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Silver coordination hypotheses and structural model in the glassy semiconductor $Ag_{0.04}As_{0.38}Se_{0.58}$ by X-ray diffraction

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Abstract

The radial atomic distribution was studied in the amorphous alloy $Ag_{0.04}As_{0.38}Se_{0.58}$, using X-ray diffraction data of samples obtained by quenching of the molten material. The short-range order proposed was determined through the interpretation of the radial distribution function, using a theoretical expression which takes into account the variation in the atomic scattering factors with s (the scattering vector module), and approximating them to polynomic functions. The existence of tetra- and three-coordinated silver atoms, suggested in the literature for glassy alloys containing this element, was found to be compatible with the experimentally obtained structural information. A spatial atomic distribution model was generated, using the conveniently modified Monte Carlo random method. The model obtained exhibits tetrahedral units on silver and arsenic atoms, forming a compact network. A comparative analysis of the parameters of this model showed good agreement with the values given in the literature for similar alloys.

1. Introduction

The study of the structure, properties and behaviour of non-crystalline solids is relatively new, although man has been using them since ancient times and, in some cases, in large quantities. Solid state and crystallinity were traditionally treated as synonyms in texts on condensed matter, but since the sixties one of the most active research fields in solid state physics has been the study of non-crystalline materials, in which the atomic distribution has no trace of long-range order. These solids do, however, have short-range order in their bonds with first neighbours, up to a few atomic diameters, showing a characteristic spectrum in the diffraction diagram. An understanding of the spatial atomic distribution and establishment of the short-range order structure of a material are of great interest when trying to explain its macroscopic properties.

The change from the amorphous to the crystalline phase means a release of energy, but in order for this to happen an energy barrier (activation energy) must be overcome; when this is high enough, compared to the thermal agitation energy, the non-crystalline solid is stable and can maintain its properties at room temperature for thousands of years [1]. In the case of chalcogenides with polivalent elements, stability is due precisely to the presence of this type of element, which modifies the properties because of the formation of tridimensional structural units. The polivalent atoms which stabilize the structures of the chalcogenides are mainly arsenic and germanium, as they form spatial units with chalcogens, breaking their complex structural formation and contributing to the establishment of more homogeneous structures for the alloys belonging to this kind of system, a fact which can explain some of their properties.

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This work analyzes the local order of the semiconducting glassy alloy $Ag_{0.04}As_{0.38}Se_{0.58}$, from data obtained from the radial distribution function (RDF) determined from X-ray diffraction intensities. The experimental value of the area under the first RDF peak was compared to that obtained theoretically [2–4] as a coordination function of silver and taking into account that the functions $R_{ij}(s)=f_i(s)f_j(s)/[\Sigma_i x_i f_i(s)]^2$ depend on the scattering angle [5] and cannot always be approximated by a constant value $Z_iZ_j/(\Sigma_i x_i Z_i)^2$. Based on the above analysis and on the geometrical restrictions imposed by the experimental RDF, a spatial atomic distribution model was generated, using the Monte Carlo random method. An analysis of the parameters of the model (coordinations, bond lengths and angles) shows good agreement with the values quoted in the literature for similar alloys.

2. Experimental details

The bulk samples of the glassy alloy $Ag_{0.04}As_{0.38}Se_{0.58}$ were prepared from commercial 99.999% pure Ag, As and Se, which were pulverized to a grain size of less than 40 μm, and weighted to obtain 7 g of the compound. The material was homogeneously mixed and put into quartz tubes which were submitted to an iterative process of filling and emptying with inert gas (He) to avoid possible oxidation of the samples. The capsules were sealed with an oxyacetylene burner, while the residual pressure was less than 10^{-3} torr. The resulting ampoules were kept at 800°C for 7 days in a rotary furnace, rotating at 1/3 rpm, and then quenched in ice water, which supplied the necessary cooling rate for obtaining the glass. The density of the material was determined from pieces of adequate size, using a pycnometric method at a constant temperature. The average value obtained from series of measurements carried out was 4.87 g cm^{-3}, with a relative error of less than 3%.

Part of the alloy was pulverized to a particle size of less than 40 μm and pressed into $20\times20\times1$ mm^3 bricks. The absence of crystalline peaks was checked by X-ray diffraction, confirming the glassy nature of the solid. The intensities of the radiation diffracted by the sample were measured in an automatic Siemens D500 powder diffractometer, equipped with a bent graphite monochromator and a scintillation detector. Mo Kα radiation was used ($\lambda=0.71069$ Å). Four series of measurements were done in the $5°\leqslant2\Theta\leqslant110°$ range, two for increasing and two for decreasing scattering angles, using an angular interval of 0.2° in the 5–70° scan and of 0.5° in the 70–110° scan. These measurements were done fixing the number of counts at 4000, and digitally registering the time it took to detect them. The average value of the four measurements was taken as the radiation intensity at each observation point.

3. Obtaining the radial distribution function. Local order hypotheses

The observed intensities were corrected, as usual, for background, polarization, absorption and multiple scattering [6], in order to eliminate the portion of radiation which does not carry structural information. The correction of incoherent intensities and the determination of the interference function make it necessary to express the experimental intensities in electronic units (eu), as the atomic factors and Compton intensities are tabulated in these units. The normalization to electronic units was done using the high angle technique [6], and the normalized intensities were corrected for the Compton component, obtaining the spectrum of coherent intensities $I_{eu}(s)$ used to determine the interference function

$$F(s)=si(s)=s\,\frac{I_{eu}(s)-\Sigma_i x_i f_i^2(s)}{[\Sigma_i x_i f_i(s)]^2}\,, \qquad (1)$$

where x_i and $f_i(s)$ are the atomic fraction and the scattering atomic factor of element i in the alloy. The function $F(s)$ was extended up to $s_{max}=30$ Å^{-1}, in order to avoid the spurious oscillations which appear in the RDF when small values of r are considered, due to the lack of experimental data for high values of s. The extension was done using the method described by D'Anjou and Sanz [7], based on the one proposed by Shevchik [8]. A Fourier transformation was applied to the extended interference function, obtaining the radial distribution function

$$4\pi r^2\rho(r)=4\pi r^2\rho_0+rG(r)\,, \qquad (2)$$

where ρ_0 is the average experimentally measured density of the material, $\rho(r)$ represents the local atomic

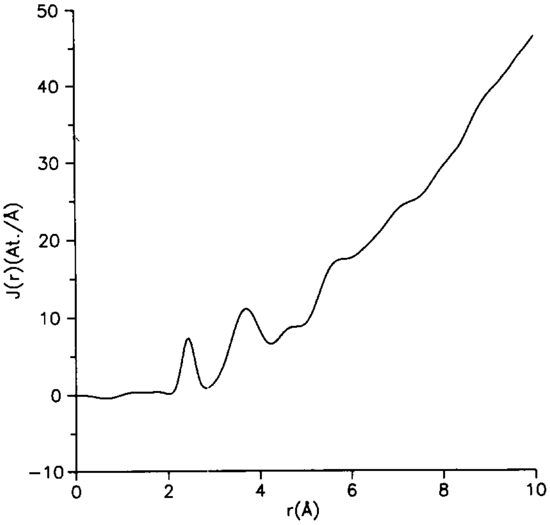

Fig. 1. Radial distribution function.

density affected by the Fourier transformation of products $R_{ij}(s)$, and the function $G(r)$ is given by

$$G(r)=\frac{2}{\pi}\int_{0}^{s_{\max}} F(s)\,\sin(sr)\,\mathrm{d}s\,. \tag{3}$$

The experimental RDF, shown in Fig. 1, supplied the structural information shown in Table 1. The interval defined by the first RDF peak, corresponding to the distances between first neighbours, is such that bonds are possible between all pairs of elements in the material.

A parameter of great interest, when postulating short-range models of a glassy solid, is the area enclosed under the first RDF peak, as it represents the average coordination number of the material. Bearing in mind the physical meaning of this area, and the fact that the products $R_{ij}(s)$ are functions of the scattering angle, Vázquez and Sanz [5], following the method described by Warren [6], deduced that the area under the first RDF peak is related to certain structural parameters, the relative coordination numbers n_{ij}, through the expression

$$\text{Area}=\frac{2}{\pi}\sum_{i}\sum_{j}x_i\frac{n_{ij}}{r_{ij}}\int_{a}^{b} rP_{ij}(r)\,\mathrm{d}r\,, \tag{4}$$

where r_{ij} is the average distance between an i-type atom and a j-type atom, a and b are the limits of the first RDF peak, and $P_{ij}(r)$ is a function defined by

$$P_{ij}(r)=\frac{1}{2}\int_{0}^{s_{\mathrm{m}}} R_{ij}(s)\,\cos[s(r-r_{ij})]\,\mathrm{d}s\,, \tag{5}$$

where s_{m} is the upper limit of the measurement.

The structural information obtained by analyzing the experimental RDF, together with the physical–chemical properties of the alloys and of their constituent elements, make it possible to postulate the nature of the local order of the glassy materials. These hypotheses, which are reflected in the relative coordination numbers and, therefore, in the number of chemical bonds between the different pairs of elements in the material, have made it possible for Vázquez et al. [4] to deduce the following relation from Eq. (4):

$$\text{Area}=\frac{1}{50\pi}\Bigg[(h+\beta A_{22}-\delta Q)N+\alpha A_{22}+\gamma Q+P\Bigg(\sum_{i=j\neq 1}A_{ij}-\sum_{\substack{i,j\neq 1\\ i\neq j}}A_{ij}\Bigg)a_{ij}\Bigg]\,, \tag{6}$$

where h, α, β, γ and δ are parameters that depend on the alloy and on the coordination hypotheses, N is the coordination attributed to a certain element in the material, P is a parameter equal to 2 when, in the variable a_{ij}, $i=j$ and equal to -1 if $i\neq j$, and A_{ij} is determined by:

$$A_{ij}=\frac{1}{r_{ij}}\int_{a}^{b} rP_{ij}(r)\,\mathrm{d}r\,, \tag{7}$$

being

Table 1
RDF characteristics

	Maximum	
	1	2
position (Å)	2.43	3.70
limits (Å)	2.01–2.81	2.81–4.24
averaged angle (deg)	99.16	
area (atoms)	2.60	7.91
error	±0.1	±0.2

Table 2
Bond lengths and A_{ij} parameters

Pair	r_{ij} (Å)	Ref.	A_{ij}
1–1	2.68	[9]	2.9856
1–2	2.55	[10]	2.2810
1–3	2.50	[9]	2.3198
2–2	2.49	[11]	1.4744
2–3	2.38	[9]	1.5164
3–3	2.34	[9]	1.5673

$$Q=\delta_{ij}\sum_{\substack{i,\,j\neq 1\\ i\neq j}} A_{ij}+(1-\delta_{ij})\sum_{i=j\neq 1} A_{ij}$$

(δ_{ij} = Kronecker's delta).

This work evaluates parameters A_{ij} by adjusting functions $R_{ij}(s)$ by the corresponding straight regression lines, thus obtaining the values shown in Table 2, which were calculated through the method described by Vázquez and Sanz [5]. The distances between the different pairs used are also shown in Table 2, together with the corresponding references.

In order to express the area under the first RDF peak as a function of the coordination N, assigned to the silver atoms in this alloy, the characteristic parameters ($h=12.3192$, $Q=3.0328$), and those depending on the coordination hypotheses, were calculated [4]: $\alpha=-1.17$, $\beta=-0.83$, $\gamma=113.58$, $\delta=-2.42$ for $N=3$ and $N=4$. From these data, the tabulated A_{ij} and using Eq. (6), the following expressions were obtained:

$$\text{Area}=2.5338+1.1\times10^{-4}a_{33}\,,\quad \text{for } N=3\,;$$

$$\text{Area}=2.6511+1.1\times10^{-4}a_{33}\,,\quad \text{for } N=4\,,\qquad (8)$$

and used for postulating the short-range order of the alloy. These relations may be observed to be functions of the number of Se–Se bonds, a_{33}, a fact which makes it possible to limit the variability of the theoretical area.

In order to generate a local order model of the alloy $Ag_{0.04}As_{0.38}Se_{0.58}$, it is necessary to establish the average coordinations of its constituent elements, which implies attributing a certain coordination to the silver. This is a relatively complicated question, as there is not just one coordination hypothesis in the literature for this element in other compounds. Whereas some authors [12–14] propose tetrahedral coordination for silver in ternary alloys with chalcogens, others [15,16] attribute three-coordination to the silver in these types of compounds, so both hypotheses must be considered.

Bearing in mind that relationship (8) for each value of N varies linearly with the number of Se–Se bonds, and that the relative coordination numbers n_{22} and n_{23} also depend on N, it is possible to obtain, according to the literature [17], an adequate coordination of silver, by determining the variation interval for a_{33} in which the relative coordination numbers are positive and, at the same time, the theoretically obtained area within the margin of error of the experimental area. Table 3 shows the expressions for n_{ij}, $i, j\neq 1$, as functions of a_{33} for the tetra- and tri-coordinated silver hypotheses, as well as variation intervals for the number of Se–Se bonds defined by positive nature of the n_{ij} and by the margin of error of ±0.1 atoms in the experimental area, together with the intersection of these intervals.

In order to illustrate our calculations, Fig. 2 shows the theoretically calculated areas versus the number of Se–Se bonds for the two valid silver coordination hypotheses in $Ag_{0.04}As_{0.38}Se_{0.58}$. This figure shows the variation intervals of a_{33} in which the theoretical areas are simultaneously compatible with the experimental area and with the corresponding coordination numbers.

Table 3
Theoretical results obtained for the coordination hypotheses of the silver atom

N	Coordination numbers n_{ij}, $i,j\neq 1$	Variation intervals for parameters a_{33}		Intersection of intervals
		defined by the n_{ij} parameters	defined by limits of error of the experimental area	
3	$n_{22}=(-19/15+2a_{33})/38$ $n_{23}=(34162/300-2a_{33})/38$	$0.63\leqslant a_{33}\leqslant 56.94$	$0\leqslant a_{33}\leqslant 1510.9$	$0.63\leqslant a_{33}\leqslant 56.94$
4	$n_{22}=(-13/10+2a_{33})/38$ $n_{23}=(11397/100-2a_{33})/38$	$0.65\leqslant a_{33}\leqslant 56.99$	$0\leqslant a_{33}\leqslant 444.55$	$0.65\leqslant a_{33}\leqslant 56.99$

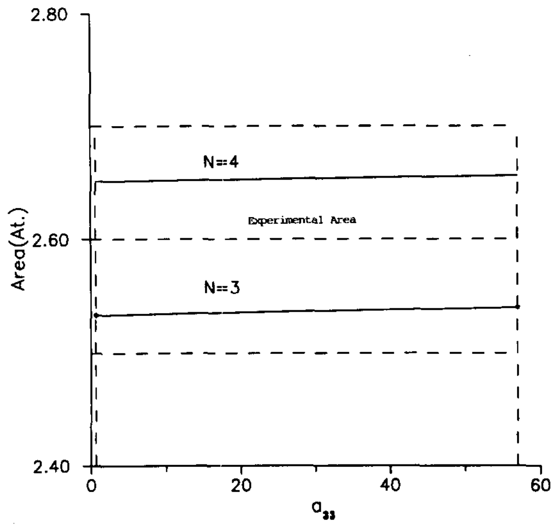

Fig. 2. Areas of the first peak plotted against the number of Se–Se bond.

An analysis of the interval intersections leads to the conclusion that in this alloy, the tetra- and tri-coordinated silver hypotheses are compatible with the structural information obtained from the experimental data. Therefore, the most probable short-range order may be described as a three-dimensional network of covalent bonds, arranged tetrahedrally and three-fold coordinated around silver and arsenic atoms.

4. Generation and analysis of a structural model

The basic aim of determining the structure of glassy solids is to build spatial atomic distribution models which verify the experimentally obtained structural information and, at the same time, agree with the physical–chemical properties of the materials. This model was generated using a variation of the Monte Carlo method, similar to the procedure followed by Rechtin et al. [18] and described at length by Vázquez et al. [19], which seems to be the most adequate for describing the short-range order of a glassy material obtained through quenching. The variations of this procedure refer to the geometrical and coordination conditions imposed by the experimental RDF, which imply a certain semi-randomness in the building of the atomic configuration.

The mathematical space considered suitable for generating the possible structural model of the alloy $Ag_{0.04}As_{0.38}Se_{0.58}$ is the volume limited by a 10 Å radius spherical surface, which is large enough to statistically represent the sample, and small enough not to require too much calculation time. The number of atoms which, according to the experimental density, can be located in this volume is 156, distributed as follows: 6 silver atoms, 59 arsenic atoms and 91 selenium atoms.

The atomic positions were generated by finding their Cartesian coordinates from three random numbers [19] and bearing in mind all the geometrical and coordination conditions deduced from the analysis of the experimental RDF, and which in this case are the following:

(i) The distance between first neighbours must be within the interval defined by the first experimental RDF peak.

(ii) The bond angle between an atom and two of its first neighbours may vary between 60° and 180°, as may be deduced [20] from the extreme radii of the first two coordination spheres represented by the limits of the first two RDF peaks.

(iii) The coordination attributed to each element must be such that the average coordination of the model agrees with the experimentally obtained coordination.

Considering the aforementioned geometrical and coordination conditions, 250 positions were generated and reduced to 156, the number predicted from the experimental density, by eliminating those with the lowest coordination. The next step was to assign the atoms to their positions, placing the silver atoms in the positions with maximum coordination, the other elements being randomly placed in the rest. The reduced RDF of the initial configuration $rG_{\text{mod}}(r)$, was determined, simulating a diffraction process in the configuration. This function was compared to the $rG_{\text{exp}}(r)$ multiplied by the expression proposed by Mason [21], and the two RDFs were compared by mean-square deviation, used as a criterion for deciding on the validity of the generated configuration. The initial model was considered to be suitable for obtaining a relatively speedy adjustament of the theoretical and experimental RDFs; so the positions were refined by successive atom movements of arbitrary amplitude P and in random directions. During the position refining process, the model evolved as shown in Table 4 where the mean-square deviation refers to the last movement in each interval. The position refining process was considered

Table 4
Position refining process

P (Å)	Movement intervals	Squared deviation (Å)
0.5	1–271	0.0319
0.3	272–307	0.0206
0.1	308–358	0.0167

finished when the number of rejected movements became too high and the mean-square deviation did not significantly improve. Fig. 3 shows the experimental reduced RDF and the model RDF, after the process of refining the positions and the thermal factors was completed.

Fig. 4 is a spatial representation of the generated atomic configuration, in which one may observe tetrahedrons centered on silver atoms which coexist with other tetrahedrons centered on those arsenic atoms whose coordination has increased to four. Both structural units are interlinked, forming a network which constitutes the possible structure of the alloy.

Dangling bonds are observed in this spatial distribution, as is frequent in amorphous materials. Many of these dangling bonds belong to atoms which are less than a first neighbour's distance away from the surface of the sphere, and may be saturated with atoms situated outside it. In the case of elements with two or more dangling bonds, they may be due to the finite size of the model, when the atom in question is less than 1.1 Å away from the surface limiting the configuration. This possibility takes into account both the distance between first neighbours and the average bond angle. 14% of dangling bonds observed in the model belong to atoms which are not in a position allowing them to be saturated with possible external neighbours. However, the existence of dangling bonds is a consequence inherent to the preparation of chalcogenide glasses.

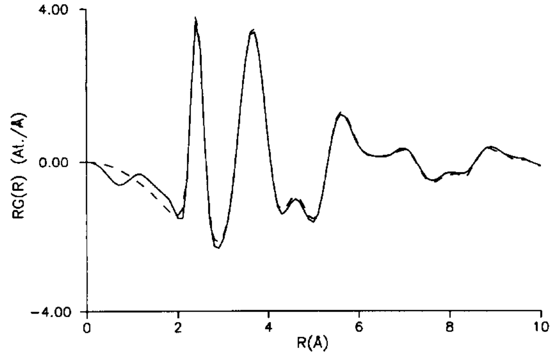

Fig. 3. Representation of (- - -) calculated and (—) experimental RDFs.

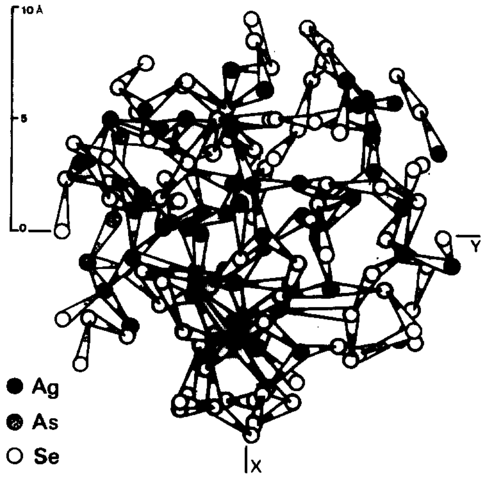

Fig. 4. Spatial representation of the model of the $Ag_{0.04}As_{0.38}Se_{0.58}$ alloy.

One way of estimating the concordance between the generated atomic configuration and the actual structure of the alloy under study, is by analysing the structural parameters (bond lengths and angles) obtained from the model, and relating their values to those quoted in the literature for similar compounds. Table 5 shows the average bond lengths between the different pairs of elements. The values calculated for the bond lengths may be observed to agree very acceptably with the bibiographical data.

Another interesting parameter which supplies information on the true structure of a glassy solid is the average bond angle between each element and two of its first neighbours. The average values of these angles are therefore usually compared to those given in the literature. Table 6 shows these values for the model, together with those quoted in the literature for similar alloys. All the calculated values can be considered acceptable, bearing in mind that a distortion of the bond angle is typical of glassy materials and that, in the most unfavourable case, the difference between the bond angles in the model and the values quoted in the literature was less than 4%.

Table 5
Averaged bonding distances

Bond	Material	$\langle d_{ij} \rangle$ (Å)	Ref.
Ag–As	$Ag_{0.04}As_{0.38}Se_{0.58}$	2.50	present work
	sum of covalent radii	2.55	[9]
Ag–Se	$Ag_{0.04}As_{0.38}Se_{0.58}$	2.46	present work
	sum of covalent radii	2.50	[9]
	Ag_3AsSe_2 crystal	2.53	[22]
	Ag_2Se	2.52	[15]
As–As	$Ag_{0.04}As_{0.38}Se_{0.58}$	2.44	present work
	As_4Se_4	2.41	[23]
	$As_{0.20}Se_{0.50}Te_{0.30}$	2.47	[24]
As–Se	$Ag_{0.04}As_{0.38}Se_{0.58}$	2.43	present work
	As–Se system	2.43	[25]
	$Cu_{0.26}As_{0.37}Se_{0.37}$	2.42	[26]
Se–Se	$Ag_{0.04}As_{0.38}Se_{0.58}$	2.42	present work
	$As_{0.40}Se_{0.30}Te_{0.30}$	2.38	[27]
	amorphous Se	2.40	[28]

Table 6
Averaged bonding angles

Type	$\langle \alpha \rangle$ (deg)	Material	Ref.
Ag	106.2	$Ag_{0.04}As_{0.38}Se_{0.58}$	present work
	109.5	tetrahedric angle	
As	109.8	$Ag_{0.04}As_{0.38}Se_{0.58}$	present work
	109.9	$As_{0.40}Se_{0.30}Te_{0.30}$	[27]
	109.5	$As_{0.20}Se_{0.50}Te_{0.30}$	[24]
Se	111.8	$Ag_{0.04}As_{0.38}Se_{0.58}$	present work
	107.7	$As_{0.45}Se_{0.10}Te_{0.45}$	[29]
	107.5	Se glass	[30]

5. Conclusions

According to the radial atomic distribution function of the alloy studied, obtained from X-ray diffraction data and by analysing the silver coordination hypotheses quoted in the literature, both tetrahedral and tricoordinated silver were found to be possible in this alloy, as they correctly explain the experimentally determined average number of first neighbours.

By using the most approximate expression of the area under the first RDF peak, a number of Se–Se bonds was found for each of the silver's coordinations such that, while keeping the coordination numbers, n_{22} and n_{23} positive, the theoretical area is within the margin of error of the experimental area.

Considering the tetra-coordinated silver hypothesis, spatial atomic distribution model of the alloy was built, using the Metropolis Monte Carlo random method, allowing the silver atoms to evolve to three-coordination, and bearing in mind the geometric conditions deduced from the radial atomic distribution function.

According to the analysis of the generated model, the three-dimensional structure of the studied alloy can be described as a network of tetrahedra centered on silver atoms, coexisting with other tetrahedra whose centres are occupied by tetracoordinated arsenic atoms, making the network more compact.

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