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Relationship between polytetrahedral crystals and glasses by using anomalous X-ray diffraction technique and geometrical modelling

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Résumé. — Les fonctions d'interférence et de distributions radiales sont déterminées en utilisant la technique de diffraction anomale des rayons X pour l'alliage Cu2Y. Ces résultats permettent d'inclure cette structure dans une large famille A2B où A est du Co, Fe, Cu ou Ni et B est du Zr ou Y. Par comparaison des nombres de coordination et des distances interatomiques obtenus expérimentalement avec ceux de modèles géométriques, nous analysons l'ordre icosaédrique et la présence de réseaux de disinclinaison dans ces phases de Frank et Kasper, vitreuses ou cristallines.

Abstract. — Partial interference functions and radial distribution functions are determined using the anomalous X-ray diffraction technique for the amorphous alloy Cu2Y. These results are generalized for the amorphous family of A2B amorphous alloys where A is Co, Fe, Cu, or Ni and B is Zr or Y. By comparing the coordination number and interatomic distances obtained experimentally with those of geometrical models, the icosahedral order and the occurrence of disclination networks in these Frank and Kasper crystalline and glassy phases are analysed.

1. Introduction.

To explain the complex structure of the intermetallic phase of alloys, between small and large atoms, Frank and Kasper (F. K.) proposed the concept of icosahedral coordination in 1955. Since the icosahedron point group symmetry is not a crystallographic symmetry, these structures must contain other local coordination.

Frank and Kasper analyzed these structures in terms of tetrahedral packing (polytetrahedral phases). However, regular tetrahedra cannot tile the space thus they introduced non-regular tetrahedra and local fluctuations in the coordination number which is needed to fill the space with tetrahedra [1].

In a theoretical study [2] of the structure of amorphous alloys, similar concepts (Sadoc, Rivier [3]) are developed. In both cases the structure could be reduced to a skeleton: the Frank and Kasper lines running from a non-icosahedral site to another non icosahedral site, or the disclination lines introduced in order to describe the deviation from the icosahedral
order in amorphous alloys. It is now well understood that F. K. crystalline phases have an ordered skeleton of disclination lines whereas amorphous structures are characterised by a disordered skeleton. So, in structure studies, the real focal interest is this network of disclinations lines.

Disclination lines have to respect geometrical and topological rules, which impose a local order at a scale different from the atomic size. This local order results in a long crystalline range order in F. K. phase, and remains purely local in amorphous alloys. For instance it has been shown that the density of disclinations (defect) can be evaluated, and actually it is related to the coordination number in metallic alloys. In these alloys the coordination number is usually $Z = 12$, $Z = 14$ and $Z = 16$ ($Z_{12}$, $Z_{14}$, $Z_{16}$ sites). Large atoms are supposed to be on disclination sites ($Z_{14}$ or $Z_{16}$ sites) and small atoms on the $Z_{12}$ sites (with icosahedral coordination) as it is observed in the F. K. intermetallic phase.

Hence the vital information needed to understand the « genetic » relationship between the structure of an alloy of a F. K. phase and its amorphous alloys has to characterize the properties of a disclination network.

2. Review of recent works on these amorphous alloys by X-ray diffraction using the anomalous dispersion effect.

The possibility of obtaining a precise partial function using the anomalous diffraction technique has been shown [4]. In this technique an atom scatters the X-ray with an amplitude and a phase that can be represented by a total atomic scattering factor of $f_{\text{tot}}(K, E) = f_0(K) + f'(K, E) + if''(K, E)$ in which $K = \frac{4 \pi}{\lambda} \sin \theta$ and $f_0$ is the atomic scattering factor for radiations with a frequency ($\omega$) much higher than the absorption edge. The other two terms of this equation (anomalous dispersion) depend on $E = h\omega$.

This principle has been applied by Waseda et al. (1976) to deduce the partial interference functions in amorphous Cu-Zr alloys. After this attempt very few applications were performed to show the useful aspect of anomalous dispersion of the structural studies in disordered material. A major difficulty was to obtain reliable data. The energy dependence of diffraction intensity is relatively small therefore a very high accuracy of measurement was required to obtain a very high quality of the Radial Distribution Function (R.D.F.).

The recent availability of synchrotron radiation (S.R.) as a tunable source of X-rays, with a very high intensity, allows one to maintain other tasks, on the base of the frequency modulated X-ray diffraction (Shevchik 1977). The method called the differential anomalous scattering has been based upon this idea. By this method only a partial function for the dominant species has been reported. It has been preferred to analyse $I(K, \omega)$ as a function of $K$, obtained for different energies. By this classical way, reliable interference functions can be determined. The degree of reliability is increased by minimizing the experimental errors.

For this purpose, a synchrotron X-ray universal powder diffractometer has been designed to be adapted with the polarized and the parallel beam of the synchrotron (for details see Refs. [10, 15]) radiation at DCI (LURE).

The very simple geometrical construction of this diffractometer (in contrast with the ideal classical diffractometer) is due to the parallel beam of S.R., and the optical arrangement. The diffractometer can be optimized to reduce the deviation of the observed diffraction profile line from the ideal profile (Delta function) without any background. This system allows a new technique to be created called the anomalous diffraction, which has also been developed for the purpose of obtaining partial interference functions of different component in a material. This method gives similar results to those found with the isomorphous replacement technique.
In binary alloys (A-B), the total interference function $Y(K)$ can be expressed in the following form:

$$Y(K) = C_{AA}(K) Y_{AA}(K) + C_{BB}(K) Y_{BB}(K) + 2 C_{AB}(K) Y_{AB}(K).$$

To deduce the partial interference function $Y_{jj}(K)$ three different experiments with different energies are done. For each energy the values of $C_{jj}(K)$ are changed. One value far away from the $K$ absorption edge of A or B element, one very close to this absorption edge and one close to the $K$ absorption edge of A.

It is known that a good resolution in the Radial Distribution Function needs a short wavelength in order to have a large $K_{\text{max}}$ value. This condition can not be carried out for all kinds of binary (A-B) alloys.

If the wavelength close to the $K$-absorption edge of the B-atom is large (in the case of elements with relatively small atomic number) the $K_{\text{max}}$ is small and consequently the resolution is poor.

But for a diluted (A-B) alloy the low value of the B content leads to a very small contribution of the B-B partial function ($Y_{BB}$) to the total $Y(K)$ function. So it is possible to assume a very simple function for the B-B contribution, and then to estimate other contributions ($Y_{AA}$, $Y_{AB}$) using $Y_{BB}$ as an adjustable parameter.

This hypothetical function is obtained by Fourier transform of a hypothetical first peak in the B-B radial distribution function at an atomic diameter position.

By inversion, the linear system can be solved with two unknowns; the partial interference functions of A-A and A-B. This method was used to obtain the partial interference functions of Cu-Y amorphous alloys for the composition Cu$_5$Y [4]. For this composition the $Y_{Y-Y}$ function can be taken as an adjustable parameter. For instance the two numerical coefficients relating partial functions for $K = 14 \text{ Å}^{-1}$ are shown:

$$Y_{\text{Cu-Cu}} = 1.79 Y_1 - 0.81 Y_2 + 0.02 Y_{Y-Y}$$
$$Y_{\text{Cu-Y}} = -3.50 Y_1 + 4.67 Y_2 - 0.17 Y_{Y-Y}.$$  

The coefficient of $Y_{Y-Y}$ is small, so the influence of the selection of the hypothetical $Y_{Y-Y}$ function remains small.

Figure 1 shows the partial interference functions for Cu-Cu and Cu-Y derived by this method.

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![Graph](https://via.placeholder.com/150)

**Fig. 1.** — The partial interference function for Cu-Cu and Cu-Y of amorphous Cu$_5$Y.
Figure 2 shows the two reduced radial distribution functions of $W_{\text{Cu-Cu}}$ and $W_{\text{Cu-Y}}$. These functions permit us to find distances occurring in the Cu-Cu and Cu-Y pairs and the coordination number (see Tabs. I and II).

These results and those obtained with another diluted alloy Fe$_9$Zr demonstrate that by assuming a simple hypothetical function in the case of the diluted alloy [5], it is possible to obtain a precise partial function.

![Graph showing radial distribution functions](image)

**Fig. 2.** — The reduced radial distribution functions $W_{\text{Cu-Cu}}$ and $W_{\text{Cu-Y}}$ of amorphous Cu$_5$Y.

**Table I.** — *Interatomic distances in amorphous Cu$_5$Y obtained in reference [4] (in Å).*

<table>
<thead>
<tr>
<th></th>
<th>First nearest neighbour</th>
<th>Second</th>
<th>Third</th>
<th>Fourth</th>
<th>Fifth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Cu</td>
<td>2.50 (3.32)</td>
<td>4.3</td>
<td>4.9</td>
<td>6.7</td>
<td>7.8</td>
</tr>
<tr>
<td>Cu-Y</td>
<td>3.0</td>
<td>4.9</td>
<td>5.5</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>Y-Y</td>
<td>3.40 (¹)</td>
<td></td>
<td></td>
<td></td>
<td>7.2</td>
</tr>
</tbody>
</table>

(¹) Hypothetical.

**Table II.** — *The theoretical and experimental coordination numbers in amorphous Cu$_5$Y alloy.*

<table>
<thead>
<tr>
<th>Atom taken as origin</th>
<th>Number of Cu atoms around it</th>
<th>Number of Y atoms around it</th>
<th>Total ($Z$)</th>
<th>Mean coordination number ($Z$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>$7.4 + 3 = 10.45$</td>
<td>2.8</td>
<td>13.2</td>
<td>13.75</td>
</tr>
<tr>
<td>Y</td>
<td>14.39</td>
<td>2 (¹)</td>
<td>16.5</td>
<td></td>
</tr>
</tbody>
</table>

(¹) Hypothetical.
3. The A$_2$B amorphous alloys.

In the present work we mainly use information on the different coordination shells which is extracted from pair-pair correlation functions.

Our aim in this work is to analyse the way of propagation of the icosahedral order by comparison of the structure of amorphous and crystalline F.K. phase, where the forthcoming point is the size factor. Cu$_2$Y is chosen in this system. Cu$_2$Y is not reported to be a crystalline Laves phase [6], nevertheless its composition, A$_2$B, and its ratio of atomic diameters corresponds to that of Laves phases; as the case of Ni$_2$Y or Fe$_2$Y. The advantage of comparing both systems Cu-Y and Ni-Y is that the Haucke phase (Cu$_5$Y-Ni$_5$Y) [7] is present in both of them. Experimental results presented here are obtained by X-ray diffraction using the contrast variation of atomic scattering factors due to the anomalous dispersion effect. Structural information for amorphous Ni$_2$Y has been obtained by neutron diffraction [8] and that for Cu$_2$Y is obtained in the present work by anomalous diffraction. Hence such a comparison may be taken forth.

3.1 ANOMALOUS X-RAY DIFFRACTION STUDY OF THE Cu$_2$Y AMORPHOUS ALLOY. — In the case of Cu$_2$Y it is not possible to obtain the precise partial functions, if a simple hypothetical function is used, since the Y$_{Y-Y}$ coefficients are larger than in Cu$_5$Y for instance ($K = 14$ Å$^{-1}$):

\[
Y_{Cu-Cu} = 3.023 Y_1 - 2.260 Y_2 + 0.237 Y_{Y-Y} \\
Y_{Cu-Y} = -2.021 Y_1 + 3.554 Y_2 - 0.533 Y_{Y-Y}.
\]

Therefore the effect of $Y_{Y-Y}$ cannot be negligible on the other two partial functions. For this reason we have supposed a realistic $Y_{Y-Y}$ function obtained from a theoretical model.

We could consider amorphous Cu$_2$Y as polytetrahedral amorphous phase [9]. The structure of all these alloys can be described as a packing of small atoms (Cu) and large atoms (Y) with tetrahedral interstices. In modelling the structure, an adequate hypothesis is to consider large atoms located on the disclination nodes (mainly coordination 16) and small atoms with coordinations equal to 12 or in a few cases equal to 14. This is clearly what happens in crystalline polytetrahedral phases with similar components (Haucke, Laves phases).

So in a geometrical model of these structures it is possible to consider small atoms on the Z12 sites and large atoms on Z16, or other larger sites.

We have used a model derived from the $\{335\}$ polytope which is a template for dense icosahedral metallic structures. The polytope is then partially decurved using a disclination network. Cu atoms are supposed to be on the Z12 sites and Y atoms are located on Z16 sites which are nodes of the disclination network.

In this model there are 600 Y atoms and 1560 Cu atoms Hence the composition is $A_{0.72}B_{0.27}$ which is between A$_2$B and A$_5$B compositions.

The three theoretical interference partial functions, $Y_{Cu-Cu}$, $Y_{Y-Y}$ and Cu-Y appear in figure 3.

This figure shows that the partial interference function of Y-Y has common features with the interference function of amorphous silicon (Si).

This could be related to the fact that the partial B-B diffraction pattern in crystalline A$_2$B Laves phase is identical to the crystalline silicon diffraction pattern. In these Laves phases, the disclination lines are interconnected exactly in the same way as bonds in a diamond structure. They go straight from a « Y » atom to a « Y » atom and form angles on all the « Y » atoms.
Hence a tetracoordinated network of intersecting disclination lines is formed. It should be indicated that the atomic distances of Y-Y derived from this phase is 3.11 Å, hence smaller than the Y-Y in pure hexagonal yttrium (3.60 Å). We need a knowledge of this distance to select a theoretical Y-Y partial function.

It is therefore necessary to determine experimental partial functions (Y_Cu-Cu, Y_Cu-Y) we used the theoretical Y_Y function as a known function. However the scale of this function must be adjusted. In this model, if the Cu-Cu first neighbours distance is given, all other distances are geometrically imposed. We have supposed a first Cu-Cu distance equal to 2.55 Å leading to a first Y-Y neighbour distance equal to 3.40 Å. This choice of the Cu-Cu distance is coherent with the experimental determination.

The influence of the selection of Cu-Cu distance will be discussed in a section on the accuracy of partial W_Cu-Cu and W_Cu-Y.

3.2 EXPERIMENTAL DETAILS. — The ductile amorphous alloys were prepared using a triode sputtering technique on Cu substrate maintained at 78 K. By optimising different parameters we could obtain a ductile foil of amorphous alloys with 10 μm thickness and a lateral dimension of 70 × 10 mm. In order to check the glassy state of the sample a very sensitive photographic method (Guinier technique) was used.

The experiment was carried out at DCI at LURE, which is equipped with an X-ray universal powder diffractometer [10] and a Channel-cut Si(220) single crystal as a monochromator. This system provides a high quality monochromatic parallel beam with 2 to 3 eV wide in energy (E = 6 500 eV).

The diffracted intensity I(K) was measured using a goniometer θ - 2θ with a vertical axis at two energies 16 338 eV, and 17 028 eV (10 eV and 700 eV below the absorption edge of Y).

In order to avoid fluorescence and Compton radiations, the scattering beam was recorded by an energy dispersive detector, of lithium-drifted silicon.

The sample was scanned from 2θ = 1°-160° in reflection geometry 2θ = 1°-90° in transmission mode. The scanning step was 0.25°. The part of the diagram (2θ < 60°) that was obtained by transmission and the part of the diagram (2θ > 60°) that was obtained by reflection were used to obtain a precise interference function. As the energy resolution of the solid state detector is about 180 eV for a photon energy near 8 000 eV; it is sufficient to resolve the fluorescence line Kα and Kβ, but not adequate enough to resolve Kβ from the elastically scattered photon. (When the energy of the incident beam is close to the absorption
An accurate estimation of the Kβ intensity is necessary to be subtracted from the diffracted beams. The Kα intensity has been measured and then the Kβ intensity is deduced from the ratio \( Kβ / Kα = 0.19 \) (Ref. [11]). Diffracted intensities were normalized with the fluorescence intensity of CuKα in order to take into account the time decrease of the beams. In order to normalize the scattered intensity, the value of \( f' = -2 \) e.u. at \( E = 16\,338\) eV and \( f' = -6.6 \) e.u. for \( E = 17\,028\) eV were assumed. These values were obtained from the theoretical value calculated in reference [12] from the Cormed and Liberman relationship.

After absorption corrections the interference functions were derived from the data using the classical procedure of normalization; dividing the experimental intensity by a calculated gaseous scattering intensity adjusted to a large \( K \). Small errors in this normalization are detected and corrected by taking into account the low \( R \) contribution to the radial distribution function obtained by the Fourier transform. In other words, the experimental \( I(K) \) was analytically corrected. According to this argument, there are no interatomic distances smaller than the nearest neighbourhood distances. This indicates that the curve below the first peak of the R.D.F. has a slope of \( -1 \).

**Fig. 4.** — The total interference functions for the amorphous alloy, Cu₂Y, which are used to obtain the partial functions. a) \( E = 16\,338\) eV, 700 eV below the yttrium K-edge, b) \( E = 17\,028\), 10 eV below the yttrium K-edge.
4. Results.

The total interference functions $Y(K, \omega)$ have been measured for two energies. Two reduced interference (Fig. 4) functions $F(K) = K[Y(K) - 1]$ were derived from $Y(K, \omega)$ with the above correction and normalization procedure. The reduced radial distribution function $W(R)$ is the Fourier transform of the $F(K)$ function (see Fig. 5).

![Fig. 5. - The reduced radial distribution functions derived by Fourier transform from figures 4a and 4b functions.](image)

These functions show that using synchrotron radiation is an immense improvement in R.D.F.'s over those yielded in conventional X-ray tube experiment. Such high quality of R.D.F., is achieved due to the fine quality of monochromatic beam and specification of anomalous diffraction technique. Because of a missing background in the X-ray pattern the elastic and inelastic components of the scattered X-ray beams can be characterized carefully. So, in high $(K)$ we can get a real signal from the disordered material. This possibility gives a hope to achieve a better normalization of R.D.F. and to be more confident in the details observed on this function.

4.1 Total Radial Distribution Functions. — The radial distribution function derived from $F(K)$ exhibits main peaks centered around 2.56, 3.0 and 3.60 Å. These peaks are usually attributed to Cu-Cu, Cu-Y and Y-Y first neighbour distances, the atomic radius of Cu is $R_{Cu} = 1.28$ Å and the atomic radius of yttrium $R_Y = 1.80$ Å then, $R_{Cu} + R_{Cu} = 2.56$, $R_{Cu} + R_Y = 3.06$, $R_Y + R_Y = 3.60$ Å, these are very close to the experimental results, but in the discussion of partial function we concluded that the peak at 3.60 Å results from a mixture of Cu-Cu, Cu-Y and Y-Y distances.

4.2 The Partial Interference Function and the Distribution Function. — Figure 6 shows the three partial interference functions for the amorphous alloy evaluated from the two independent functions (as mentioned above).

The information on the atomic distribution functions in real space is given by the Fourier transform of each partial interference function.

Figure 7 shows three partial radial distribution functions $W(r)$ of Cu-Cu, Cu-Y and Y-Y which are derived from the partial interference functions $Y(K)$. These functions permit us to find the characteristics of Cu-Cu, and Cu-Y correlation functions.
The first peak of the Cu-Cu partial radial distribution function corresponds to the distance at 2.53 Å. The first peak of the Cu-Y partial function is at 3.0 Å. Table III shows interatomic distances obtained from these curves. Interatomic distances and coordination number of nearest neighbours of Ni$_2$Y and Cu$_2$Y can be compared in table IV.

4.3 ACCURACY OF PARTIAL FUNCTION. — Specific procedures have been used to minimise the data collection errors, due to synchrotron X-ray universal powder diffractometer and data analysis uncertainties. By these procedures, interference functions with great precision, essential for obtaining precise partial functions, can be produced. The details of these procedures have been described elsewhere [4, 10]. For instance, to measure the exact value of the wavelength ($\lambda$) and scattering factor $f_{\text{tot}}$ is a delicate problem in such experiments.

To understand the effect of this uncertainty, $f'$ was systematically varied for yttrium and Cu atom.
Table III. — Interatomic distances in amorphous Cu$_2$Y obtained in this work (in Å).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Cu</td>
<td>2.53 (3.50)</td>
<td>4.40</td>
<td>5.4</td>
<td>6.4 (6.9)</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>Cu-Y</td>
<td>3.0 (3.7)</td>
<td>5.0</td>
<td>5.7</td>
<td>6.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y-Y (*)</td>
<td>3.40 (3.9)</td>
<td>5.4</td>
<td>5.9</td>
<td>6.51</td>
<td>7.0 (7.6)</td>
<td></td>
</tr>
</tbody>
</table>

(*) From the theoretical partial function of Y$_{yy}$.

Table IV. Interatomic distance (in Å) and the coordination number of nearest neighbours in amorphous Ni$_2$Y and Cu$_2$Y.

<table>
<thead>
<tr>
<th></th>
<th>Ni$_2$Y</th>
<th>Cu$_2$Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline</td>
<td>Amorphous</td>
<td>Phase</td>
</tr>
<tr>
<td>Laves phase</td>
<td>Neutron and X-ray Diffraction (7)</td>
<td></td>
</tr>
<tr>
<td>Nc</td>
<td>RA</td>
<td>Nc</td>
</tr>
<tr>
<td>6Ni</td>
<td>2.54</td>
<td>5.5 Ni</td>
</tr>
<tr>
<td>6Y</td>
<td>2.98</td>
<td>5Y</td>
</tr>
<tr>
<td>Z=12</td>
<td>Z=11.5</td>
<td>Z=12</td>
</tr>
<tr>
<td>12Ni</td>
<td>2.98</td>
<td>12Ni</td>
</tr>
<tr>
<td>4Y</td>
<td>3.11</td>
<td>4Y</td>
</tr>
<tr>
<td>Z=16</td>
<td>Z=16</td>
<td>Z=16</td>
</tr>
</tbody>
</table>

* From the theoretical partial function of Y$_{yy}$.

The change of the $f'$ value from $-6$ to $-7$ e.u. does not modify significantly the interatomic distances in the partial R.D.F. The effect on the coordination number (Tab. IV) remains smaller than 0.2 atoms, thus the uncertainty on the coordination number which results from the $f'$ uncertainty does not exceed 5%.

In this new procedure for obtaining partial interference functions using two independent experiments with a theoretical partial function, the first distance of Cu-Cu is given as a known parameter. This known parameter fixes the scale of the theoretical partial function. The Y-Y first distance is then 3.40 Å.

This value must be justified. The first argument for this choice comes from other similar amorphous materials: Cu$_3$Y presents in the total R.D.F. a clear peak at this distance (Fig. 8).
Hence in Ni2Y amorphous alloy studied by EXAFS [13] and neutron diffraction [8] the Y-Y first distance is also reported to be at 3.40 Å.

In order to have a better confirmation of this conclusion we have tried to use in the theoretical partial function determination an Yₙₘ-Y function which gives by Fourier transform a first neighbour distance at 3.60 Å corresponding to the position of a peak in the total experimental R.D.F. This needs in the model a Cu-Cu first distance equal to 2.70 Å which is never observed in amorphous transition elements and rare-earth alloys.

Fig. 8. — The reduced radial distribution functions of amorphous Cu₅Y. This figure shows that the Y-Y distance is also well resolved (3.40 Å).

Fig. 9. — The reduced radial distribution functions obtained by fixing in the model the Cu-Cu distance at 2.70 Å, allows us to get the Y-Y first distance at 3.60 Å. The « refusal » of the 2.70 Å first distance by the partial Cu-Cu function can be demonstrated by the usage of the new Y-Y partial function and solving the system with two unknowns. Comparing with figure 7 it can be concluded that partial Cu-Cu and Cu-Y functions are relatively insensitive to large change in the Yₙₘ-Y function. Comparing this figure with figure 5 confirms that the choice of the Y-Y distance at 3.40 Å is reasonable, since the 3.60 Å peak arises from the Cu-Cu partial function.
If the peak at 3.60 Å of the total R.D.F. results only from a Y-Y contribution, the peak close to this distance observed, on Cu-Cu and Cu-Y partial R.D.F. should decrease drastically when a $Y_{Y-Y}$ function related to the 3.60 Å Y-Y distance is used in place of the one related to the 3.40 Å distance. This is not the case as shown in figure 9.

5. Discussions and conclusions.

The model used to describe the structure is the hierarchical model reported by Sadoc and Mosseri (S. M.) [16] (its simplest form: the first iteration). In this model B (Y) atoms are on the vertices of a \{533\} polytope. Cells of this polytope are dodecahedral cages which are filled by icosahedral clusters of 13 copper atoms (A). All Cu atoms have 12 neighbours in an icosahedral configuration which are 12 Cu or (7 Cu + 5 Y) atoms. All Y atoms have 16 (12 Cu + 4 Y) atoms as neighbours. Consequently edges of the \{533\} polytope form the disclination network.

The geometrical distances between atoms are fixed by the choice of the Cu-Cu first distance: (2.55 Å) then 3.00 Å and 3.40 Å respectively for Cu-Y and Y-Y distances are obtained.

The model contains 600 Y atoms and $120 \times 13 = 1560$ Cu atoms. So the composition corresponds to $\text{Cu}_{0.722}\text{Y}_{0.278}$ which is intermediate between the two compositions $\text{Cu}_{0.666}\text{Y}_{0.333}$ and $\text{Cu}_{0.833}\text{Y}_{0.166}$ studied in this paper.

This structure is not completely decurved. Hierarchical models obtained after complete decurving present interlaced networks of disclination which look locally like the \{533\} network of edges, but with some intermediate Z14 sites. Certainly in real material such sites could occur and be occupied by Cu atoms leading to some Cu-Cu first neighbours distances larger than the usual one, but also if some adjustment of the composition is needed these sites could be occupied by Y atoms leading also to an increase in the Cu-Cu first neighbours distances of the Cu atoms close to the considered Y atoms. It is clearly what is observed on both experimental R.D.F. for Cu$_5$Y and Cu$_2$Y which show some Cu-Cu distances close to 3.5 Å (3.32 Å in Cu$_5$Y).

They are two ways for comparing a model with experimental results: i) compare the interference functions with their corresponding experimental curves and ii) to compare the radial distribution functions with their corresponding experimental values. Since there was a possibility to compute the interference function in the curved space, the two methods were systematically used.

The comparison of partial interference functions deduced from the hierarchical model of Sadoc and Mosseri with partial interference function of Cu$_5$Y and Cu$_2$Y obtained by the anomalous diffraction technique indicates a strong correlation between their peak positions (see Fig. 10). It is interesting to remark that the small humps or oscillations on experimental interference functions have a counterpart with theoretical functions. However it should be noticed that the functions obtained from the (S. M.) model are broadened, but they still exhibit larger oscillations than the experimental functions.

From the partial radial distribution functions, the interatomic distances and coordination number can be obtained. The comparison of these values with the one predicted by the (S. M.) model supports the viability of such a description of the polytetrahedral structures. With such a model the structure of Cu$_5$Y and Cu$_2$Y could be sketch by a skeleton of F. K. lines (disclinations) linking Y-Y atoms.

As a conclusion it can be added that Cu-Y amorphous alloys have a structure which covers the whole family of amorphous alloys like (Co, Ni, Fe, Cu)-(Y, Zr), which are defined as large atom and small atom alloys in which small atoms are richer in composition. In the crystalline state these alloys have often the Frank and Kasper type (or more generally are
polytetrahedral close packed) but not always. It seems that the amorphous state gives more flexibility in keeping the local coordination of F. K. structure in order to accommodate all local chemical constraints and the efficiency of a tetrahedral packing.

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Fig. 10. — The comparison of the partial interference functions of Cu$_2$Y (a) and Cu$_5$Y (c) with the model (b).
References