	397.4
240	130.3
042=402	95.5
024=204	96.6

Note: From Mazzi et al., 1976.

dral twins are contained within pseudomerohedral domains in which c is normal to the film (i.e., $l = 0$) and the image is formed from overlapping 420 and 240 spots. Conversely, when c is in the plane of the specimen, the contrast among the merohedral twins is virtually zero. Thus, the 420 spots simultaneously reveal merohedral twin shapes and pseudomerohedral boundaries.

It is apparent from Figure 4 that the merohedral twin boundaries are conspicuously curved, unlike their pseudomerohedral counterparts. The starkly different shapes of the two twin types may be explained by considering elastic strain energies. Structural misfit at the pseudomerohedral boundaries will give rise to strain along the boundary if it is a coherent interface. In fact, at the interface itself the atoms may assume the high leucite configuration, just as the atoms in the regions separating the Dauphiné twins of low quartz may take on the high quartz arrangement (Liebau and Böhm, 1982). The resulting interfacial strain energy can be minimized by reducing the area of the interface and by placing the interface in an exact lattice-fit orientation; flat surfaces oriented along $\{101\}$ result. On the other hand, no lattice misfit occurs at the merohedral twin boundaries, regardless of their orientation. Thus, these surfaces are irregular, arcuate, and strain-free. A rigorous analysis of variations in pseudomerohedral twin orientations resulting from spontaneous strain due to the phase transition is presented by Palmer et al. (1988).

The behavior of the merohedral domain walls as they meet the pseudomerohedral boundaries has been a source of some disagreement. Whereas Amelinckx and Van Landuyt (1976) and Palmer et al. (1988) claim that the merohedral walls transect the pseudomerohedral interfaces, Rüscher et al. (1987) imply that the merohedral twins are engaged in a pseudomerohedral prison. Our bright-field images using only the primary beam have shown unambiguously that the merohedral boundaries can indeed cross the pseudomerohedral walls without interruption (Fig. 5A). High-resolution images (Fig. 5B) confirmed this observation, and they also demonstrated the complete coherency of the lattices across both types of boundaries (Fig. 5C). It should be noted that in some micrographs the merohedral twin boundaries appear to terminate at their junction with the pseudomerohedral twin boundaries. However, the axial transformations involved at the twin domain intersections imply that such merohedral twin boundaries must actually follow along one limb of the pseudomerohedral twin interfaces; they cannot simply disappear.

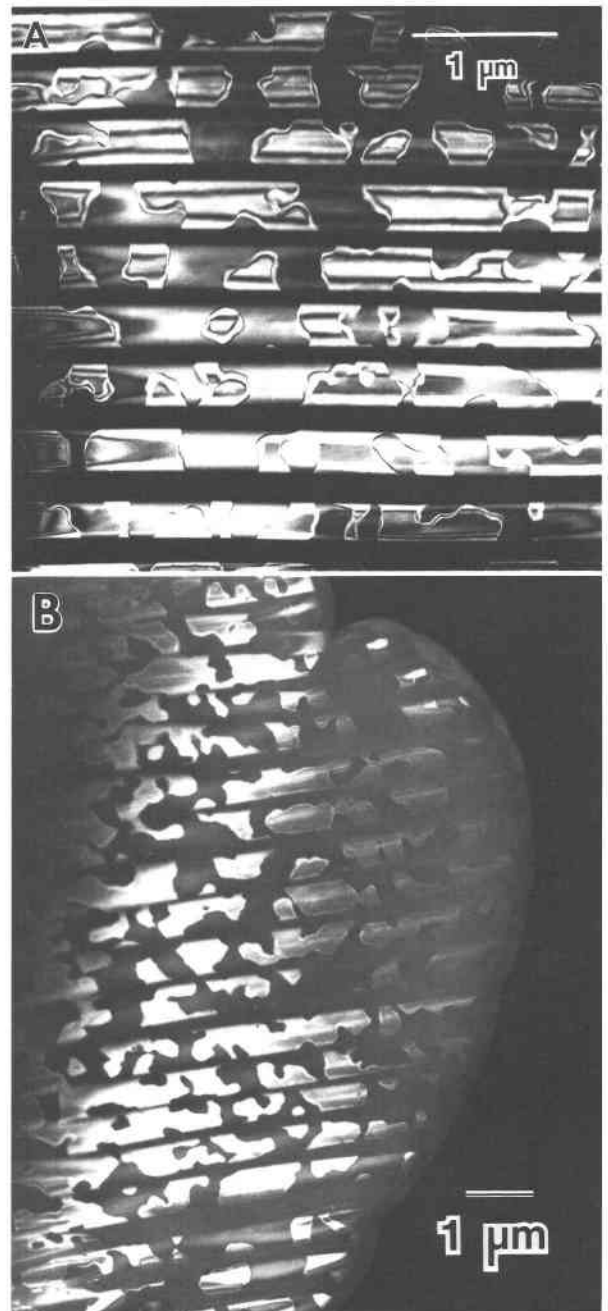


Fig. 4. (A) A dark-field micrograph using the 420 diffracted beam. Merohedral twins occur as irregularly shaped domains within one set of pseudomerohedral twin domains. (B) At temperatures of approximately 500 °C, contrast among the pseudomerohedral twins diminishes, revealing the merohedral twins more distinctly.

In situ heating experiments

Existence of an intermediate phase. Before the heating experiments were begun, the leucite crystals studied were replete with both pseudomerohedral and merohedral twins, as revealed not only through TEM images but

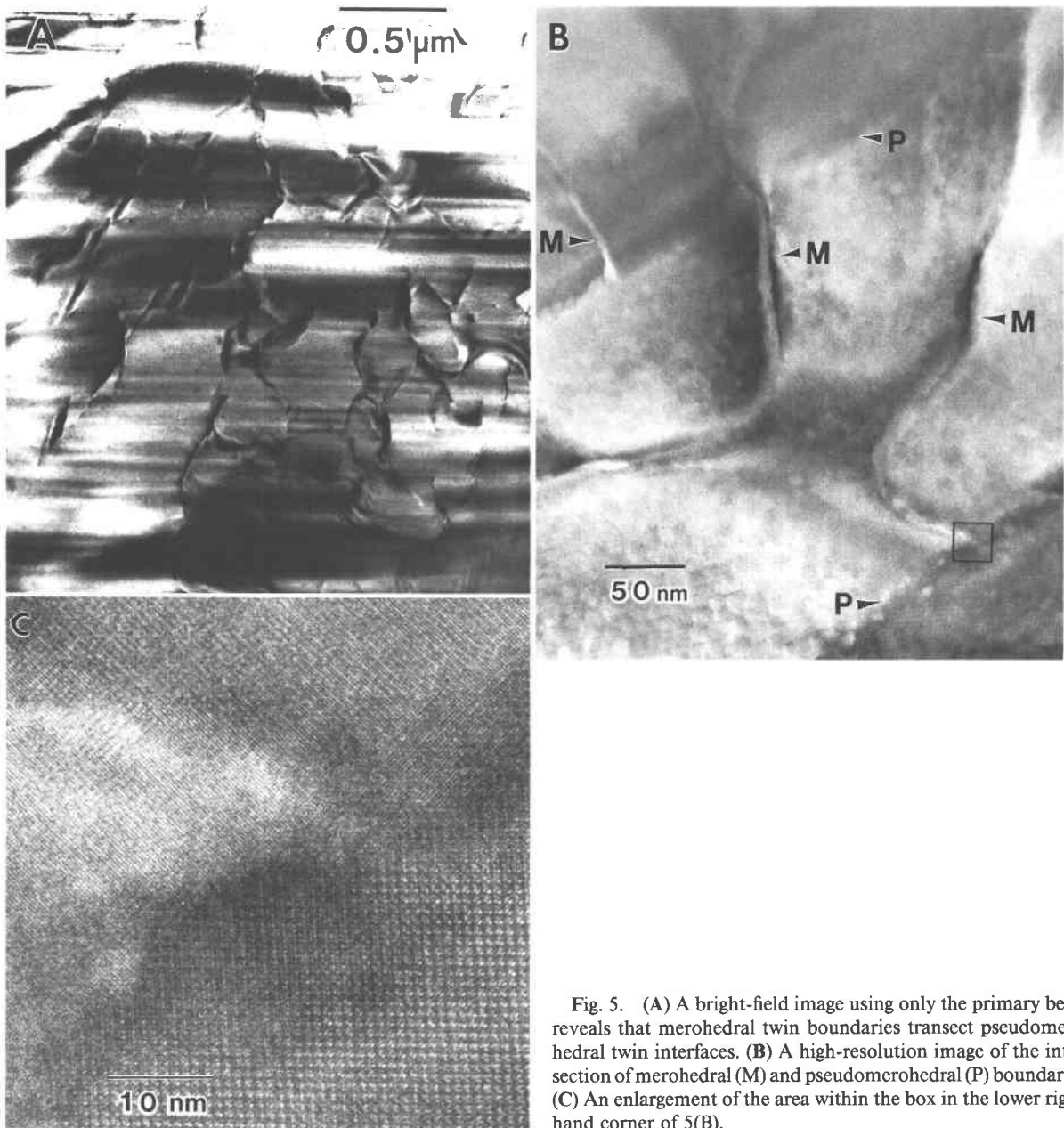


Fig. 5. (A) A bright-field image using only the primary beam reveals that merohedral twin boundaries transect pseudomerohedral twin interfaces. (B) A high-resolution image of the intersection of merohedral (M) and pseudomerohedral (P) boundaries. (C) An enlargement of the area within the box in the lower right-hand corner of 5(B).

through electron diffraction patterns as well. The presence of pseudomerohedral twins was ascertained from the splitting of diffractions in SAED patterns, and merohedral twins were evident in reciprocal space through the occurrence of $hk0$ spots where either h or k is odd; a transition to a polymorph of higher symmetry would require the introduction of a diamond glide, causing those reflections and the twins to disappear. Although diffractions forbidden by glide planes commonly are introduced in electron-diffraction patterns through dynamical interactions with higher-order Laue zones, this phenomenon was not observed in our zone-axis patterns.

Samples were observed along two zone axes: $\{001\}$ and $\{113\}$. As the foils were heated, the angle of splitting between reciprocal lattice vectors that are equivalent in the cubic phase decreased gradually and continuously. The ratio c/a can be computed from this splitting angle, and the shape of the plot of c/a versus temperature (Fig. 6) closely resembles those obtained from X-ray diffraction by Wyart (1938), Sadanaga and Ozawa (1968), and Peacor (1968). Over the first several hundred $^{\circ}\text{C}$, the splitting angle decreased slowly but steadily, but at ~ 200 $^{\circ}\text{C}$ below the transition temperature the slope steepened sharply. As the spots converged, the $hk0$ diffractions with h or k

odd became perceptibly weaker until they no longer could be observed at the critical point itself. Their disappearance seemed to coincide exactly with the coalescence of the split spots, suggesting that the unit cell became at least metrically cubic when the diamond glide was introduced (Fig 7).

Thus, information obtained from electron-diffraction experiments is fully consistent with the results of the previous X-ray work. However, direct electron imaging can reveal subtleties not easily discerned through diffraction techniques (Fig. 8). Pseudomerohedral boundaries grew increasingly diffuse as the specimens were heated, and the contrast between merohedral twins grew steadily weaker. At the actual transition, the merohedral twins could not be imaged at all, but, contrary to our expectations, the pseudomerohedral twins still could be identified above the transition temperature determined from our c/a versus T plots.

The existence of the twins above T_c was manifested in three ways: (1) the Bragg extinction contours were scalloped, with each indentation corresponding to the position of a pseudomerohedral twin lamella (Figs. 8D and 9A); (2) intensity variations among the two pseudomerohedral twin orientations were evident in bright field images obtained at appropriate orientations (Fig. 9A); and (3) under special diffracting conditions the pseudomerohedral boundaries themselves were apparent in one micrograph (Fig. 9B). As the temperature was raised approximately 150 °C above the transition, the intensity variations gradually became imperceptible and the Bragg contours smoothed out. Although it was impossible in these experiments to gauge the absolute temperatures of the specimens themselves, it is certain from c/a plots such as that in Figure 6 that the specimens were well above T_c .

These results demonstrate that leucite passes through an intermediate phase that must have space group $I4_1/acd$. The appearance of a d -glide at the transition temperature is confirmed by the extinction of the $hk0$ spots with h or k odd in both our electron diffraction experiments and all previous X-ray diffraction experiments. That the introduction of the d -glide is not accompanied by a threefold rotational axis along $[111]$ is supported by the persistence of pseudomerohedral twins above the transition temperature. The threefold axis is the twin element of the pseudomerohedral twin law; when the pseudomerohedral twins are present, the threefold rotation must be absent as a symmetry element by the definition of a twin law. However, the presence of threefold axes along $[111]$ is required by cubic symmetry. Therefore, even though this intermediate phase appears to be metrically cubic (i.e., $c = a_1 = a_2$), it cannot possess a cubic point group or space group.

Explanation of the memory effect. The occurrence of a tetragonal intermediate phase may account for the memory effect of leucite. Like Wyart (1938) and Lee and Peacor (personal communication, 1983), we noted that when our foils were cooled below the transition temperature, the orientations and positions of the pseudomerohedral

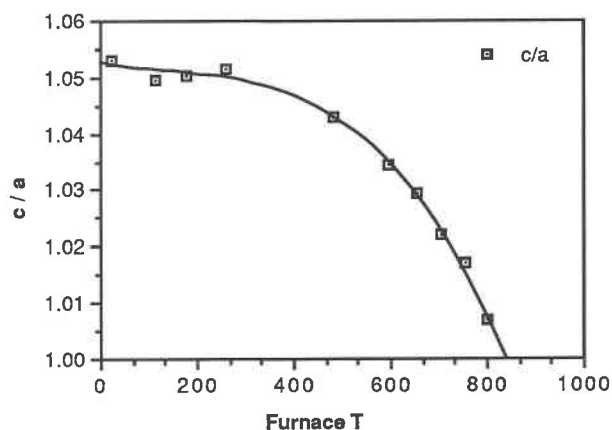


Fig. 6. A plot of the ratio of axial lengths c/a versus furnace temperature. T_c is defined as the point at which $c/a = 1.00$, about 850 °C in this experiment.

twin boundaries were closely preserved (Fig. 10). However, since our experiments suggest that the pseudomerohedral twins never actually disappeared, the fact that they returned to their original locations is unsurprising.

It should be noted, however, that at the thin edges of the specimens the twin configuration after quenching bore no resemblance to the original one; typically, these twins were extremely fine and multidirectional, giving rise to a parquet pattern as in Figure 11. The cause of this fine-scale twinning remains uncertain, but it may be related to volatilization of K at the thin edge of the foil. On the other hand, fine twins also have been observed at the thin edges of quartz foils after cycling specimens about the α - β transition (Heaney and Veblen, in preparation), and this twinning has been interpreted to result from strain associated with the specimen surfaces.

For reasons not fully understood, the merohedral twins could not be imaged with enough contrast after the experimental runs for decisive comparisons to be made of boundary positions before and after heating cycles. Consequently, it is not clear whether the merohedral twins retained a memory of their boundary locations. However, it was evident from dark-field images of a quenched specimen treated with additional ion thinning that the average shapes and sizes of the merohedral twins were unchanged.

The existence of an intermediate phase with space group $I4_1/acd$ may explain the anomalously high amplitudes of thermal vibration obtained by Peacor (1968) when he attempted to refine high leucite using cubic symmetry. Further, it should be noted that no evidence could be found for an intermediate modulated structure such as that observed in quartz (Van Tendeloo et al., 1976). Both merohedral and pseudomerohedral twin boundaries remained stationary with increasing temperature, and contrast differences among each type of twin grew gradually less distinct as they approached their separate points of disappearance.

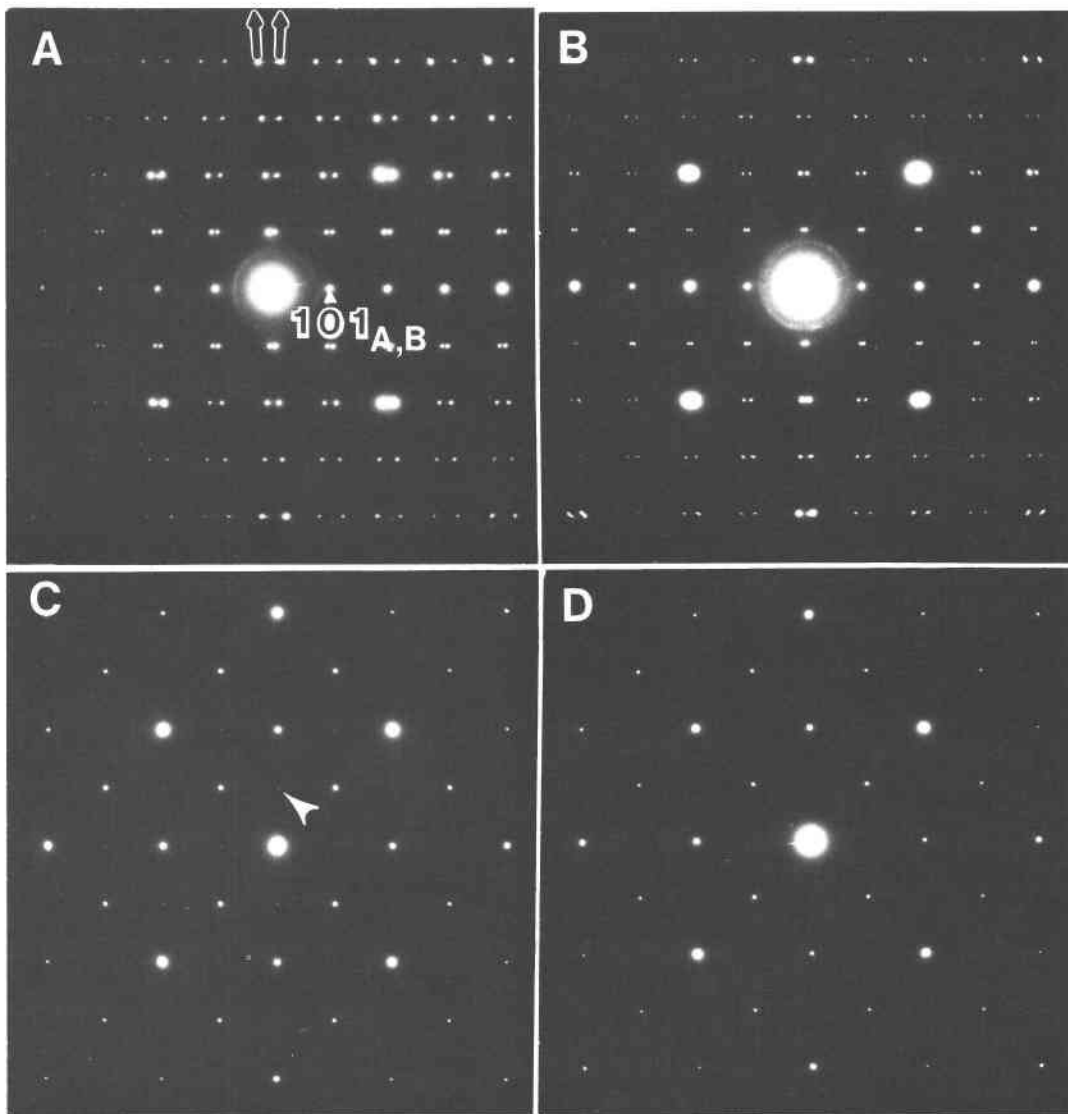


Fig. 7. A series of SAED patterns taken at increasingly higher furnace temperatures: (A) 22 °C; (B) 659 °C; (C) 993 °C; (D) 1041 °C. Split spots can be seen to converge, and $hk0$ spots with h or k odd grow dimmer and disappear in (D) due to the introduction of the d -glide. A weakened pair of $hk0$ spots with h or k odd is arrowed in (C).

CONCLUSIONS

Our experiments indicate that leucite does not transform directly from a structure with space group $I4_1/a$ to one with space group $Ia3d$; rather, leucite transforms to a polymorph with space group $I4_1/acd$. Our TEM work and the single-crystal X-ray diffraction experiments of Peacor (1968) and Sadanaga and Ozawa (1968) suggest that the transition from the $I4_1/a$ phase to the $I4_1/acd$ phase is displacive and second-order. On the other hand, the considerable hysteresis observed about the lower-temperature absorption peak in the DSC experiments of Lange et al. (1986) seems more consistent with first-order transition behavior.

Further, it remains unresolved whether the $I4_1/acd$ polymorph has a true field of thermodynamic stability; proof of this assertion would require the growth of the $I4_1/acd$ phase from cubic leucite above the displacive transition temperature. Unfortunately, our own TEM observations of the subtle features that distinguish the tetragonal from the cubic phase required rather special imaging conditions (e.g., Fig. 9), and these features were indistinct at very high temperatures.

Nevertheless, we believe that the observed behavior of leucite may be explained by Al/Si order among the tetrahedral sites. Though tetrahedral order was not detected by Peacor (1968) and Mazzi et al. (1976), we suggest that it is plausible, even likely, that short-range order would

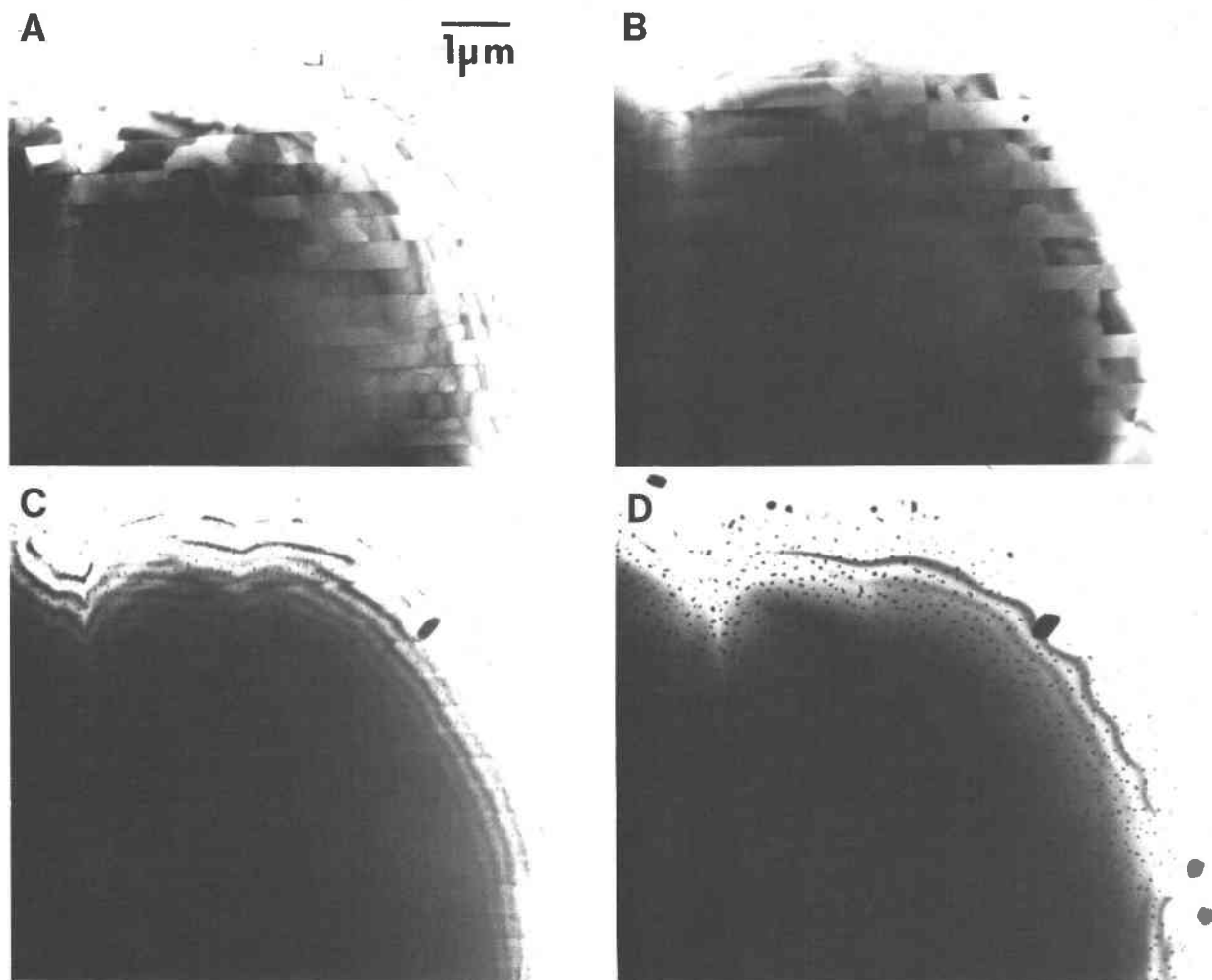


Fig. 8. A series of images of the same area at increasing furnace temperatures: (A) 22 °C; (B) 813 °C; (C) 923 °C; (D) 1041 °C. The specimen in (D) is about 50 °C above T_c , but scalloping of the Bragg contours is evident. The fine black particles in (C) and (D) are tantalum evaporated from the furnace.

be overlooked by X-ray diffraction techniques, especially in light of the complex microtwins that are so pervasive in leucite. Further, strong support for such order arises from the ^{29}Si NMR experiments described earlier (Brown et al., 1987; Murdoch et al., 1988).

Tetrahedral order is not compatible with the symmetry constraints of the $Ia3d$ space group, and the diffusion

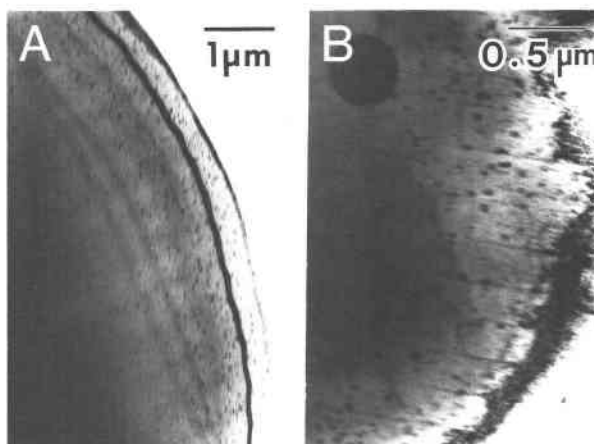


Fig. 9. Both specimens are about 100 °C above the transition temperature. In (A) the pseudomerohedral twins are apparent as bands of alternating light and dark intensities, and the extinction contours are scalloped. The pseudomerohedral twin boundaries themselves can be seen in (B).

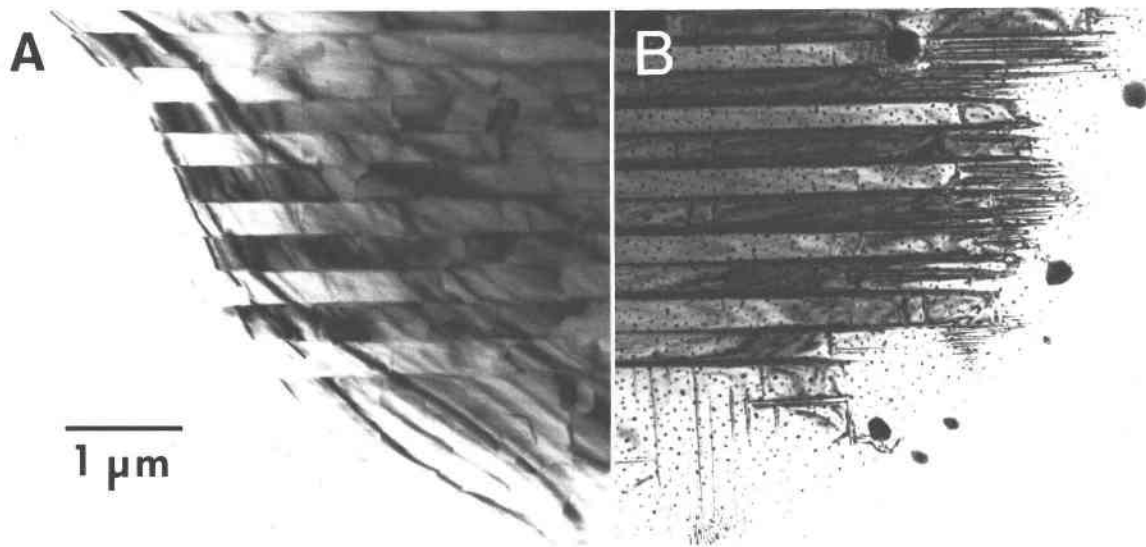


Fig. 10. The same area of a specimen before and after heating above T_c , with (B) printed backwards for simplified comparison. The pseudomorph boundaries have returned close to their original positions. Small discrepancies in boundary locations are due to changes in orientation of the specimen from warping of the foil during the heating experiment.

coefficients for Al and Si in framework silicates at 1000 °C are below the limits of detection by conventional means in dry systems (Freer, 1981). Therefore, in contrast to Grögel et al. (1984), it seems improbable that rapid disordering of Al and Si at the lower transition temperature would transform tetragonal leucite to a cubic polymorph. Instead, the presence of Al/Si order might inhibit a transition to the cubic phase, in much the same way that the topochemically triclinic Al/Si ordering scheme may prevent the inversion of $C\bar{1}$ albite to $C2/m$ monalbite at the equilibrium analbite-monalbite transition temperature (Grundy and Brown, 1969; Okamura and Ghose, 1975; and Prewitt et al., 1976). It appears, then, that during our experiments kinetic factors would have favored the transformation from the $I4_1/a$ phase to the $I4_1/acd$ polymorph, even if the $I4_1/acd$ polymorph is metastable with respect to cubic leucite.

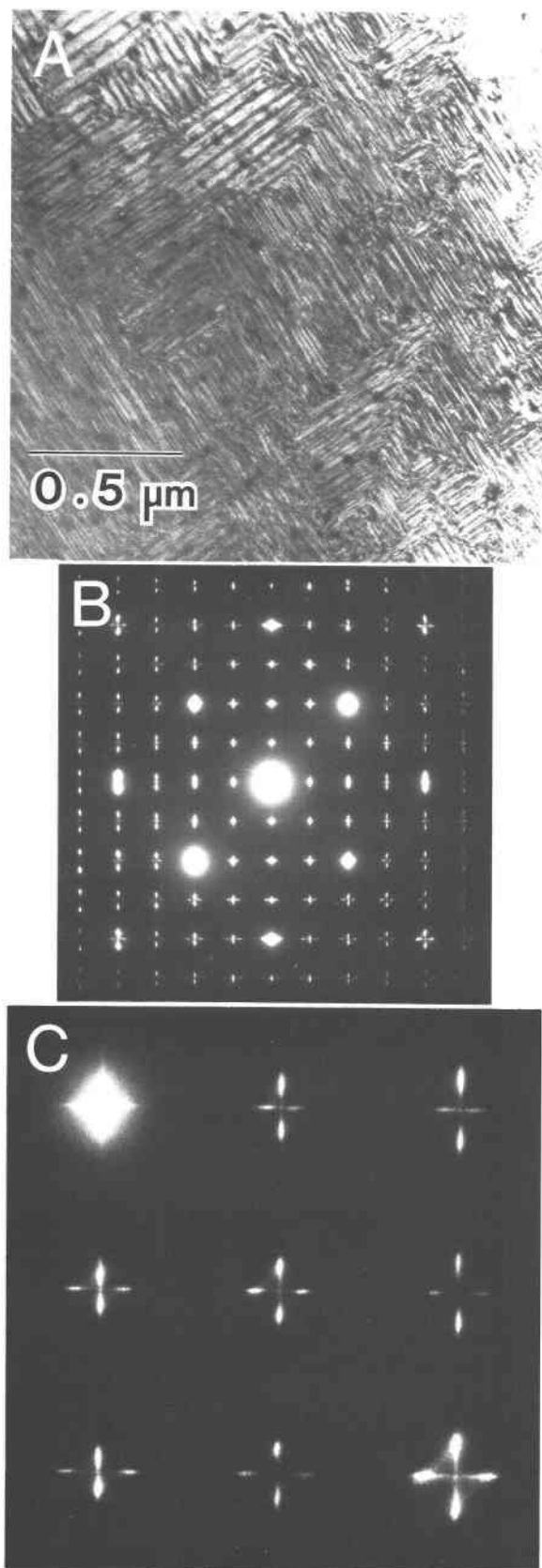
Nevertheless, our experiments clearly did show that a leucite phase with space group $I4_1/acd$ can exist. On the other hand, it remains to be demonstrated that high leucite actually does attain true cubic symmetry. Some ^{29}Si NMR experiments (Murdoch et al., 1988; Stebbins, personal communication) indicate that short-range Al/Si order persists well above the displacive transition temperature: leucite specimens with local Al/Si order that were annealed for nearly a week at 1400 °C displayed no change in tetrahedral partitioning. If these results are correct, it would appear that either the transition from tetragonal to cubic leucite occurs at an extremely high temperature or that high leucite actually is tetragonal, with space group $I4_1/acd$. If high leucite is tetragonal, then the pseudomorph boundaries in leucite should be classified as growth twins rather than transformation twins. However, the periodic and polysynthetic quality of the pseudomero-

hedral twins seems more consistent with transformation than with growth twinning.

The second absorption event in the experiments of Faust (1963) and Lange et al. (1986) remains enigmatic. It seems unlikely that it represents an Al/Si disordering phenomenon, since even this higher-temperature absorption episode occurs with rapid heating and at relatively low temperatures (about 673 °C in synthetic leucites and from 584 to 633 °C in natural leucites in the study of Lange et al.). We therefore doubt that this second peak is related to an $I4_1/acd$ to $Ia3d$ transformation, as suggested by Lange et al. (1986) and Palmer et al. (1988). It also is questionable whether this second peak corresponds to a discontinuity in thermal expansion. Like potassium-aluminum leucites, potassium ferrileucites exhibit three distinct stages of unit-cell expansion; but unlike potassium-aluminum leucites, potassium ferrileucites display only a single peak on DSC traces. Perhaps the second peak is related to sudden shifts in alkali cation positions in light of the dc-conductivity results of Rüscher et al. (1987), but a rigorous resolution of this and the many other problems involving leucite awaits further experimental work.

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REFERENCES CITED

- Amelinckx, S., and Van Landuyt, J. (1976) Contrast effects at planar interfaces. In H.-R. Wenk, Ed., *Electron microscopy in mineralogy*, p. 68–112. Springer-Verlag, Berlin.
- Brown, I.W.M., Cardile, C.M., MacKenzie, K.J.D., Ryan, M.J., and Meinhold, R.H. (1987) Natural and synthetic leucites studied by solid state ^{29}Si and ^{27}Al NMR and ^{57}Fe Mössbauer spectroscopy. *Physics and Chemistry of Minerals*, 15, 78–83.
- Buerger, M.J. (1951) Crystallographic aspects of phase transformations. In R. Smoluchowski, Ed., *Phase transformations in solids*, p. 183–211. Wiley, New York.
- Faust, G.T. (1963) Phase transition in synthetic and natural leucite. *Schweizerische Mineralogische und Petrographische Mitteilungen*, 43, 165–195.
- Freer, R. (1981) Diffusion in silicate minerals and glasses: A data digest and guide to the literature. *Contributions to Mineralogy and Petrology*, 76, 440–454.
- Fudali, R.F. (1963) Experimental studies bearing on the origin of pseudoleucite and associated problems of alkalic rock systems. *Geological Society of America Bulletin*, 74, 1101–1126.
- Grögel, T., Boysen, H., and Frey, F. (1984) Phase transition and ordering in leucite (abs.). *Acta Crystallographica A*, 40S, C256–C257.
- Grundy, H.D., and Brown, W.L. (1969) A high-temperature X-ray study of the equilibrium forms of albite. *Mineralogical Magazine*, 37, 156–172.
- Heaney, P.J., and Veblen, D.R. (1988) A transmission electron microscope study of the low-high leucite phase transition. *Geological Society of America Abstracts with Programs*, A103.
- Henderson, C.M.B. (1981) The tetragonal-cubic inversion in leucite solid solutions. *Progress in Experimental Petrology*, 5, 50–54.
- Hirao, K., Soga, N., and Kunugi, M. (1976) Thermal expansion and structure of leucite-type compounds. *Journal of Physical Chemistry*, 80, 1612–1616.
- Lange, R.A., Carmichael, I.S.E., and Stebbins, J.F. (1986) Phase transitions in leucite (KAlSi_3O_6), orthorhombic KAlSi_4O_8 , and their iron analogues (KFeSi_2O_6 , KFeSi_4O_8). *American Mineralogist*, 71, 937–945.
- Liebau, F., and Böhm, H. (1982) On the coexistence of structurally different regions in the low-high quartz and other displacive phase transformations. *Acta Crystallographica*, A38, 252–256.
- Martin, R.F., and Lagache, M. (1975) Cell edges and infrared spectra of synthetic leucites and pollucites in the system KAlSi_3O_6 – $\text{RbAlSi}_3\text{O}_6$ – $\text{CsAlSi}_3\text{O}_6$. *Canadian Mineralogist*, 13, 275–281.
- Mazzi, F., Galli, E., and Gottardi, G. (1976) The crystal structure of tetragonal leucite. *American Mineralogist*, 61, 108–115.
- Murdoch, J.B., Stebbins, J.F., Carmichael, I.S.E., and Pines, A. (1988) A silicon-29 nuclear magnetic resonance study of silicon-aluminum ordering in leucite and analcite. *Physics and Chemistry of Minerals*, 15, 370–382.
- Náray-Szabó, von, S. (1942) Die struktur des leucits KAlSi_3O_6 . *Zeitschrift für Kristallographie*, 104, 39–44.
- Okamura, F.P., and Ghose, S. (1975) Analbite-monalbite transition in a heat treated twinned Amelia albite. *Contributions to Mineralogy and Petrology*, 50, 211–216.
- Palmer, D.C., Putnis, A., and Salje, E.K.H. (1988) Twinning in tetragonal leucite. *Physics and Chemistry of Minerals*, 16, 298–303.
- Pankratz, L.B. (1968) High-temperature heat contents and entropies of dehydrated analcite, kaliophilite, and leucite. U.S. Department of the Interior, Bureau of Mines, Report of Investigations, 7073.

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Fig. 11. (A) Fine, parquet-like twinning at the thin edge of the foil. (B) A SAED pattern taken from an area such as that in (A), showing spot splitting and diffuse intensity caused by very fine-scale twinning. (C) An enlarged view of the diffraction crosses in the pattern shown in (B). Close inspection reveals the presence of superstructure spots; these indicate a periodicity among the microtwins of about 375 Å.

- Papike, J.J. (1988) Chemistry of the rock-forming silicates: Multiple-chain, sheet, and framework structures. *Reviews of Geophysics*, 26, 407–444.
- Peacor, D.R. (1968) A high temperature single crystal diffractometer study of leucite, $(K,Na)AlSi_2O_6$. *Zeitschrift für Kristallographie*, 127, 213–224.
- Phillips, B.L., and Kirkpatrick, R.J. (1986) Increased resolution for solid-state ^{27}Al NMR. Abstracts of the Fourteenth General Meeting of the International Mineralogical Association, 198–199.
- Prewitt, C.T., Sueno, S., and Papike, J.J. (1976) The crystal structures of high albite and monalbite at high temperatures. *American Mineralogist*, 61, 1213–1225.
- Rüscher, C., Papendick, M., Boysen, H., Putnis, A., and Salje, E. (1987) Dielectric and electron-microscopical studies on leucite $KAlSi_2O_6$. *Zeitschrift für Kristallographie*, 178, 195–196.
- Sadanaga, R., and Ozawa, T. (1968) Thermal transition of leucite. *Mineralogical Journal*, 5, 321–333.
- Taylor, D., and Henderson, C.M.B. (1968) The thermal expansion of the leucite group of minerals. *American Mineralogist*, 53, 1476–1489.
- Taylor, W.-H., (1930) The structure of analcite $(NaAlSi_2O_6 \cdot H_2O)$. *Zeitschrift für Kristallographie*, 74, 1–19.
- Van Tendeloo, G., Van Landuyt, J., and Amelinckx, S. (1976) The alpha-to-beta phase transition in quartz and $AlPO_4$, as studied by electron microscopy and diffraction. *Physica Status Solidi*, 33, 723–735.
- Wyart, J. (1938) Étude sur la leucite. *Bulletin de la Société française de Mineralogie*, 61, 228–238.
- (1940) Étude cristallographique d'une leucite artificielle. Structure atomique et symétrie du minéral. *Bulletin de la Société française de Mineralogie*, 63, 5–17.
- Yund, R.A., and Tullis, J. (1980) The effect of water, pressure, and strain on Al/Si order-disorder kinetics in feldspar. *Contributions to Mineralogy and Petrology*, 72, 297–302.

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