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X-ray diffraction study on uniformly oriented quasicrystals

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Résumé. — Nous présentons des résultats de diffraction des rayons X sur des quasi-cristaux Al-Li-Cu ayant une seule orientation. L'observation des taches de diffraction au moyen de diagrammes de Laue monochromatique et de clichés de précession est compatible avec les règles de parité correspondant à un quasi-réseau icosaédrique primitif. Des diffusions diffuses complexes, respectant la symétrie de l'état quasicristallin ont été observées pour la première fois. Des coquilles sphériques de diffusion sont présentes dans l'espace réciproque ; les plus intenses sont centrées en des points situés sur les axes de symétrie d'ordre 5.

Abstract. — X-ray diffraction results on several uniformly oriented quasicrystals of an Al-Li-Cu alloy are reported. By means of long exposed monochromatic Laue and precession photographs, we confirm the parity rules for a primitive icosahedral quasilattice. Moreover, for the first time, complex diffuse scattering related to the icosahedral symmetry has been observed. Spherical shells of diffuse scattering appear in reciprocal space : the centres of the most intense shells are located on the five-fold axes.

The discovery by Shechtman et al. [1] of a metallic phase with long-range icosahedral orientational symmetry has revealed a new class of ordered structures. The icosahedral symmetry is inconsistent with three-dimensional crystallographic periodicity. The discrete diffraction patterns found experimentally imply a quasi-periodicity which was related to a periodic six-dimensional protolattice, see e.g. [2]. The new quasicrystalline phase has been observed mainly in micron size grains of quenched alloys. Therefore, the structural studies have been limited to electron diffraction on single domain and X-ray and neutron on powder samples. Very recently, large quasicrystals of uniform orientation have been prepared in the aluminium-lithium-copper system [3]. These stable quasicrystals with a chemical composition near to Al₆CuLi₃ show triacontahedral morphology. A typical sample size of a few 100 μm diameter is perfectly adapted for the detailed exploration of the reciprocal space by X-ray diffraction. In this paper we report the results obtained by monochromatic Laue and precession techniques.

The quality of the samples was tested by X-ray rotation photographs in order to check a possible contamination by crystalline phases and/or the presence of differently oriented quasicrystalline domains. In this way, two specimens were selected ; pseudo-spherical in shape, they are formed by natural « golden rhombus » faces (each perpendicular to a 2-fold axis) resulting in an almost perfect triacontahedron. Figure 1 shows one of the samples of about 300 μm diameter glued on a glass fiber with a 2-fold axis A aligned along its direction. We observe a macroscopic 5-fold symmetry at the vertex formed by five rhombus faces perpendicular to the 2-fold axis A. The tested samples have been studied using two kinds of X-ray experiments : monochromatic — Laue and precession photographic techniques ; the sensibility of long exposed X-ray photographs gives us information on very weak diffraction peaks and on some interesting diffuse scattering. First results have already been published elsewhere [4]. All details are presented and discussed on the basis of the indexing method proposed by J. W. Cahn, D.
Fig. 1. — Photograph of an Al₆Cu₃Li sample glued on a glass fiber. The triacontahedral morphology of the quasicrystal is visible with a 5-fold axis being perpendicular to the plane of the figure.

Shechtman and D. Gratias [2]. The same samples have been used for quantitative measurements of peak intensities for structure determination, on a four-circle diffractometer [5].

Monochromatic Laue transmission photographs of very long exposure time were taken using MoKα (0.711 Å) as well as CuKα radiation (1.54 Å) with the 2-fold axis A perpendicular to the incident beam direction. In a systematic manner, the sample orientation was varied in turning around A with steps of 2°. In figure 2 (a, b, c), the patterns recorded for special orientations of the sample are shown: they correspond respectively to the 2-, 3- and 5-fold axes parallel to the incident beam. In this way, we were able to prove the icosahedral symmetry. The results are typical for a uniformly oriented quasicrystal. The striking general features of all patterns are:

i) The high density of diffraction peaks; due to the sensibility of the method we are able to distinguish between peak intensities up to a ratio of more than 1 000. Some peaks are strongly anisotropic in shape, even, composed out of several distinct components, and different line shapes are observed for different symmetry directions. Our findings are in good agreement with the results of a high resolution X-ray scattering study on independently grown monodomain Al₆Cu₃Li₃ quasicrystals [6]. Horn et al. discuss this phenomenon in terms of strains resulting from phason dislocations.

ii) In addition to the diffraction peaks, the patterns show clear evidence for complex diffuse scattering which obeys the icosahedral symmetry. Several kinds of diffuse features have been observed [4], the most spectacular ones being circles which are clearly visible when the 3-fold axis of the sample is aligned parallel to the incident beam (Fig. 2b).

To be able to compare the diffraction peak distribution in the reciprocal space for Al₆Cu₃Li₃ directly with the calculated diffraction patterns for an icosahedral quasicrystal, given by J. W. Cahn et al. [2], we have performed largely overexposed monochromatic precession photographs using MoKα radiation. In these experiments, another sample was used which shows, besides a very small contamination from crystalline grains, some indication of a small second quasicrystal domain with different orientation. In figure 3 (a, b, c), we present the results obtained for the zero level with the 2-, 3-, and 5-fold axes parallel to the precession axis. Once again, all peaks are enlarged/composed, and different shapes are observed for different symmetry directions. Each pattern is explored in the form of schematic drawings with a differentiation between the peak intensities.

i) All reflections can be indexed on the basis of the reciprocal quasi-lattice, using the notation introduced by J. W. Cahn et al. [2], with a quasilattice constant \( d_{0} = 19.20 \text{ Å} \). Following these authors, we were able to decide from the pattern of the 2-fold zone axis, that the parity rules for a primitive icosahedral quasilattice (P) are fulfilled.

ii) Important deviations between our experimental intensities on an Al₆Cu₃Li₃ quasicrystal and those calculated from the inverse distances of the spots in the six-dimensional primitive reciprocal lattice from the cut plane [2] are found. Some prominent reflections which are predicted by the model with a very strong intensity, as e.g. 4/6 2/4 0/0 or 3/4 3/5 2/3 are not visible on the patterns of figures (3a, 3c), others such as e.g. (4/6 4/6 0/0) or (2/4 2/4 0/0) are visible but with only a very small intensity (cf. Fig. 3a). On the other hand, many more diffraction peaks of smaller intensities appear in the photographs as a result of the very long exposure. The intensity modulations are certainly related to the atomic ordering (decoration) in the Al₆Cu₃Li₃ quasicrystal, which is not yet known.

iii) The precision of measurements allowed a differentiation between a description based on an icosahedral symmetry and the Pauling interpretation [7] using icostwins of a primitive cubic lattice with a lattice constant of about 25 Å. We have demonstrated that Al₆Cu₃Li₃ quasicrystals can be perfectly described with a primitive icosahedral quasilattice.

iv) Using the results of the precession experiments, we have been able to identify the peaks in the Laue patterns of figure 2 (a, b, c): some characteristic reflections are indexed in the figure description.

In perfect agreement with the monochromatic-Laue results on the first sample, we observed again diffuse scattering in form of rings in the precession photographs of figure 3b. From a systematic study, we were able to prove that these rings result from
Fig. 2. — Monochromatic transmission X-ray Laue diffraction patterns obtained with a) a 2-fold axis, b) a 3-fold axis, c) a 5-fold axis of the sample parallel to the incident beam. The CuKα radiation (λ = 1.54 Å) has been selected using (002) reflection of a pyrolitic graphite monochromator. For some typical reflections, N and M values, multiplicities and indexes are given, following the indexing method proposed by J. W. Cahn et al. [2].

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<td>36</td>
<td>60</td>
<td>0/2 2/4 0/0</td>
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</table>

The λ/2-contamination is negligible, except for a few diffraction peaks of very small intensity; the point labelled 6 on the photograph corresponds to a centre of diffuse circle; it can be indexed as 1/1 1/2 0/0 (N = 7, M = 11, multiplicity = 12); its very small intensity is not due to a violation of the parity rules given in [2] for icosahedral primitive quasilattice (i.e. h + k' = 2 n, k + I' = 2 n, l + h' = 2 n) but to a very small λ/2 contamination. A small contamination from residual crystalline phases is revealed in form of punctuated powder rings. These spots directly give the order of magnitude of the experimental resolution.

The most intense shells are located on the 5-fold axis. The centres of these twelve spherical shells are points of the reciprocal quasilattice which are forbidden by parity rules (see Fig. 3a (1/1 1/2 0/0)), the corresponding distance in the direct space being 3.86 Å. From the radius of the circle, a characteristic distance of 16.3 Å can be deduced. There is some indication for similar diffuse scattering located at a larger distance from the origin in the reciprocal space; their intensity is much lower (centres of circles at e.g. 1/1 3/4 0/0 or 2/3 3/5 0/0). This diffuse
Fig. 3. — Monochromatic X-ray precession photographs obtained for the zero-level reciprocal planes with a) a 2-fold axis, b) a 3-fold axis and c) a 5-fold axis parallel to the precession axis; each pattern is explored in form of a schematic drawing with differentiation between peak intensities: strong, medium and small according to the size of the circles. Three types of symbols are used: full circles •, dotted circles ○, and combined full and open circles ◐. In this form, we give a comparison between the experimental results and the calculated intensities (see [2]). • ◐ both correspond to observed reflections; ◐ stays for peaks which are not present in the calculated patterns [2]; ○ denotes peak positions present in the calculated patterns for which no intensity was observed.

scattering in form of spherical shells related to icosahedral symmetry is a new and exciting feature for quasicrystals. In order to test a possible explanation by a density wave, a X-ray small angle scattering experiment has been performed; the research of a possible diffuse spherical shell centred on the origin of the reciprocal lattice has been unsuccessful. We think of the only tentative explanation by a displacement wave. A temperature dependent investigation of the diffuse scattering is now in progress in order to decide on the static or dynamic character of this phenomenon.

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