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Crystal Structure of α-$Li_{2.5}Al_{0.5}SiO_4$

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The crystal structure of α-$Li_{2.5}Al_{0.5}SiO_4$, refined from neutron HRPD data, is derived from that of γ-$LiAlO_2$. Oxygens form a distorted tetragonal packed array with cations in fully occupied tetrahedral sites; one such site contains Li and Al at random. The tetrahedra form edge-sharing pairs which link up at their corners to form infinite columns and the columns then link up to form a 3D framework. The high temperature phase, α-$Li_{2.5}Ga_{0.5}SiO_4$, appears to be isostructural. These structures are compared with others that have tetragonal packed anions. © 1991 Academic Press, Inc.

Introduction

The new phase, α-$Li_{2.5}Al_{0.5}SiO_4$, was synthesized during a study of lithium ion conducting solid electrolytes based on doped Li_4SiO_4 (*1*). Li_4SiO_4 forms extensive solid solutions with trivalent Al,Ga by the mechanism $3Li \rightleftharpoons Al,Ga$ (*1, 2*). These have formulae $Li_{4-3x}(Al,Ga)_xSiO_4$ with $0 < x < 0.6$. Various pieces of evidence suggested that the stoichiometry $x = 0.50$, corresponding to $Li_{2.5}(Al,Ga)_{0.5}SiO_4$, may be regarded as an ideal stoichiometry rather than as simply one composition in a solid solution series. In particular, the conductivity passed through a minimum at $x = 0.50$, indicating the absence of defects, such as Li vacancies or interstitials, which are present at other x values (*3*).

The structures of two members of the Ga-containing solid solution series, $x = 0.20$ and $x = 0.33$, have been refined using high resolution neutron powder diffraction data (*4, 5*). These show an essentially continuous transition from the monoclinic structure of Li_4SiO_4 ($x = 0.20$) to an orthorhombic structure ($x = 0.33$) that can be regarded as derived from the tetragonal structure of γ-Li AlO_2 (*6*). We were interested in determining the structure of one of the $x = 0.50$ phases and to compare it with that of γ-$LiAlO_2$. Since the α phase in the Ga system is stable only > 1090°C for $x = 0.50$ (*3*), it was easier to study the Al-containing phase. This can be obtained by quenching in air from the reaction temperature of 1100°C to room temperature.

Experimental

Sample Preparation

α-$Li_{2.5}Al_{0.5}SiO_4$ was prepared by solid state reaction of $^7Li_2CO_3$ (AERE Harwell, Stable Isotope Unit, 99.99% ^7Li), Al_2O_3 (BA Chemicals Ltd., Baco Cera Alumina, 99.9%) and SiO_2 (Thermal Syndicate quartz

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powder, particle size < 100 μm, 99.98%). Appropriate quantities were weighed out and finely ground using an agate mortar and pestle, with acetone added to form a paste. After drying, the reactants were placed in a Pt crucible and heated in an electric muffle furnace at 700°C for 4 hr to expel CO_2. This was followed by firing at 1000°C for 65 hr and 1100°C for 72 hr. The sample was removed from the furnace and reground daily in order to speed up formation of the desired product.

Data Collection

High resolution, time-of-flight powder neutron diffraction data were collected on the HRPD diffractometer at ISIS, Rutherford Appleton Laboratory. Details of data collection and manipulation are similar to those given in (*4*), but with the exception that the time-of-flight range used for structure refinement was from 25,000 to 90,000 μs (0.5 to 1.9 Å *d*-spacing). The normalized diffraction profile was fitted using a modified Rietveld method, with the experimentally observed peak shape modeled by a convolution of a Voigt and two decaying exponential functions (*7*).

Results

Structure Refinement

Examination of the diffraction profile indicated that the structure may have an orthorhombic unit cell similar to that of $Li_{3.00}Ga_{0.33}SiO_4$ (*5*), rather than to the tetragonal cell of γ-$LiAlO_2$ (*6*). Manual extraction of the highest 40 observed *d*-spacings, and use of the autoindexing program VISSER (*8*), fitted these reflections to a *C*-centered orthorhombic cell of dimensions, after Rietveld refinement, $a = 7.1930(1)$, $b = 7.2319(1)$, and $c = 6.2328(1)$ Å. Systematic absences confirmed the space group to be the same as that observed in $Li_{3.00}Ga_{0.33}SiO_4$, $C222_1$ (No. 20) (*9*).

The starting structural model was very similar to that used for the refinement of $Li_{3.00}Ga_{0.33}SiO_4$. The oxygen, lithium, aluminum, and silicon positions were obtained by applying an orthorhombic distortion to the unit cell of γ-$LiAlO_2$, expanded so that its [110] and [1$\bar{1}$0] face diagonals become the orthorhombic *a* and *b* edges. Li sites in γ-$LiAlO_2$ were assumed to contain Li only in $Li_{2.5}Al_{0.5}SiO_4$; Al sites in γ-$LiAlO_2$ were split into two sets of sites, one set containing Si only, the other containing equal numbers of Li and Al atoms. All sites were fully occupied.

Initial refinements, where scale factor, background parameters, unit cell parameters, peak shape parameters, and oxygen positional parameters were allowed to refine, showed the oxygen array to be very similar to that observed in Li_4SiO_4, $Li_{3.4}Ga_{0.2}SiO_4$, and $Li_{3.00}Ga_{0.33}SiO_4$. Further refinements, where positional and site occupation parameters for Li(1), Li(2), Li(1*a*)/Al, and Si atoms were varied, confirmed the distribution of cations assumed in the starting model. A difference Fourier map showed no evidence for the occupation of any other sites.

During the later refinements, when temperature factors were refined, the B_{iso}'s for the Li(1), Li(2), and Li(1*a*)/Al sites had to be constrained to the same value, otherwise the refinement was unstable. Anisotropic temperature factors were refined for oxygen and silicon.

In the final refinement, a total of 40 positional, thermal, and instrumental parameters was refined to a final $R_{wp} = 8.86\%$, $R_{ex} = 4.71\%$, $\chi^2 = 3.54$ for 7604 data points (Table I). For a definition of *R*-factors, see Ref. (*10*).

Description of the Structure

The oxygen array in α-$Li_{2.5}Al_{0.5}SiO_4$, Fig. 1, is closely related to the ideal, tetragonal-packed (tp) array characterized by an anion–anion coordination number of eleven

TABLE I

REFINED UNIT CELL AND ATOMIC PARAMETERS FOR $Li_{2.5}Al_{0.5}SiO_4$

Atom	Position	x	y	z	B_{iso} (Å^2)	Site Occupancy
O(1)	8*a*	0.3078(3)	−0.0071(9)	0.2155(3)	—	1.0
O(2)	8*a*	0.0392(3)	0.1798(3)	0.0008(12)	—	1.0
Si	4*c*	0.1760(5)	0.0	0.0	—	1.0
Li(1a)	4*b*	0.0	0.733(6)	0.25	2.11(12)	0.5
Al(1)	4*b*	0.0	0.733(6)	0.25	2.11(12)	0.5
Li(1)	4*b*	0.0	0.298(2)	0.25	2.11(12)	1.0
Li(2)	4*a*	0.805(1)	0.0	0.0	2.11(12)	1.0

	Anisotropic temperature factors (Å^2)					
	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
O(1)	0.59(7)	2.48(11)	0.27(7)	0.54(16)	−0.20(6)	−0.57(21)
O(2)	1.47(9)	1.10(8)	0.47(7)	−0.26(18)	−0.24(20)	0.66(7)
Si	0.53(13)	−0.08(12)	0.92(13)	1.08(29)	—	—

Note. $Li_{2.5}Al_{0.5}SiO_4$ $C222_1$ (no 20), $Z = 4$, $a = 7.1930(1)$, $b = 7.2319(1)$, $c = 6.2328(1)$ Å.

(*11*). Corrugated tp layers are seen perpendicular to the ⟨110⟩ directions in Fig. 1.

Within a tp anion array there are relatively undistorted tetrahedral and octahedral "framework" sites and there are also distorted interstitial or channel sites. In α-$Li_{2.5}Al_{0.5}SiO_4$, only the tetrahedral sites of the framework are occupied, by Si, Li(1), Li(1a)/Al, and Li(2). The Li(1*a*) sites contain a random distribution of equal numbers of Li and Al ions. The sites occur in edge-sharing pairs such that SiO_4 and Li(2)O_4 tetrahedra share a common edge, as do Li(1)O_4 and Li(1*a*)/AlO_4 tetrahedra. These edge-sharing pairs link at their corners to form columns parallel to the *c* axis.

Si–O bond distances and angles are reasonable and regular, Table II. Li(2)O_4 tetrahedra show considerable distortion with bond lengths between 1.951 and 2.128 Å and angles between 75.3 and 130.8°. This distortion is caused largely by the constraints imposed on the 0(2)–0(2)′ edge which is common to the adjacent SiO_4 tetrahedra. This short edge reduces the corresponding 0(2)–Li(2)–0(2)′ angle to 75.3° and repulsion by Si increases the Li(2)–0(2), 0(2)′ bond lengths to 2.128 Å.

The Li(1*a*)/Al site also shows a large distortion, presumably due to the presence of two different sized cations. The individual Li–O and Al–O bond distances are likely to differ somewhat from the values given in Table II; these values therefore represent an average for this site. The Li(1) site contains only one cation type and shows the least distortion of all the Li-containing tetrahedral sites.

Comparison of α-$Li_{2.5}Al_{0.5}SiO_4$ with γ-$LiAlO_2$, β-BeO, Li_4SiO_4, and $Li_{4-3x}Ga_xSiO_4$ Solid Solutions

The structure of α-$Li_{2.5}Al_{0.5}SiO_4$ is closely related to that of γ-$LiAlO_2$, with similar cation sites in the two structures. Al sites in γ-$LiAlO_2$ split into two groups and are occupied by Si and Li(1*a*)/Al, respectively. This splitting is associated with the reduction in symmetry from tetragonal to orthorhombic. Li sites in γ-$LiAlO_2$ correspond to fully occupied Li sites (Li(1) and Li(2)) in α-$Li_{2.5}Al_{0.5}SiO_4$.

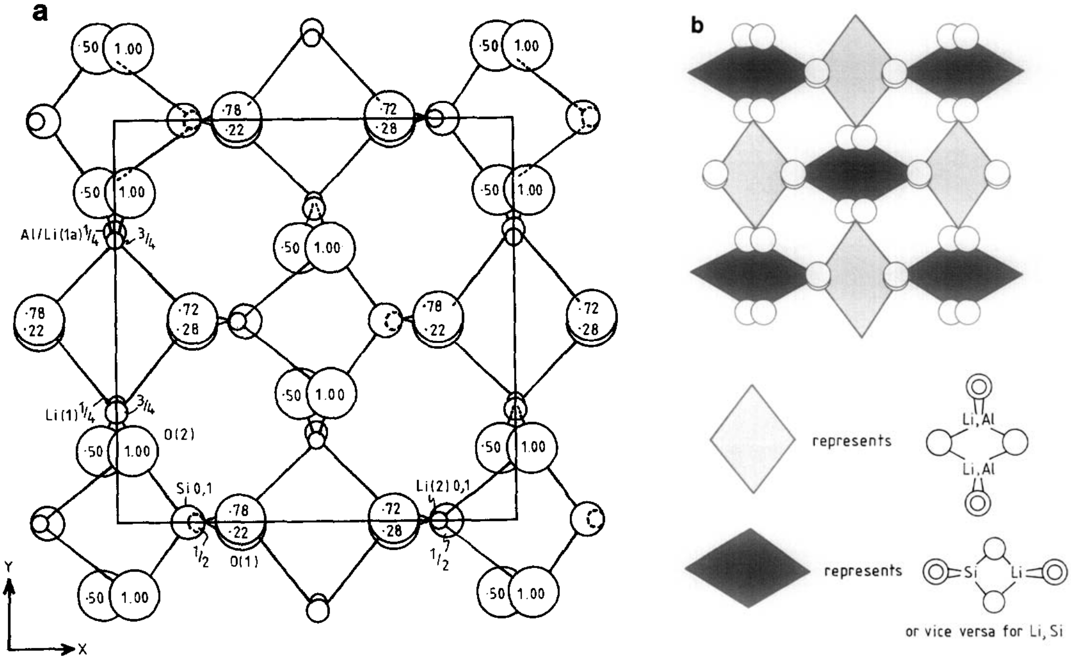

FIG. 1. Projection of crystal structure of $Li_{2.5}Al_{0.5}SiO_4$ showing (a) atomic coordinates, (b) coordination polyhedra.

The oxygen–oxygen environments in α-$Li_{2.5}Al_{0.5}SiO_4$, Figs. 2a and 2b, differ slightly from those in γ-$LiAlO_2$, Fig. 2c, and are very similar to those seen in Ga-containing α and Li_4SiO_4 solid solutions (*4, 5*), and also in Li_4SiO_4 itself (*12–14*). All these arrangements can be described as a distortion of tetragonal packing which is shown ideally in Figs. 2d and 3a.

TABLE II

SELECTED BOND DISTANCES AND ANGLES

Si coordination	Al/Li(1a) coordination
Si-O(1) 1.645(3) ×2	Al/Li(1a)-O(1) 1.710(18) ×2
-O(2) 1.630(3) ×2	-O(2) 2.228(35) ×2
O(1)-Si-O(1') 109.6(3)	O(1)-Al/Li(1a)-O(1') 77.8(14)
-O(2) 111.7(3) ×2	-O(2) 107.6(9) ×2
-O(2') 109.0(3) ×2	-O(2') 105.9(9) ×2
O(2)-Si-O(2') 105.8(3)	O(2)-Al/Li(1a)-O(2') 136.5(29)
Li(1) coordination	Li(2) coordination
Li(1)-O(1) 1.988(11) ×2	Li(2)-O(1) 1.951(5) ×2
-O(2) 1.794(9) ×2	-O(2) 2.128(8) ×2
O(1)-Li(1)-O(1') 89.4(6)	O(1)-Li(2)-O(1') 130.8(6)
-O(2) 110.7(2) ×2	-O(2) 108.4(3) ×2
-O(2') 108.8(2) ×2	-O(2') 110.1(3) ×2
O(2)-Li(1)-O(2') 123.3(8)	O(2)-Li(2)-O(2') 75.3(4)

Note. Bond distances in Ångstroms, bond angles in degrees, e.s.d.'s in parentheses.

Two types of oxygen atom can be seen on projection along the 2_1 axis (c in $Li_{2.5}Al_{0.5}SiO_4$ and α solid solutions, b in Li_4SiO_4 and its solid solutions), Fig. 1. With the first type, 0(1), oxygen atoms at different heights project almost directly on top of each other. In $Li_{2.5}Al_{0.5}SiO_4$ and α solid solutions, their centers on projection are separated by less than 0.05 Å; in Li_4SiO_4 and its solid solutions these oxygen atoms at different heights are related by a mirror plane and superpose one another. The second type of oxygen atom, 0(2) (0(2) and 0(3) in Li_4SiO_4 solid solutions), shows a separation on projection of 0.6 Å between the centers of atoms at different heights.

This structural difference can be explained in terms of the nature of the cations

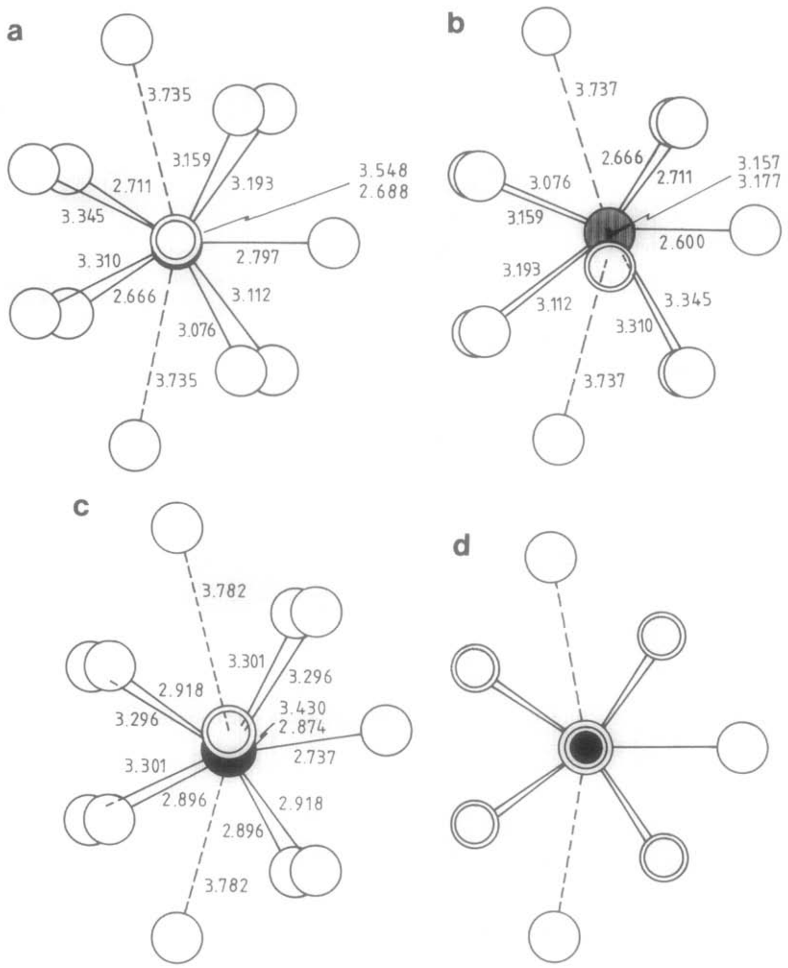

FIG. 2. Oxygen–oxygen environments in (a,b) $Li_{2.5}Al_{0.5}SiO_4$, (c) γ-$LiAlO_2$, (d) ideal tp.

which occupy the edge-sharing MO_4 tetrahedra: both types of oxygen atom are involved in the edge sharing. $Li_{2.5}Al_{0.5}SiO_4$, along with gallium-containing α and Li_4SiO_4 (*4, 5*) solid solutions, contains two types of columns, built from pairs of edge-sharing tetrahedra, Figs. 3b and 3c. In the first type, type A, Fig. 3b, the edge-sharing tetrahedra contain different sized atoms, Li and Si. The Si–O bond distances are much less than the Li–O distances; thus the oxygen atoms of the shared edge are displaced toward the Si atom. The presence of the 2_1 screw axis parallel to the column axis means that there is an alternating sequence of cations . . .–Li–Si–Li–Si–. . . in this direction, Fig. 3b. The direction of displacement of the shared edges alternates along the column axis, and consequently on projection, the centers of these 0(2)/0(3) atoms are displaced significantly.

In the second type of column, type B, Fig. 3c, edge-sharing tetrahedra contain similar sized cations, Li(1) and Li(1*a*)/Al or Li(1*a*)/Ga. In Li_4SiO_4 solid solutions, these pairs of sites contain, on average, identical Li(1)/Ga

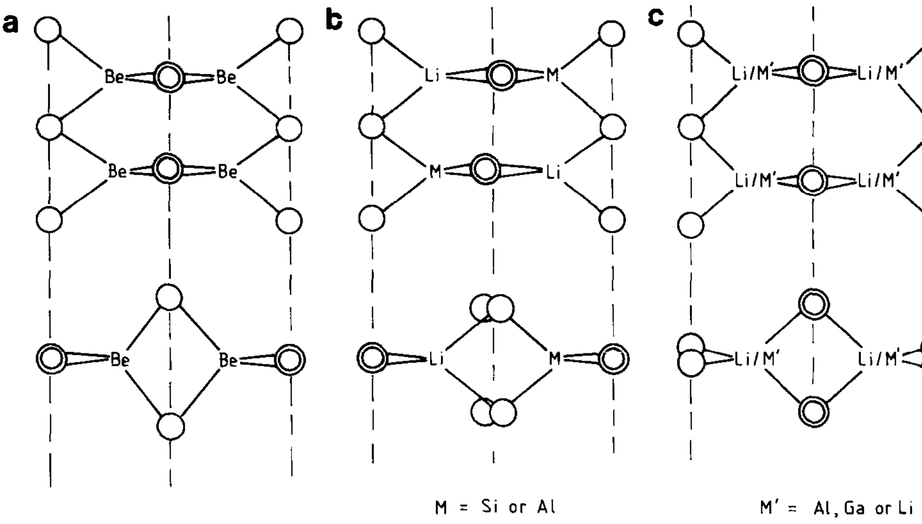

FIG. 3. Schematic projections of (a) the columns in β-BeO and (b,c) the two types of columns present in $Li_{4-3x}(Ga,Al)_xSiO_4$ solid solutions. The top part of each diagram shows a section through the column with the column axis vertical. The bottom part shows the appearance of each on a projection down the column axis.

atoms (*4*). This means that these tetrahedra are of the same, or very similar, size. Thus, there will be little or no displacement of the oxygen atoms involved in edge-sharing toward either of the cation sites. These type B columns therefore show pseudomirror symmetry along the shared edges, a formal mirror plane actually existing in the Li_4SiO_4 solid solutions, Fig. 3c. Consequently, the shared edges, and thus the 0(1) atoms involved in edge sharing, project almost directly on top of each other, or are superposed in Li_4SiO_4 solid solutions, when viewed along the axis of the columns.

In these structures, exhibiting distorted tetragonal packing, type A and type B columns are linked by corner sharing of individual tetrahedra to form the framework. Additional complications in the Li_4SiO_4 and α solid solutions, with $x < 0.5$, should be noted, however. First, the lithium and gallium tetrahedral sites making up these columns are not all fully occupied. Second, octahedral sites, present between the linked tetrahedral pairs, are partially occupied in the type B columns. Third, channels between the framework columns also contain lithium atoms in partially occupied sites.

The structures of $Li_{2.5}Al_{0.5}SiO_4$ and the different solid solutions show various distortions from ideal tp because of the complexities of their cation arrangements. The situations in γ-$LiAlO_2$ and β-BeO are somewhat simpler. Both these structures contain the columns built up from edge-sharing tetrahedral pairs observed in $Li_{2.5}Al_{0.5}SiO_4$ and α and Li_4SiO_4 solid solutions. In β-BeO (*15*), all the tetrahedral sites contain the same cation, Be. Therefore, all the columns of edge-sharing tetrahedra are of type B, and consequently the shared edges all project on top of each other and only 0(1) type oxygens are observed. The β-BeO structure is closest to exhibiting an ideal t.p. anion array.

In γ-$LiAlO_2$ (6), different cations are present in each edge-sharing pair, i.e., Li and Al, but again all the columns are identical, type A. Thus, in projection, all the shared edges are staggered and all the oxygens in γ-$LiAlO_2$ are of type 0(2).

Correlation of Structural and Conductivity Data

The above structural results show that the α structure with $x = \frac{1}{2}$ is tp and has fully occupied tetrahedral framework sites containing Si, Li, and Li/Al. There is no evidence, from the Rietveld refinement, for any significant occupancy of the channel sites. This correlates well with the results of conductivity measurements (*3*) which show a pronounced minimum, with very low Li^+ ion conductivity, at the $x = \frac{1}{2}$ composition. It also indicates the absence of defects such as Li^+ vacancies/interstitials at $x = \frac{1}{2}$.

The combined structural/conductivity results indicate that the $x = \frac{1}{2}$ composition may well be an "ideal" composition, even though it contains some cation disorder (Li/Al on Li(1*a*) sites). It may be possible to achieve a fully ordered structure, by low temperature annealing, but as yet we have seen no evidence for this.

Conclusions

The crystal structure of α-$Li_{2.5}Al_{0.5}SiO_4$ is related to that of γ-$LiAlO_2$. All the cations are tetrahedrally coordinated in a distorted tetragonal-packed oxygen framework. The distortion from ideal tp is caused by the different sizes of the three cations.

The splitting of the Al sites in γ-$LiAlO_2$ into two sets of sites in α-$Li_{2.5}Al_{0.5}SiO_4$, one containing silicon, the other containing equal amounts of lithium and aluminum, causes a reduction in symmetry from tetragonal to orthorhombic. Lithium is also located on the remaining tetrahedral framework sites, analogous to the lithium sites in γ-$LiAlO_2$. The partial ordering of cations that is found differs from a previously proposed model (*1*). There it was suggested that these two materials may be isostructural, with the Al sites of γ-$LiAlO_2$ occupied by a disordered mixture of (Al + 2Si + Li) in α-$Li_{2.5}Al_{0.5}SiO_4$.

The structural results presented here are consistent with earlier conductivity results which suggested an absence of lithium ion vacancies or interstitials at this composition.

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