Computation of ring statistics for network models of solids

D. S. Franzblau
Department of Mathematics, Vassar College, Poughkeepsie, New York 12601
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In random-network models of amorphous solids, ring statistics provide a measure of medium-range order. However, many criteria used so far to determine the set of rings to count have serious drawbacks. Here, a "shortest-path" (SP) criterion is shown to give ring statistics that agree well with intuition, and to avoid problems inherent in other criteria. The SP criterion arises naturally in a hierarchy of criteria for "irreducible" rings. It falls exactly midway between the least restrictive and most restrictive criteria in the hierarchy, suggesting that it may give the optimal balance between the two extremes. Since SP rings are simple to characterize and enumerate, SP ring statistics appear to be the most promising means for characterizing network topology.

I. INTRODUCTION

Amorphous solids are difficult to characterize, because they have no long-range order. In random-network models, information on the short-range order can be obtained from the distributions of coordination (number of neighbors per atom), bond length, and bond angle, while ring statistics have become the generally accepted measure of medium-range order.[1–8] Ring statistics may also help explain physical properties of the solids represented.[8,9]

A standard method for computing ring statistics is simply to count all possible rings up to some predetermined size.[2,3,5–7] However, each set of intersecting rings combines to form many larger rings. In an early paper, King[10] pointed out that because of these redundant rings, the number of rings per atom increases rapidly with the ring size, making such statistics of little use for characterizing network structure. On the other extreme, if one counts only the shortest rings in the network, many rings that one intuitively would call "primitive," i.e., not composed of smaller rings, are omitted.

Thus, to compute ring statistics that give meaningful information, a central problem is to determine a criterion that includes all such primitive rings, but excludes redundant, or "compound," rings. A natural approach is to introduce some kind of irreducibility test to eliminate rings with "shortcuts" across them. Applying this rule symmetrically to all shortest paths in the ring gives the "shortest-path" (SP) criterion. This criterion was also suggested in Ref. 11.

Here, the SP criterion is shown to yield ring statistics that are exactly what intuition would suggest, in contrast to other definitions that have been used. More formally, the SP criterion is shown to lie in the center of a natural hierarchy of possible irreducibility criteria, which explains why it may be the most appropriate criterion for computing ring statistics.

The remainder of the paper is organized as follows. General terminology is given in Sec. II. SP rings are defined in Sec. III, and examples are given showing that SP ring statistics match what one expects in a reasonable measure of network topology. In Sec. IV a hierarchy of irreducibility criteria is introduced, obtained by systematically weakening a very restrictive but natural criterion, until all rings are included. The SP ring criterion is shown to be in the center of the hierarchy, which explains why it is the one that should give the best results. In Sec. V other criteria that have appeared in the literature are examined, showing that although they may have uses in special cases, they are not useful as general measures of network topology. A practical algorithm for computing SP ring statistics is outlined in Sec. VI. The conclusions are summarized in Sec. VII.

II. TERMINOLOGY

Most of the terms used here are standard in graph theory (see, e.g., Ref. 12). Terms from the noncrystalline-solid literature are included as well.

A *graph* (or *network*) $G=(V,E)$ consists of a set V of vertices and a set E of edges (usually representing atoms and bonds between atoms). Each element of E is an unordered pair $[x,y]$ of distinct vertices in V. If $[x,y]$ is an edge, y is a *neighbor* of x (or is *adjacent* to x) and vice versa.

Given vertices y and z, a *y-z path* length k in G is a chain of k edges joining y to z, in which at most two edges share any vertex, i.e., a subgraph containing distinct vertices $y=x_0,x_1,x_2,\ldots,x_k=z$ and k edges $[x_0,x_1]$, $[x_1,x_2],\ldots,[x_{k-1},x_k]$. One can represent a path simply by listing the sequence of vertices, $x_0x_1x_2\cdots x_k$.

A *ring* of length k is a closed loop with k edges, a path of length k except that the path returns to its starting point $(x_0=x_k)$. At most one edge per vertex pair is allowed in the definition of a graph, so the smallest possible ring is of length 3.

The *distance* between vertices y and z, $\mathrm{dist}(y,z)$ is the minimum k such that there is a *y-z* path of length k in G. When emphasizing that distance depends on the graph G, one writes $\mathrm{dist}_G(y,z)$. A shortest *y-z* path is one of length $\mathrm{dist}(y,z)$.

The *diameter* of a graph is the maximum distance between any pair of vertices. The diameter of a ring of length k is $k/2$ if k is even, and $(k-1)/2$ if k is odd.

If P is a y-z path in a ring R, let Q be the y-z path obtained by deleting all vertices and edges of P, except y, z, from R. Then Q is the *complementary path* for P. In other words, $P \cup Q = R$ and $P \cap Q = \{y,z\}$.

III. SP RINGS AND STATISTICS

There is no general theory that explains which rings are relevant to the physical properties of the solid represented. Because of the complicated geometry of three-dimensional networks, there is also no obvious characterization of what are called here "primitive" rings, those which cannot be decomposed into smaller rings. However, at least for simple examples, there is not much controversy about which rings should be called primitive. For example, in the graph of Fig. 1, one clearly would count rings *abcfea*, *bdfcb*, and *dgfd* as primitive. One would not count *abdgfea*, because the path *dgf* has a shortcut (*df*).

The goal of this paper is to show that a definition based on the shortest-path (SP) criterion is the only one out of many possible definitions that captures the intuitive concept of a primitive ring, and has desirable formal properties. The same criterion was proposed independently in a recent article,[11] and applied to various crystalline forms of SiO_2. The present work shows explicitly why the criterion is the best available, and gives a simple algorithm to implement it.

The definition, which is given below, is first motivated by the simple example in Fig. 1. It is then shown to give desirable results on a variety of networks. In Sec. IV the definition is shown to arise naturally from a hierarchy of irreducibility criteria. The analysis there provides evidence that the criterion is "optimal" in a certain formal sense.

The purpose of the SP criterion is to include only rings which have no shortcuts (paths which shorten the ring). Notice that each pair of vertices in a ring divides the ring into two complementary paths. For example, in Fig. 1, vertices b and f divide the ring *abdfea* into paths *bdf* and *feab*. In the example of Fig. 1, if one counts only the rings with no shortcut of *any* of these paths, one ends up with only the ring *dgfd*, excluding too many rings. The SP criterion allows only rings having no shortcut of any *shortest* path on the ring. This leads to the following.

Definition. Given a graph G and a ring R in G, R is a *shortest-path ring* (SP *ring*) if R contains a shortest path for each pair of vertices in the ring. That is, $\mathrm{dist}_G(y,z)=\mathrm{dist}_R(y,z)$ for each pair y,z in the ring.

Under this definition, four of the six possible rings in Fig. 1 are SP rings. The rings *abdgfea* and *bdgfcb* are not SP rings because the distance between d and f is one, rather than two. (Although it may not be obvious that one would want to include *abdfea*, it is essentially equivalent to *abcfea*.)

To illustrate that SP-ring statistics correspond to intuition, it is useful first to consider simple, well-known graphs. In the 2D square lattice, the only SP rings are the squares of length 4 (one per atom). In the 3D cubic lattice, the only SP rings are cube faces of length 3 (three per atom), and "chairs" of length 6 (four per atom). (See Fig. 2.) In the diamond lattice, there are two SP rings per atom of length 6, but no others. (Note that each ring is counted only once. If one counted a ring once for each atom on the ring, one would get four rings per atom in the square lattice and 24 chairs per atom in the cubic lattice.)

In all these examples, the SP-ring statistics turn out to be exactly what one would expect of a good measure. Although these results may appear trivial, we show in Secs. IV and V that many other possible criteria give counterintuitive results even for these simple networks.

Since a primary object of computing ring statistics is to capture order in *amorphous* structures, SP-ring statistics were computed for a random network modeling amorphous silicon. This model, which has been studied extensively, was obtained from a diamond lattice by a "bond-switching" algorithm.[13] The results, shown in Fig. 3, are remarkably close to what one would desire in a reasonable measure of medium-range order. The diamond lattice has two SP rings of size 6 per atom; in the amorphous Si network the total number of SP rings per atom

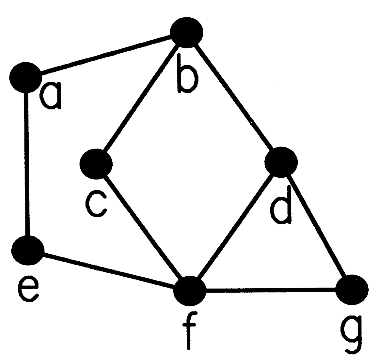

FIG. 1. Graph with seven vertices, labeled a–g, used to illustrate ring criteria. The SP rings are *abcfea*, *abdfea*, *bdfcb*, and *dgfd*.

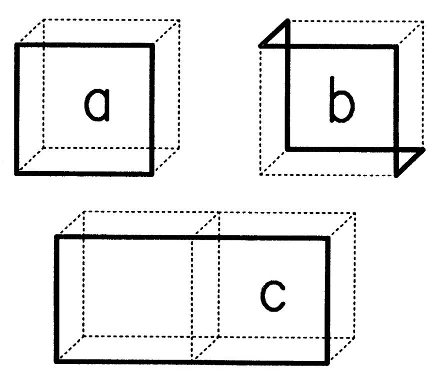

FIG. 2. Rings in the cubic lattice. The only SP rings are the length-4 square, formed by the heavy lines in (a), and the length-6 chair, formed by the heavy lines in (b). The length-6 ring shown in (c) is a K ring but not a SP ring.

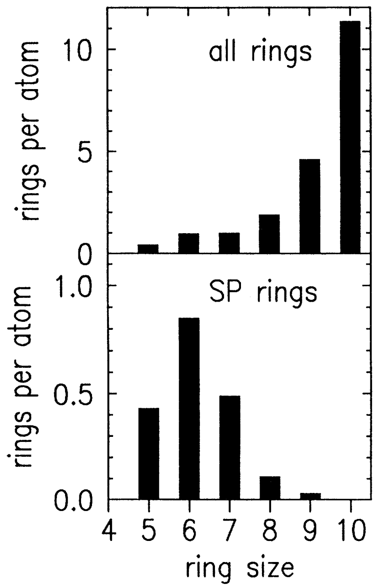

FIG. 3. Ring statistics (rings per atom vs ring length) for the amorphous Si network of Ref. 13. Statistics for all rings (top) are contrasted with SP ring statistics (bottom). Note the very different vertical scales.

is 1.9, with a peak at size 6, but a broader distribution of ring sizes: There are substantial numbers of rings of sizes 5 and 7, no rings smaller than length 5, and no rings larger than length 9 (verified up to length 20).

By contrast, if one counts *all* rings in the same amorphous Si network, the number of rings per atom grows rapidly with ring size, as shown in Fig. 3. Clearly, such a count yields little useful information.

IV. A HIERARCHY OF IRREDUCIBLE RING CRITERIA

In order to determine whether there are other definitions which give good results, it is worth searching systematically for irreducibility criteria. A natural approach is to generalize the concept of a ring with no shortcut, described as follows.

Definition. Given a ring R and a path P contained in R, R is P *irreducible* if R is a shortest ring containing P (no shorter ring contains P).

Definition. Given a non-negative integer m-, R is m *irreducible* if R is P irreducible for every path P in R of length m.

For example, in Fig. 1, *abdfea* is 3 irreducible; it is not 2 irreducible because the length-2 path *bdf* is contained in a ring of length 4. The ring *dgfd* is the only 0-irreducible ring.

In general, a 0-irreducible ring R is "vertex minimal": For each vertex v, R is the shortest ring containing v. A 1-irreducible ring R is "edge minimal": For each edge e, R is the shortest ring containing e.

If $\lambda=\lambda(R)$ is the length of ring R, and $m \geq \lambda-1$, then R is m irreducible, since any path of length $\lambda-1$ already contains all the distinct vertices of R. Thus, the set of $(\lambda-1)$-irreducible rings is the set of all rings.

Thus, if one treats m as a function of the ring R, and allows m to range between 0 and $\lambda(R)-1$, one obtains a hierarchy of classes of irreducible rings, starting with a very restricted set of rings and ending with all rings. Note that if R is m irreducible, then R is $(m+1)$ irreducible, since any path of length $m+1$ contains at least one path of length m.

The following notation will be used in showing that SP rings occupy an interesting position in this hierarchy. Let d denote the diameter of the ring R, and let $d^*=d$ if λ is even, and $d^*=d+1$ if λ is odd. Then, if P is a path of length d, the complementary path has length d^*. SP rings are characterized precisely within the hierarchy by the following theorem, which is proved in the Appendix.

SP-ring theorem. R is an SP ring if and only if R is d^* irreducible.

The SP ring theorem shows that SP rings are exactly in the center of the hierarchy. In order to determine whether the criterion is indeed "optimal," let us study the result of strengthening the criterion slightly, then of weakening it slightly.

Intuitively, each vertex v in some ring should also be in a primitive ring. For example, the shortest ring containing v is in fact a SP ring (the proof is similar to that of the SP ring theorem). To study the effect of strengthening the SP criterion, consider the set of (d^*-1)-irreducible rings. In Fig. 1, *dgfd* is the *only* such ring; for example, the ring *abcfea* (length 5, $d^*=3$) is not 2 irreducible, since the path *bcf* is contained in a smaller ring. In general, this means that there will exist primitive rings that are not (d^*-1) irreducible. Thus, the SP criterion includes at least one primitive ring for each vertex, but all stronger criteria in the hierarchy will, in general, exclude primitive rings.

To see the effect of weakening the criterion, now consider (d^*+1)-irreducible rings. In the square lattice, recall that the SP rings (d^*-irreducible rings) are the squares of length 4. The (d^*+1)-irreducible rings also include squares of length 8. Thus, in general, relaxing the SP criterion leads to rings one would regard as compound rather than primitive. In this sense, SP rings are exactly at the threshold-separating criteria that are clearly too restrictive from those that are clearly too inclusive.

V. OTHER RING DEFINITIONS

There have been few other irreducibility criteria in the published literature on ring statistics. Possibly the first clearly stated criterion to appear was that of King,[10] which is called the "K-ring" criterion here. The criterion, which is stated in the following definition, is equivalent to requiring that R be P irreducible for a *specified* path $P=wxy$.

Definition. Given a vertex x and two of its neighbors w and y, a *K-ring generated by wxy* is any ring containing edges $[w,x],[x,y]$ and a shortest w-y path in $G-x$. (If x is a vertex in G, $G-x$ is the graph obtained by deleting x from V and all edges containing x from E.)

In Fig. 1, *cbd* generates the *K*-ring *cbdfc*, and *gfe* generates *gfeabdg*. (Note that although there are two possible *K*-rings of length 5 generated by *eab*, only one would be counted in Ref. 10, since the focus there was on ring length rather than number of rings.)

The criterion may work well when applied to the network for which it was proposed (SiO_2), because all pairs of neighbors have the same angle between them. However, the *K*-ring criterion does not in general admit only the primitive rings. For example, in the square lattice, each pair of neighboring edges with an angle of 180° yields two *K*-rings of length 6, formed from two rings of length 4 sharing one edge. These certainly should not be called primitive. In the cubic lattice, each such pair generates four *K* rings of length 6 of this type [Fig. 2(c)], but no pair of edges generates a length-6 chair [Fig. 2(b)], which should be counted as a primitive ring.

A notable feature of King's criterion is that it is not symmetric; i.e., the definition depends on the origin of the ring. (This may be because the motivating problem was only to count the proportion of rings of each size *containing* a given atom.) However, it makes sense to avoid nonsymmetric definitions because they introduce an ambiguity when one tries to compute the number of rings per atom: Should one count each ring exactly once, no matter how many origins generate it, or should one count a ring each time it is generated? Since a *K*-ring can be generated by any number of origins (between 1 and the ring length), the choice can have a significant effect on the statistics. (Note that if one makes the definition symmetric by requiring the criterion to hold for each path of length 2, the 2-irreducible rings are obtained, which is too restrictive a class).

There is also a ring definition which is often used in the study of two-dimensional networks, but which appears to be irrelevant in three dimensions. A network which is embedded in the plane with straight-line edges and no crossings (a planar graph) can be regarded as a partition of a plane region into polygons; in this case, a set of natural "irreducible" rings is the set of boundaries of the polygons (the faces of the planar graph). In Fig. 1, these boundaries are *abcfea*, *bdfcb*, and *dgfd*. Note that the set of faces depends on the particular embedding as well as the topology. This definition could be generalized for networks that partition a 3D region into polyhedra (e.g., the cubic lattice), but not for arbitrary 3D networks.

VI. COUNTING SP RINGS EFFICIENTLY

A. Outline of basic strategy

Given a finite graph, a simple strategy for enumerating all SP rings up to a given length m is the following.

(1) Select an (arbitrary) vertex z.

(2) Generate each ring containing z, of length at most m, and test whether it is a SP ring (if so record its size).

(3) Delete z from the graph. (Form $G-z$.)

(4) Repeat $1-3$ until all vertices are deleted from graph.

Without step 3, each ring of length k would be enumerated k times. It is possible to remove this inefficiency only because the definition of SP ring is independent of the origin z.

Section VI B gives an efficient method for generating candidate rings. Section VI C presents a test for the shortest-path property which can be performed in time $O(k)$ on a ring of length k.

It is easy to modify the scheme to compute the number of rings per atom for an infinite but periodic graph with a specified unit cell (such as any of the networks studied in Sec. III). It suffices to enumerate all SP rings containing at least one vertex in the unit cell, since the number of rings divided by the number of atoms in the cell is the same for any cell. However, some caveats are given at the end of Sec. VI B.

B. Generating candidate rings

There is a standard method for generating all rings containing z, called *backtracking*.[14] If vertices are linearly ordered, then rings are examined in lexicographic order. One keeps a current path stored on a stack (last in, first out); if the current end point is x, then at each step one either finds an edge $[x,z]$ to close a ring, extends the path with a new edge $[x,y]$, or, if all neighbors of x have been explored, discards x from the stack (backtracks).

Since the number of rings can grow exponentially with the number of vertices, even in graphs of small degree, one would like to restrict the search to promising candidates only. SP rings satisfy a "unimodal labeling" property, described below, which makes this feasible.

Given vertex z and a SP ring R containing z, label each vertex u in R with $\text{dist}(z,u)$. If the labels are listed in the order encountered starting at z, the sequence must be *unimodal,* i.e., either $012\cdots(k-1)k(k-1)\cdots210$ (for an even ring) or $012\cdots(k-1)kk(k-1)\cdots210$ (for an odd ring). In Fig. 1, the SP ring *abdfea* has labels 012210; *bdfcb* has labels 01210. The ring *dgfcbd* has labels 011210, and hence is not an SP ring. Thus, when implementing the backtracking scheme, one need only consider a new vertex if adding it to the current path maintains the unimodal labeling.

Given a vertex z, one can compute $\text{dist}(z,u)$ for all u by labeling vertices in order of their distance from z, starting with the neighbors, then neighbors of neighbors, and so on, i.e., performing a *breadth-first search* from z.[15] If the average number of neighbors per atom (the "average degree") is δ, the time required is proportional to the number of edges, $\delta n/2$, where n is the number of vertices. If the graph is small enough, one can precompute a look-up table containing the distance between each pair of vertices in this way. A table of size n^2 can be generated in $O(n^2)$ steps for bounded δ.

Even if one modifies the backtracking strategy with the heuristic above, one will still enumerate each SP ring containing z twice. If necessary, one can avoid this using a simple strategy. For each neighbor y of z, after all the SP rings containing the edge $[z,y]$ have been enumerated, omit this edge from the graph during further enumeration. When z has exactly one neighbor remaining, each SP ring containing z has been enumerated once.

Care is needed when counting rings in an infinite periodic graph. A small piece of such a graph is illustrat-

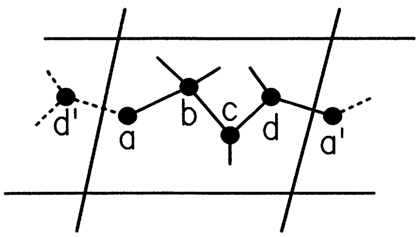

FIG. 4. Piece of an infinite periodic network, with a unit cell represented by the parallelogram. If the network is represented by a finite graph in which $a=a'$ and $d=d'$, the path *abcda'* becomes a ring, so care must be taken in counting rings.

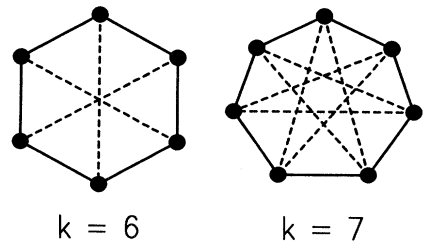

FIG. 5. Antipodal pairs shown joined by dashed lines. The ring length is k; if $k=6$, there are $k/2=3$ pairs; if $k=7$, there are $k=7$ pairs. If the true distance between each pair of antipodes is the ring diameter, then the ring is an SP ring.

ed in Fig. 4. A standard representation is obtained by imposing periodic boundary conditions on the finite graph determined by an arbitrary unit cell. (The parallel sides of the cell are "identified," yielding an embedding of the graph in a three-dimensional "torus.") In the graph of Fig. 4, this means that vertices a' and a are considered equivalent, as are vertices d' and d and edges $[d',a]$, and $[d,a']$. Notice that in the finite representation *abcda* is a ring; however, this is *not* a ring in the infinite graph. If the maximum ring size is larger than the "diameter" of the cell, many such spurious rings will be counted. One way to avoid this problem is to store the coordinates of each vertex as rings are generated. Another solution, which allows one to save time by precomputing the distance table, is simply to increase the size of the finite graph sufficiently, by replicating the unit cell.

C. An efficient test for SP rings

Although there are $k(k-1)/2$ pairs of vertices on a ring of length k, it is sufficient to check only pairs of *antipodes,* vertices whose distance in R is the diameter of R. (Antipodal pairs are illustrated in Fig. 5.) It is not hard to show that if $\text{dist}_R(x,y)=\text{dist}_G(x,y)$ for every pair of antipodes x,y, then R is an SP ring; i.e., $\text{dist}_R(u,v)=\text{dist}_G(u,v)$ for *every* pair u,v. The test requires only $O(k)$ distance checks, since there are $k/2$ antipodal pairs if k is even, and k pairs if k is odd.

If distance labels are maintained as described in Sec. VI B, when the distance labels have stopped increasing, the test can be performed for the antipode(s) of each new vertex just before it is added to the current ring. This allows one to discard candidates more efficiently than testing all antipodes after each ring is completed.

VII. CONCLUSION

By excluding rings which contain shortcuts, one arrives naturally at the shortest-path criterion. Not only does the criterion produce the ring statistics that one would want intuitively, but within a natural hierarchy of irreducibility criteria, it lies on the threshold between definitions which are too restrictive and those that are too inclusive. Since the criterion is independent of the origin of the ring there is no ambiguity in counting SP rings. Moreover, their statistics can be computed easily. Thus, at present, SP ring statistics are the most natural general measure of medium-range order.

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APPENDIX: PROOF OF THE SP RING THEOREM (SEC. IV)

First, assume R is an SP ring. Let P^* be any path in R of length $\lambda(P^*)=d^*$, and let P be the complementary path, with u,v as their common end points. Observe that the length of P is d. Given any ring R' containing P^*, let Q be the complementary path of P^* in R'. Since R is an SP ring, P must be a shortest u-v path; hence $\lambda(Q)\geq\lambda(P)$, which implies $\lambda(R')\geq\lambda(R)$. Since P^* and R' were arbitrary, R is d^* irreducible.

Now assume that R is d^* irreducible. Let u and v be any distinct vertices on R; we want to show that R contains a shortest u-v path, i.e., $\text{dist}_R(u,v)\leq\text{dist}_G(u,v)$. Let Q be any shortest u-v path. Let $u=x_0,x_1,\ldots,x_j=v$ $(j\geq 1)$ be all the vertices contained in both Q and R, in the order they appear in Q. Let Q_i be the segment of Q which contains $\{x_i,x_{i+1}\}$, and let R_i be the shortest segment in R containing $\{x_i,x_{i+1}\}$.

By the definition of the x_i, Q_i and R intersect only at x_i and x_{i+1}; thus, if R_i^* is the complementary path for R_i, $R_i^*\cup Q_i$ is a ring. Al$_s\sigma$, the length of R_i^* is at least d^*. R is d^* irreducible, so the length of Q_i is at least the length of R_i. The sum of the lengths of the R_i is at least $\text{dist}_R(u,v)$. However, since Q is a shortest u-v path, the sum of the lengths of the Q_i is $\text{dist}_G(u,v)$. Hence, $\text{dist}_R(u,v)\leq\text{dist}_G(u,v)$ as desired.

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