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ANALYTICAL DETERMINATION OF THE AREA BELOW THE FIRST PEAK IN THE RDF FOR AMORPHOUS ALLOYS

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An analytical expression has been obtained for the area below the first peak in the radial distribution function of an amorphous material, in which on one hand, the products of atomic factors, $f_if_j/(\sum_i x_if_i)^2$, are approximated by the polynomial which is best fitted to the tabulated values and on the other, the parameters reflecting structural properties are introduced, on which hypotheses permitting the elaboration of a short-range order model of the alloy may be carried out.

1. Introduction

In the interpretation of the radial distribution function (RDF), obtained from the diffraction intensities of an amorphous solid, the area enclosed by the first peak of the curve is related to certain structural parameters with which attempts are made to propose a short-range structural model for the material.

As is seen in the literature, the following is frequently taken for the value of the area

$$\text{area} = \frac{1}{(\sum_i x_i Z_i)^2} \sum_{i,j} x_i n_{ij} Z_i Z_j \,, \tag{1}$$

which can only be applied when the products $R_{ij}(s) = f_if_j/(\sum_i x_if_i)^2$ remain practically constant and do not differ greatly from the values $Z_iZ_j/(\sum_i x_iZ_i)^2$ in the interval s where the measurements are carried out.

In those cases where the functions $R_{ij}(s)$ move away significantly from the constant values mentioned above, Vázquez and Sanz [1] have obtained an expression for the aforementioned area, following the process described by Warren [2], considering that the functions $R_{ij}(s)$ may be approximated by nth order polynomials.

Likewise, as has been described previously, the area is related to the structural parameters, n_{ij}. In a first approximation, Vázquez et al. [3] proposed an expression for the mentioned area, as a function of the coordination of one of the elements in the alloy and the number of bonds between pairs of the same elements in it, considering the atomic scattering factors, f_i, to be constant and equal to Z_i.

In the present paper an analytical expression has been determined for the area under the first peak in the RDF, which takes into account the variation with s of the atomic factors, as well as the possible hypotheses regarding coordination and bonding of the different elements present in the material.

2. Analytical determination of the area

When the products $f_if_j/(\sum_i x_if_i)^2$ vary appreciably with s, the area under the first peak of the RDF is given by [1]

$$\text{area} = \frac{2}{\pi} \sum_{i,j} x_i \frac{n_{ij}}{r_{ij}} \int_a^b r P_{ij}(r)\, \mathrm{d}r \,, \tag{2}$$

where x_i is the atomic fraction of element i, n_{ij} the mean number of atoms of type j at distance r_{ij} from atom i, a and b the limits of the first peak in the RDF, and $P_{ij}(r)$ a function defined by

$$P_{ij}(r)=\frac{1}{2}\int_0^{s_m}\frac{f_i f_j}{(\sum_i x_i f_i)^2}\cos[s(r-r_{ij})]\,\mathrm{d}s\,, \tag{3}$$

s_m being the highest measurement limit.

If the ternary amorphous composition $A_{a'_1}B_{a'_2}D_{a'_3}$ is considered for each hundred atoms of material, in which the elements A, B and D are designated by the subindexes 1, 2 and 3 respectively, the mean coordination numbers may be expressed by

$$n_{ij}=a_{ij}/a'_i\ , \quad n_{ii}=2a_{ii}/a'_i\ ,$$

where a_{ij} is the number of bonds between species i, j and from which relation (2) becomes

$$\text{area}=\frac{2}{50\pi}\sum_{\substack{i,j\\ i\leqslant j}} a_{ij}A_{ij}\ , \tag{4}$$

with

$$A_{ij}=\frac{1}{r_{ij}}\int_a^b rP_{ij}(r)\,\mathrm{d}r\,. \tag{5}$$

Supposing that element A has coordination N in the alloy and the mean coordination numbers, n_{1k}, of this element, with all those bound to it, are proportional to their respective percentual concentrations, the following is obtained:

$$\sum_k n_{1k}=N\,,\quad \frac{n_{1k}}{a'_k}=K\ (K=\text{constant})\ ,$$

from which expression (4) becomes

$$\text{area}=\frac{1}{50\pi}\left[\frac{Na'_1}{\sum_k a'_k}\left(\sum_k a'_kA_{1k}+\sum_{k\neq 1} a'_kA_{1k}\right)+2\sum_{\substack{i,j\neq 1\\ i\leqslant j}} a_{ij}A_{ij}\right]\ , \tag{6}$$

where k cannot assume the values of the subindexes representing the elements in the alloy not bound to element A.

Bearing in mind that the total number of bonds, a_i, of species i is given by [4]

$$a_i=2a_{ii}+\sum_{i\neq j} a_{ij}\ ,$$

the area may be expressed as a function of N and the number of bonds of just one type of element pairs, which in the case of pair 3–3, remains as follows:

$$\text{area}=(1/50\pi)[hN+(a_2-a_3)A_{22}+2a_3A_{23}+2(A_{22}+A_{33}-2A_{23})a_{33}]\ , \tag{7}$$

h being a specific characteristic of each alloy given by the relation

$$h=\frac{a'_1}{\sum_k a'_k}\left(\sum_k a'_kA_{1k}+\sum_{k\neq 1} a'_kA_{1k}+pa'_3(A_{22}-2A_{23})-qa'_2A_{22}\right)\ , \tag{8}$$

in which the parameters p and q are equal to 1 when multiplying concentrations, a'_k, of the elements bound to element A, and equal to zero otherwise.

If the normal coordinations of the diffferent elements in the sample are denoted by C_i and we suppose that species A presents coordination $N (N \geqslant C_1)$, the number of bonds of this species will be

$$a_1 = N a'_1 = C_1 a'_1 + x \,,$$

x being the increment in the number of bonds of the aforementioned element, when it passes from coordination C_1 to N.

As the coordination of element A increases, the coordinations of elements B and D may either be increased or reduced, and therefore the number of bonds of these elements is given by

$$a_i = C_i a'_i \pm y_i \quad (i \neq 1) \,,$$

where y_i represents the variation of the number of bonds of element i.

Taking into account these considerations and in agreement with ref. [3], expression (7) becomes

$$\text{area} = (1/50\pi)\left[(h + \beta A_{22} - 2\delta A_{23})N + \alpha A_{22} + 2\gamma A_{23} + 2(A_{22} + A_{33} - 2A_{23})a_{33}\right] \,, \tag{9}$$

where the parameters α, β, γ and δ are given by

$$\alpha = \frac{(a'_2)^2 C_2 - (a'_3)^2 C_3 + a'_2 a'_3 (C_2 - C_3) \pm a'_1 C_1 (a'_2 - a'_3)}{a'_2 + a'_3} \,, \quad \beta = \pm \frac{a'_1 (a'_3 - a'_2)}{a'_2 + a'_3} \,,$$

$$\gamma = \frac{a'_2 a'_3 C_3 + (a'_3)^2 C_3 \pm a'_1 a'_3 C_1}{a'_2 + a'_3} \,, \quad \delta = \pm \frac{a'_1 a'_3}{a'_2 + a'_3} \,.$$

These expressions present double signs, the + sign being valid when as coordination of element A is increased, the coordinations of elements B and D are reduced, and the − sign when under the first hypothesis, the coordinations of elements B and D increase.

Expression (9) obtained for the area under the first peak of the RDF is a function of the coordination of element A in the compound and the number of bonds a_{ii}, given that the parameters α, β, γ and δ are characteristic of the alloy, as they only depend on the concentration of each element in 100 atoms of material and its habitual coordination. This relation takes the form

$$\text{area} = (1/50\pi)\{[h + \beta A_{22} - \delta(A_{22} + A_{33})]N + \alpha A_{22} + \gamma(A_{22} + A_{33}) - (A_{22} + A_{33} - 2A_{23})a_{23}\} \,, \tag{10}$$

with

$$h = \frac{a'_1}{\sum_k a'_k}\left(\sum_k a'_k A_{1k} + \sum_{k \neq 1} a'_k (A_{1k} - A_{kk})\right) , \tag{11}$$

when it is expressed as a function of the number of bonds, a_{ij}, between different pairs of elements in the alloy.

Expressions (9) and (10) obtained for the area may be condensed in one, in which the double dependence of this magnitude on N and the number of bonds between pairs of elements in the sample are manifested, in cases where these pairs are made up of the same or different elements. In this general case, the following is obtained for the area below the first peak in the RDF:

$$\text{area} = \frac{1}{50\pi}\left[\left(h + \beta A_{22} - \delta \sum_{i,j \neq 1} A_{ij}\right)N + \alpha A_{22} + \gamma \sum_{i,j \neq 1} A_{ij} + P\left(\sum_{i=j \neq 1} A_{ij} - \sum_{\substack{i,j \neq 1 \\ i \neq j}} A_{ij}\right)a_{ij}\right] , \tag{12}$$

in which the terms $\delta \sum_{i,j \neq 1} A_{ij}$ and $\gamma \sum_{i,j \neq 1} A_{ij}$ must fulfill the condition $i \neq j$, should the area be expressed as a function of a_{ii}, and $i = j$ when it is expressed as a function of a_{ij}. Thus, the parameter P takes the value 2 in the first case and −1 in the second and h the values given in (8) and (11) respectively.

3. Applications

To check the goodness of the procedure described, we have applied the expression obtained, eq. (12), to different alloys, each based on different structural hypotheses, and the results obtained are in agreement with experimental values. The results of two tests are given in the present paper.

In the first case, for the alloy $As_{0.20}Se_{0.50}Te_{0.30}$ (As = 1, Se = 2, Te = 3), in which the As atoms are considered to be fourfold coordinated ($N=4$), and bonds are admitted between all the elements in the material [5], the following is obtained for the area:

$$\text{area} = 2.0636 + 0.0073 a_{33} , \qquad (13)$$

where the different values shown in tables 1, 2 and 3 have been used, and taking $h = 22.6048$, calculated from expression (8). The area obtained is a function of the number of Te–Te bonds, a_{33}.

In the second case, for the alloy $Al_{0.20}As_{0.20}Te_{0.60}$ (Al = 1, As = 2, Te = 3), in which we suppose that no Al–Al bonds exist and that $N=4$ for this type of atom, implying the presence of Te and As atoms with coordinations 3 and 4 respectively [13], the area as a function of the number of As–Te bonds, a_{23}, is

$$\text{area} = 2.2421 - 0.0023 a_{23} , \qquad (14)$$

as obtained from expression (12) with the values of the different parameters given in tables 1, 2 and 3, and $h = -25.4865$ deduced by means of expression (11) in which $k \neq 1$, as this has been based on the hypothesis of the non-existence of Al–Al bonds.

Figs. 1 and 2 represent the variation of the area obtained for each alloy with the number of Te–Te and As–Te bonds, respectively, in the interval in which the numbers of mean coordination are defined. It is seen that the calculated values are close to those determined experimentally from the RDF and always within the estimated error margin of ±0.1 atom.

Table 1
Bonding distances for both alloys

Pair	$As_{0.20}Se_{0.50}Te_{0.30}$		$Al_{0.20}As_{0.20}Te_{0.60}$	
	r_{ij}(Å)	ref.	r_{ij}(Å)	ref.
1-1	2.49	[6]	2.86	[10]
1-2	2.38	[7]	2.43	[11]
1-3	2.68	[8]	2.53	[7]
2-2	2.34	[7]	2.49	[6]
2-3	2.54	[7]	2.80	[8]
3-3	2.71	[9]	2.83	[12]

Table 2
Values obtained for A_{ij} following the process described in ref. [1] with $s_m = 12$ Å^{-1}

Pair	A_{ij}	
	$As_{0.20}Se_{0.50}Te_{0.30}$	$Al_{0.20}As_{0.20}Te_{0.60}$
1-1	1.0707	0.1417
1-2	1.1186	0.3463
1-3	1.8885	0.6354
2-2	1.1778	1.1012
2-3	1.8334	1.7829
3-3	3.0638	2.8337

Table 3
The intervals of the first peak and the characteristic parameters of the alloys

Alloy	First peak		α	β	γ	δ
	a(Å)	b(Å)				
$As_{0.20}Se_{0.50}Te_{0.30}$	2.05	2.90	55	−5	82.5	7.5
$Al_{0.20}As_{0.20}Te_{0.60}$	2.20	3.05	−30	−10	75	−15

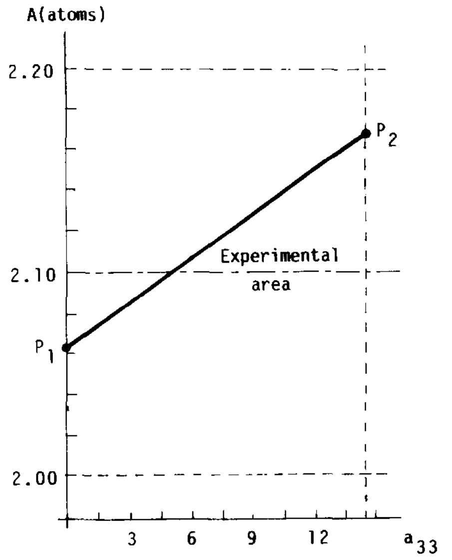

Fig. 1. Area of first peak versus number of Te–Te bonds.

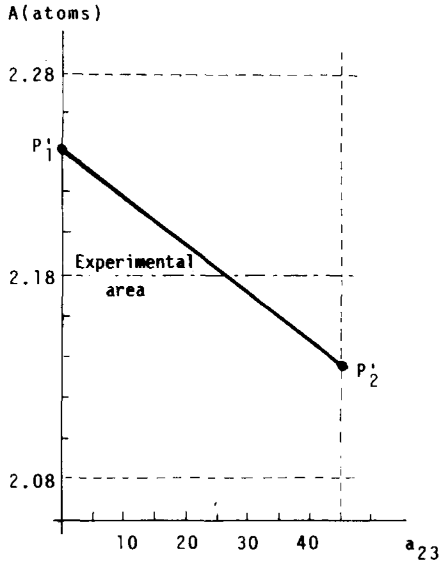

Fig. 2. Area of first peak versus number of As–Te bonds.

4. Conclusion

The expression obtained for the area below the first peak of the RDF permits the establishment of hypotheses regarding structural properties such as: coordinations, the absence of particular bonds, etc., as well as the use of polynomial functions that are better adjusted to the values of atomic products $f_i f_j/(\sum_i x_i f_i)^2$, in those cases in which the aforementioned magnitudes differ remarkably from the approximated values $Z_i Z_j/(\sum_i x_i Z_i)^2$. On the other hand, the area thus obtained may be compared to the experimental value measured for this magnitude, which in a first approximation permits the verification of the validity of previously established structural hypotheses.

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