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THE EXAFS OF QUASICRYSTALS

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Abstract - EXAFS data for a number of Al-based quasicrystalline alloys are surveyed. A comparative EXAFS study of icosahedral Al_{86}Mn_{14}, Al_{85.5}Mn_{7}Cr_{8} and Al_{86}Cr_{14} phases is presented in detail. To interpret the EXAFS results, an icosahedral model is proposed in the framework of the α (Al-Mn-Si) structure and in close relation to recent theories of Mackay icosahedron packing.

I - INTRODUCTION

"Icosahedral crystals : where are the atoms ?". This is the question asked by Per Bak, a theoretician studying the quasicrystalline structure in a recent publication (1). Since their recent discovery by Shechtman, Blech, Gratias and Cahn (2), the icosahedral crystals have generated extensive theoretical and experimental studies. A most puzzling problem is the determination of the actual atomic positions of these phases. Several X-ray and neutron scattering investigations have been performed and their diffraction patterns indexed using the 6 fivefold symmetry directions. However neither electron microscopy nor X-ray and neutron diffraction could answer the question of atomic positions within the quasilattice cell. Moreover no simple mathematical model can possibly describe the structure. The only models (3,4) based on the α (Al-Mn-Si) structure, which give reasonable agreement with the actual available data for both X-ray and neutron spectra, predict too low a mass density.

To elucidate the nature of the local structure, EXAFS has the great advantage to allow, easily enough, the reconstruction of the experimental oscillations in the k-reciprocal space using a simple formula containing the parameters of the real space : i.e. the type of the neighbour atoms around a given central atom, their distances and their numbers. EXAFS can give directly this information and try to determine the local order.

II - WHAT ARE THE QUASICRYSTALS ? = THE FORBIDDEN SYMMETRY

The quasicrystalline alloys are generally prepared by melt-spinning, so they are obtained in the form of ribbons. The microstructure of the Al based quasicrystals examined by transmission electron microscopy show quasicrystalline grains of flower shape, embedded in a fcc aluminium matrix. Their diffraction patterns show Bragg peaks as sharp as those of single crystals but they present
icosahedral symmetry, including fivefold symmetry axes. This is at variance with a well-known theorem in crystallography which states that fivefold symmetry axes can never appear in a truly long-range periodic crystal. Therefore, the new structure is like a crystal in that it has long range translational order and long range orientational order. However the translational order is not periodic. Instead, the new structure is quasiperiodic. There exists a space filling arrangement of a small number of different building blocks (Penrose tiles) with icosahedral diffraction patterns. How are these tilings related to the actual structure is the central question.

III EXAFS REVIEW = STATE OF ART

To answer this question, several EXAFS studies have been undertaken on Al Mn and Al Mn Si alloys. A pioneering work was published in November 1985 by Stern, Ma and Boulton (5). They reported a comparative study of quasicyristalline and crystalline Al₆ Mn powders. They remarked first that the amplitude of the spectrum of the quasicrystal is smaller than those of the crystal by a factor \( \tau^5 \) (\( \tau \) is the golden mean). After analysis, using the Al₆ Mn crystal as a standard, they found two types of Mn sites, the average Mn-Al bond being closely the same at the two sites, with no drastic change of the coordination number but one of the sites having a larger disorder. They also noted some change beyond \( R = 5 \) Å between the quasicrystal and the crystal which they interpreted by distortion of the bonds in the quasicrystal. They concluded that their results showed that the icosahedral phase was not related to the crystalline \( \alpha \) (Al Mn Si) phase.

Three EXAFS studies (6,7,8) have recently been reported for icosahedral Al Mn and Al Mn Si alloys and comparison made with \( \alpha \) (Al Mn Si) and to the orthorhombic Al₆ Mn phase. All these papers reported rather small intensities of the spectra of the icosahedral phases since a straightforward analysis of the data gave about 6 Al neighbours instead of 10 in Al₆ Mn (Ref. 9) and 9±12 in \( \alpha \) (Al Mn Si) (Ref. 10). So, as remarked by Boyce et al. (7) this rules out the Mn being the center of an icosahedron. The apparent loss of coordination was interpreted as the signature of a broad asymmetric distribution similar to metallic amorphous alloys (11). Different types of two subshell fits (two gaussian or two asymmetric subshells) gave approximately same results. In an attempt to quantify the distances and coordination numbers, we obtained 2.55 and 2.78 ± 0.05 Å for the first Mn-Al distances. All these models supposed Al first neighbours. We have also considered the possibility of the neighbourhood of a Mn atom to consist of Al and Mn atoms (8). This yielded fits of equivalent quality as two Al subshells although no Mn-Mn contact exists in Al-Mn compounds with up to 33 % Mn. The resulting radial distribution \( F(R) \) based on Al first neighbours showed close resemblance to those in \( \alpha \) (Al Mn Si). On the other hand, neither icosahedral phase showed much resemblance to the orthorhombic phase. Finally, Marcus et al. (6) concluded that the icosahedral Al Mn Si resembles a distorted \( \alpha \) phase and may be built of icosahedra glued together with Al atoms as in the \( \alpha \) structure. They suggested also that i-Al Mn is perhaps a more disordered version of i-Al Mn Si.

More recently, Maurer (12) has compared i-Al Mn to the hexagonal Al₆ Mn phase. As a matter of fact, the Al₆ Mn, samples consist of icosahedral grains plus some Al matrix. Therefore, the composition of the quasicrystal is near those of Al₆ Mn. Unfortunately, although the crystal structure of h-Al₆ Mn is well established, the positions of the atoms within the unit cell are not yet resolved. Nevertheless, from that EXAFS study, the icosahedral Al Mn structure could appear as a smeared version of the hexagonal phase.

While all these papers mostly concern the first neighbourhood of a Mn atom, Ma et al. (13) have studied in detail the more distant shells in connection with the \( \alpha \) (Al Mn Si) structure (10) and related models (3, 14). To interpret the peaks at large \( R \) distance in the Fourier transforms of i-Al Mn and i-Al Mn Si, they proposed a model based on structural units in the form of Mn icosahedron, with different connections of the Mn-icosahedra in the two icosahedral phases and in the \( \alpha \) (Al Mn Si) phase.
Most recently, Heiney et al. (15) have just finished a study of i-(Al Mn Ru Si) alloys where the change in the local environment with addition of Ru is discussed in the hypothesis that the Ru atoms stabilize the icosahedral phase.

IV = i-Al (Mn, Cr) SYSTEMS

IV = 1 Data collection and analysis

To get new insights into the local structure of icosahedral phases, the EXAFS above the Mn and/or Cr K-absorption edges of icosahedral Al$_{\text{x}}$Mn$_{1-x}$, Al$_x$Mn, Cr$_a$ (Fig. 1) and Al$_{\text{x}}$ Cr$_{1-x}$ alloys have been recorded. This study was done in connection with neutron scattering experiments (16) using isomorphic substitution. The negative coherent length of Mn for thermal neutrons provided a variable contrast between the alloys.

The samples were prepared by G. Regazzoni and R. Rey-Flandrin (Aluminium Pechiney, Voreppe, FRANCE). They were obtained by rapid quenching on a rotating copper wheel using a melt-spinning method and their microstructure checked by transmission electron microscopy. Similar electron diffraction patterns were obtained for the three alloys (17). In the same way, the $\chi(k)$ EXAFS spectra (Fig. 2) show a striking resemblance so that some similar local ordering has to be present in the different icosahedral alloys.

The Fourier transforms (FT) of $k^2 \chi(k)$ exhibit, for all the alloys, a main peak at about 2 Å (uncorrected for phase shift). However, in the case of i-AlCr, a noticeable peak at 4.2 Å is also observed (Fig. 3). These results have to be compared with the neutron data (16) obtained on the same samples. Strong differences exist between the diffraction patterns which cannot be simply explained by the different scattering lengths of Mn and Cr. They could be due to somewhat different mean or long range order or even to small differences in the local order (for example $\Delta R$ changes $\pm 0.02$ Å).

The peak at 4.2 Å has its exact counterpart in the FT obtained for a pure chromium foil (Fig. 3). Moreover, the inverse FT of these two corresponding peaks are in phase through all the energy range. In pure Cr, this peak is due principally to the 24 fourth neighbours at 4.78 Å. Some contribution comes, however, from the fifth shell of 8 Cr at 5.00 Å so that, when extracting experimental amplitudes and phase shifts, it was analysed as being due to 32 atoms at an average distance 4.835 Å. Then, the corresponding peak in i-Al Cr was found to be due to 5-7 Cr at about 4.85 ± 0.05 Å.

For the three alloys, similar inverse FT of the first peak (2 Å) were obtained so that the same fitting could be found with small changes of the parameters N, R and $\sigma$ ($\Delta N = \pm 0.5$, $\Delta R = \pm 0.05$ Å, $\Delta \sigma = \pm 0.02$ Å). Therefore, only the i-Al Cr results (18) will be discussed in the following. Theoretical amplitudes and phase shifts (19) were used and different types of Gaussian subshells fits were tried. For example, a single Al gaussian shell gave a coordination of only 6 Al atoms at 2.55 ± 0.03 Å. Then the fitting was performed using the $\alpha$(Al Mn Si) structure as a model.

IV = 2 $\alpha$(Al Mn Si)

Using crystallographic data (10) the cubic $\alpha$(Al Mn Si) phase has recently (3, 14) been described as a bee packing of Mackay icosahedra (20). In the basic unit, the Mn atoms are located at the vertices of an icosahedron, the centre of which is unoccupied (Fig. 4). 12 Al atoms are located at half the distance of the vectors pointing to the Mn vertices, thereby forming themselves a half-sized parallel icosahedron. Moreover, 30 Al atoms occupy the midpoints of the edges of the larger Mn icosahedron. If a labels the edge of the Mn icosahedron, the atoms surrounding a Mn atom are 1 Al at d/2, 5 Al at a/2 and 5 Mn at a. In this description, there are only 6 Al neighbours. Icosahedra of the same orientation are packed with their faces directed towards one another forming a contracted octahedron. The connection occurs along threefold axes.
Figure 1: Cr and Mn K-edge absorption curves of icosahedral $\text{Al}_{85} \text{Mn}_{15}$ alloy.

Figure 2: Experimental EXAFS spectra for icosahedral alloys. $\text{Al}_{85} \text{Mn}_{15}$ (a), $\text{Al}_{85} \text{Mn}_{15}$, $\text{Cr}_8$ (b) Mn edge, (c) Cr edge and $\text{Al}_{85} \text{Cr}_{15}$ (d).

Figure 3: Fourier transforms of $k^2 x(k)$ data for (a) pure chromium (b) icosahedral $\text{Al}_{85} \text{Cr}_{15}$ (multiplied by 10). The FT were obtained with the same $k$-window ($10 \sim 300$ eV).
IV 3 Icosahedral model

With the Mackay icosahedron description of the \( \alpha \) phase, the main contribution of neighbours around a Mn/Cr atom arises from the 5 Al atoms at \( a/2 \) and does correspond to the EXAFS distance of about 2.55 Å. This yields \( a = 5.10 \) Å, which is the edge length of the Mn/Cr icosahedron in the Audier and Guyot model (3).

To determine the missing Al atoms, we have first looked for 1 Al at about 2.40 - 2.45 Å by using a fitting program. The best fit was obtained for 5 Al at 2.60 Å (\( \sigma = 0.12 \) Å) and 1 Al at 2.425 Å (\( \sigma = 0.114 \) Å). This last distance corresponds exactly to \( d/2 = 2.425 \) Å, the distance between the Al and Mn icosahedra in the Audier and Guyot model. But there are still only 6 Al neighbours, so we have tried to find another subshell consistent with the EXAFS spectrum. This can be done with Al atoms at 2.75 ± 0.05 Å. At this distance 1 to 5 Al atoms can be found according to the \( \sigma \) parameter value (\( \sigma = 0.13 \approx 0.17 \) Å). The resulting radial distribution of the Al atoms is asymmetric (18) and compares well with the histogram of the Mn-Al distances in \( \alpha \) (Al Mn Si). We have also considered the possibility of Al and Cr first neighbours. This fit of the inverse FT of the first peak yielded a Cr-Cr distance equal to 2.59 ± 0.05 Å. The extra Cr/Mn subshell (Mn=Mn = 2.61 Å) could explain the differences obtained in the neutron diffraction patterns (16).

**Figure 4**: Schematic representation of the \( \alpha \) (Al Mn Si) structure constructed with Mackay icosahedra. It is also a possible model of the icosahedral Al (Mn, Cr) alloys. The small circles represent Cr/Mn atoms and the big ones the Al atoms.

**DISCUSSION**

It is clear that there is not a unique fit of the EXAFS due to strong correlations between parameters. Nevertheless, a number of important features can be extracted from the systematic comparison between the different EXAFS studies. First the environment around the average Mn/Cr site contains at least two shells, the first distance being 2.55 Å. Secondly, the second subshell (Al or Mn/Cr) is generally not taken into account in the theoretical works (3,4). This could explain the too small value found for the calculated density.
The farther neighborhood appears different in the several Al-based quasicrystals and different from those in $\alpha$ (Al Mn Si). This could be due to more or less disordered bondings inside the icosahedron or to different connections between the icosahedra.

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REFERENCES

17. SAINFORT, P., Private communication