

Al p-like states in highly resistive icosahedral alloys

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 L717

(<http://iopscience.iop.org/0953-8984/8/49/001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 23:02

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Al p-like states in highly resistive icosahedral alloys

Esther Belin-Ferré^{†§} and Jean Marie Dubois[‡]

[†] Laboratoire de Chimie Physique Matière et Rayonnement URA 176 and GDR CINQ, 11 rue Pierre et Marie Curie, 75231 Paris Cédex 05, France

[‡] Laboratoire de Science et Génie des Matériaux Métalliques URA 159 and GDR CINQ, Ecole des Mines, Parc de Saurupt, 54042 Nancy Cédex, France

Received 26 June 1996, in final form 1 August 1996

Abstract. This letter presents a systematic study of Al p states in various icosahedral quasicrystals by means of absorption and emission x-ray spectroscopies. For the sake of comparison, crystals showing different degrees of icosahedral order are examined as well. Direct evidence is given for the first time that the metallic character attached to the constituent atoms tends to disappear in all stable Al–3d (4d and 5d) transition metal icosahedral quasicrystals known at present. The density of conduction states at the Fermi level and beyond (up to 3–5 eV) has indeed dramatically vanished in the icosahedral quasicrystals. In crystalline approximants the same effect is observed but to a much lesser extent. This effect is strongly related to the resistivity increase observed by electron transport measurements. A discussion of the results is proposed in the light of a recent model based upon a hierarchy of quantum wells.

Quasicrystals are alloys made of good, conventional, metals, e.g. Al and Cu added to Fe. Their physical properties differ very significantly from metallic behaviour embodied by the free electron model. For instance, they show high electrical resistivity that furthermore increases with decreasing temperature (Poon 1992). Details of the many surprising properties of quasicrystals may be found in reviews and text books (Janot 1992).

The purpose of the present letter is twofold. First, we bring direct evidence that the metallic character attached to the constituent elements (Al, Cu, Fe, Ru, Pd, Mn, Re) has nearly disappeared in all stable icosahedral crystals known so far. Second, we show that these quasicrystals present a marked, deep pseudo-gap like the one observed in Hume–Rothery intermetallic crystals but which is most important in the more resistive quasicrystals. To substantiate this view, we have used x-ray emission and absorption spectroscopy techniques, able to selectively probe Al states, and we have applied these techniques to several crystalline compounds of the Al–Fe(Cu) system that show increasing icosahedral order. Similarly, we have examined stable icosahedral alloys with increasingly marked resistive behaviour. We then show that both the pseudo-gap deepening and the disappearance of conduction states take place correlated to the enhancement of the icosahedral order in the materials. As long as true quasicrystals, i.e. with a substantial degree of lattice perfection, are considered, it is therefore no longer sufficient to refer to a gap opening, Hume–Rothery-like, mechanism at the boundaries of the pseudo-Jones zone (Friedel and Dénoyer 1987). One may also be inclined to consider the condensation of electrons on critical states. The agreement of our data with such a model (Janot and de Boissieu 1994, Janot 1996) is advocated at the end of the paper.

§ Corresponding author.

To date, computation techniques cannot study the densities of states of true quasicrystals since the Bloch theorem is no longer valid for such structures and also because a complete description of all the atomic positions in the solid, that could be used for cluster type calculations, is not available yet. Calculations have been performed so far for crystalline approximants of various icosahedral as well as decagonal quasicrystals (see for example Fujiwara and Yokokawa 1991, Fujiwara 1993, Trambly de Laissardière and Fujiwara 1994, Hafner and Krajci 1992, 1993, Krajci *et al* 1995, 1996, Sabiryanov *et al* 1995). Thus, it is important to investigate by experimental means the electronic structure of this new class of solids to understand their electronic and physical properties and ascertain the respective roles of the local and long-range orders in the electronic densities of states.

For such a purpose various techniques may be used, for example photoemission and (or) x-ray spectroscopies. Photoemission spectroscopy (PES) scans the binding energies of inner levels as well as those of all the states of the occupied band in a solid whereas inverse photoemission spectroscopy (IPS) investigates unoccupied states; neither technique provides any atomic site selectivity. The spectral intensities are modulated by photoemission cross sections and the energy resolutions are generally as good as 0.4–0.6 eV. However, due to the photoemission cross sections, d- and f-like states are significantly favoured with respect to p or s ones. Since as already mentioned, most of the quasicrystalline alloys are intermetallic Al based alloys with Cu or transition metals (TMs), photoemission experiments performed so far have not investigated the conduction band. They supplied the energy distribution of Cu or TM d occupied states (Mori *et al* 1991, Stadnik and Stronik 1993) i.e. localized-like states. They could not observe the contribution of the Al states.

By contrast, x-ray emission and absorption spectroscopies allow us to analyse separately occupied and unoccupied electronic distributions around a given atomic site of a solid and for the various s, p, d, . . . spectral characters. The energy resolution which may be achieved in these experiments varies from about 0.3 eV to a few electron volts according to which inner level is involved in the x-ray transitions and to the experimental resolution. Fortunately enough for our present purpose, emission and absorption spectra for Al p states involve the 1s inner level whose energy width is less than 0.4 eV (Krause and Oliver 1979). The energy resolution of the spectrometers used for emission or absorption experiments in the energy range of the corresponding x-ray transitions is about 0.3 eV, thus ensuring a total resolution better than 0.5 eV. Consequently, the occupied Al 3p and unoccupied Al p electronic distributions can be easily investigated using the x-ray spectroscopy techniques. Since p states are of rather extended character, they are expected to be more sensitive than localized states to modifications due to changes in the atomic site neighbourhood.

These techniques were used to probe ternary Al(Cu or Pd)(Fe, Mn, Ru or Re) icosahedral quasicrystals (Belin *et al* 1994a,b, 1996, Belin-Ferré *et al* 1996, Mayou 1994). The description of the occupied and unoccupied bands of the solids imposes the adjustment of the various spectral curves on the binding energy scale, i.e. to placing the Fermi level on the x-ray transition energy scales. This was achieved by complementary measurements of the binding energies of the inner levels involved in the probed x-ray transitions.

The electronic interactions were traced in the close vicinity of the Fermi level (E_F) between Al 3p–s,d states and occupied Fe (Mn, Ru or Re) states of d character as well as the interactions between the Al states and Cu (Pd) d states at about 4 eV from E_F . In the unoccupied bands, at E_F and in a short energy range beyond, Fe (Mn, Ru or Re) d-like states interact with Al p states. Beyond about 1 eV from E_F , the Fe (Mn, Ru or Re) states are d–s hybridized; again, around 2 eV (4 eV) from E_F , Cu (Pd) d-like states, are also present, that at larger energies are also d–s hybridized. Thus, from all these results, it emerges that on both sides of the Fermi energy the occupied and unoccupied bands are

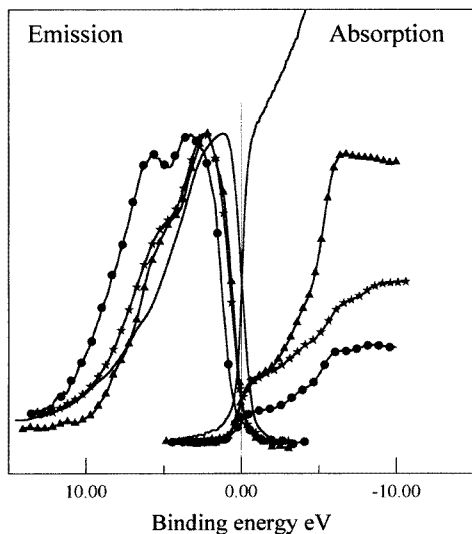


Figure 1. Occupied Al 3p state distributions in Al (full line), $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$ (stars), $\text{Al}_{71}\text{Pd}_{19}\text{Mn}_{10}$ (triangles) and $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$ (full circles) normalized so that the maximum intensity of the occupied states density is equal to unity. For simplicity, the $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$ curve is not drawn. The unoccupied Al p state density shown on the right-hand side of the figure corresponds to fcc Al (full line), $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$ (stars), $\text{Al}_{71}\text{Pd}_{19}\text{Mn}_{10}$ (triangles) and $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$ (full circles) adjusted to the occupied band intensity at E_F . See figure 2 for the other samples.

limited by TM states of rather localized character since they are d-like in interaction with the Al p-like states whereas the s-like states, pure or hybridized to d states, are pushed far away from E_F .

In this paper, we compare and discuss the occupied Al 3p and unoccupied Al p electronic distributions in highly resistive icosahedral $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$, $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$, $\text{Al}_{71}\text{Pd}_{19}\text{Mn}_{10}$ as well as $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$. For such a purpose we have probed the x-ray transitions from the occupied band to Al 1s states and from Al 1s states to the unoccupied band. In each case, the Fermi level has been placed on the x-ray transition energy scales within ± 0.1 – 0.2 eV by measurements of the Al $2p_{3/2}$ binding energy and of the Al $2p_{3/2} \rightarrow 1s$ x-ray transition energy. The various Al 3p and p spectra were taken at room temperature. The corresponding distribution curves are shown in figure 1 together with the same curves for pure fcc Al.

The Al 3p distribution curves are each normalized to arbitrary unit value at their maximum intensity. The curves for $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$, $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$ and $\text{Al}_{71}\text{Pd}_{19}\text{Mn}_{10}$ are very similar; they show a notable shoulder beyond 5 eV from E_F that is not present in the curve for pure Al. This shoulder is even much more marked for $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$, the Al 3p band is more intense and extends over a wider energy range than for the three other quasicrystals. In pure metallic Al, the intensity of the 3p edge at E_F (I_{E_F}) is half the maximum intensity of the Al 3p band as expected for a free electron conventional metal. In the icosahedral alloys, I_{E_F} is much lower than in the metal. It is found within 0.1–0.09 for $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$, $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$ and $\text{Al}_{71}\text{Pd}_{19}\text{Mn}_{10}$ on the one hand and it is 0.07 for $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$ on the other hand. This result emphasizes the non-metallic behaviour of icosahedral quasicrystals, even at room temperature, as compared to the behaviour of fcc

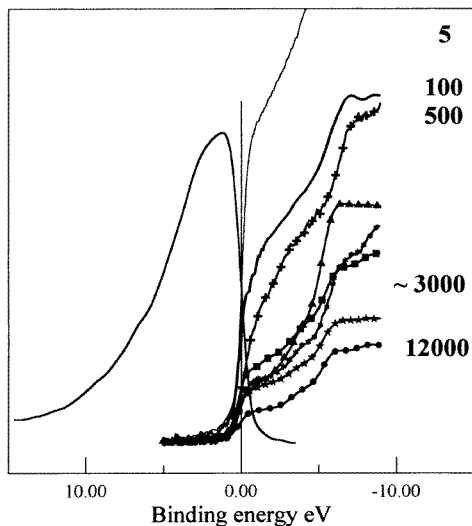


Figure 2. Occupied Al 3p and unoccupied Al p distributions in fcc Al (full thin line), Al p distributions in tetragonal $\text{Al}_7\text{Cu}_2\text{Fe}$ (thick full line), monoclinic $\text{Al}_{13}\text{Fe}_4$ (crosses), rhombohedral $\text{Al}_{62.5}\text{Cu}_{26.5}\text{Fe}_{11}$ (line with squares), icosahedral $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$ (line with sixfold stars) icosahedral $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$ (line with fivefold stars), icosahedral $\text{Al}_{71}\text{Pd}_{19}\text{Mn}_{10}$ (line with triangles) and icosahedral $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$ (full circles) adjusted to their Al 3p intensity value at the Fermi level. The Al 3p counterparts are not shown for clarity except for fcc Al. The numbers on the right of the figure are averaged values of the resistivities in microohm centimetres taken at room temperature.

Al. Note however that, due to the intensity normalization scheme used here, the actual density of states at E_F is obviously much smaller than these values referred to that of fcc Al. Very low equivalent free electron values can thus be attached to these alloys. These low values are consistent with the fact that the electronic velocity is very small in the highly resistive quasicrystals in comparison to free-electron-like metals (Mayou 1994). A significant difference between $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$, $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$ and $\text{Al}_{71}\text{Pd}_{19}\text{Mn}_{10}$ on the one hand and $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$ on the other hand arises from the important shift of the Al 3p edge far from E_F . Indeed, within the limits of the experimental precision on energies, the distance from E_F of the Al 3p edges taken at half maximum intensity, which we label δ , is zero for pure fcc Al but becomes about 0.6 ± 0.1 eV for $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$ and $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$ as well as for $\text{Al}_{71}\text{Pd}_{19}\text{Mn}_{10}$ whereas it is as large as 1.2 ± 0.2 eV for $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$.

The low I_{E_F} and large δ values lead to the formation of a noticeable pseudo-gap in all these quasicrystalline samples. It is remarkable that the decrease of I_{E_F} together with the increase of δ on the one hand and the increase of the electrical resistivity on the other hand vary in the same way from one sample to another. Values of the electrical resistivity at room temperature in microhm centimetres are reported in the right-hand side part of figure 2. It is about the same for the three first quasicrystals i.e. about $3 \times 10^3 \mu\Omega \text{ cm}$ (Klein *et al* 1991, Lanco *et al* 1992, Poon 1992) and is noticeably higher than $10^4 \mu\Omega \text{ cm}$ for $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$ (Pierce *et al* 1993, 1994). Let us recall, as mentioned above, that when going from Al to the highest-resistivity quasicrystal, the Al 3p states are not only shifted from E_F but also spread over a wide energy range so that they are of remarkable intensity where these states almost totally vanish in pure Al.

It is less easy to normalize absorption curves due to the non-finite energy range extent

of the conduction bands. Here, thanks to the band overlap at the pseudo-gap, the Al p sub-band curve may be normalized by adjusting its intensity at E_F to the value of the Al 3p sub-band. Within this adjustment scheme, a drastic reduction of the Al p conduction states is pointed out when going from pure Al to the icosahedral quasicrystals: in fcc aluminium, the intensity of the Al p states increases beyond E_F with respect to the occupied band in full agreement with the free electron picture. Conversely, this is no longer the case for the icosahedral alloys, in which the dramatic Al p state depletion is the more marked for the more resistive alloys.

In the one-electron approximation, emission or absorption x-ray processes involve respectively transitions from the occupied states to a core level and from a core level to normally empty states. The emitted or absorbed radiations are connected to the matrix element M of the transition probability that depends upon the overlap between the wave functions of the initial and final states of the system. M is usually constant or varies slowly against energy. Our adjustment of the Al p state distributions implies that at E_F M should be the same for the transitions from the occupied band to Al 1s and from Al 1s to the unoccupied band. The initial state of the Al 3p emission and the final state of the Al p absorption processes are the same, they imply a hole in the Al 1s inner level. The initial state of the absorption is the background state whereas the final state of the emission involves a hole in the outer occupied band. Thus, our adjustment in the intensity scale implies that at E_F there is no significant difference for the Al wave functions of the various alloys from the ground state with respect to a state with a hole of p-like character in the occupied bands, i.e. a hole on a specific site of the solid of not totally extended character although not fully localized. This adjustment procedure is impossible to assess theoretically because of the difficulties encountered in carrying out band structure and wave function calculations valid for true quasicrystals.

In the framework of our adjustment, we have interpreted the important depletion around E_F as the consequence of the interaction between Al p states and TM d-like states that somewhat modifies the nature of the electronic states in the energy ranges where the interactions take place. Note that the same kind of interaction with Pd or Cu could be responsible for secondary depletions that are observed in the Al distributions about 4 eV below E_F in the occupied band and about 2 eV or further above E_F in the unoccupied band.

It is now questionable whether the Hume–Rothery mechanism (see Friedel and Dénoyer 1987) is sufficient to explain the considerable depletion of the Al states observed for the highly resistive quasicrystals in both Al 3p and p distributions. Indeed, we have investigated many Hume–Rothery-like alloys as well as intermetallic approximant crystals. We have found that, although I_{E_F} may be low and δ may be large and despite the fact that d-like states may limit the occupied and unoccupied bands around E_F as in the icosahedral alloys, the Al p state reduction is much less important with respect to pure Al than it is in the very resistive quasicrystals (Dong *et al* 1994). To exemplify, we have plotted in figure 2 the Al 3p and p curves for Al_{70.5}Pd₂₁Re_{8.5}, Al₆₂Cu_{25.5}Fe_{12.5}, Al₆₅Cu₂₀Ru₁₅, Al₇₁Pd₁₉Mn₁₀ icosahedral quasicrystals and those for tetragonal Al₇Cu₂Fe (Bown and Brown 1956), monoclinic Al₁₃Fe₄ (Black 1955) and the rhombohedral approximant Al_{62.5}Cu_{26.5}Fe₁₁ (Audier and Guyot 1990) of the Al–Cu–Fe icosahedral quasicrystal. The tetragonal compound has no icosahedral order whereas monoclinic Al₁₃Fe₄ consists of planar arrangements of pentagonal tiles with atoms at vertices. These tiles are packed on top of each other so that only slightly distorted icosahedra form (see the article by Audier and Guyot (1990) for more details). The rhombohedral approximant, with giant unit cell, shows a very pronounced icosahedral order both locally and at long distance. The Al p bands for these crystalline alloys are

of noticeably higher intensity than in the quasicrystals studied above. This relatively high intensity of the Al p conduction band is in line with their electrical resistivity values at room temperature that are about 20, 500 and 2700 $\mu\Omega$ cm for Al₇Cu₂Fe, Al₁₃Fe₄ and rhombohedral Al_{62.5}Cu_{26.5}Fe₁₁, respectively, i.e. noticeably lower than for the quasicrystals analysed here. Furthermore, the temperature coefficient of the resistivity is positive in Al₇Cu₂Fe, as in metals, but is negative in the rhombohedral approximant (Berger 1994).

Our results for the occupied Al 3p and unoccupied Al p state distributions of highly resistive Al₆₂Cu_{25.5}Fe_{12.5}, Al₆₅Cu₂₀Ru₁₅ and Al₇₁Pd₁₉Mn₁₀ are in agreement with a model proposed recently (Janot and de Boissieu 1994, Janot 1996). In this model, the stability of the quasicrystals is assigned to the localization of electrons in a succession of inflated spherical quantum wells attached to successive, hierarchical, generations of aggregates. Most of the densities of states form a semi-bonded occupied band that sharply decreases at E_F , detrimentally to the extended conduction band, thus expected to be of very flat density. Both bands are separated at the Fermi level by an asymmetric valley. Again, our present results confirm the previous observations on the other very resistive quasicrystals: for the highest-resistivity Al_{70.5}Pd₂₁Re_{8.5} alloy, the occupied densities of states spread over a wider energy range than for the two other high-resistivity quasicrystals (Belin-Ferré *et al* 1996). All the same, its unoccupied band flattens more than for the two other quasicrystalline alloys. This once more supports the model of a hierarchy of quantum wells. In the Al-Pd-Re icosahedral quasicrystal, the occupied states vanish so much more markedly as compared to the other two alloys that one may even guess, if this latter model is valid, that the atomic clusters are no longer simply Mackay icosahedra, as in Al-Cu-Fe in which the inflation ratio is τ^3 (τ is the golden mean). They may rather be clusters of larger size that force the hopping distance to increase. For instance, an atomic cluster built on a Mackay icosahedron but bounded by a supplementary larger external shell such as a triacontahedron would produce a better agreement with conductivity data. This question is open until the structure of icosahedral Al-Pd-Re is solved.

From our results, we suggest that due to the screening by d-like barriers located on both sides of E_F and because of the existence of the flat conduction band, in highly resistive quasicrystals, the motion of Al electrons across extended-like states should be somewhat slowed down even in energy ranges far from E_F . This is less effective for the crystalline related counterparts for which the Al p states display much higher intensities. Consequently, tunnelling or variable range hopping to unoccupied states, as invoked by Janot (1996) and in Klein *et al* (1991) and Lanco *et al* (1992) to account for the electrical conductivity of the highly resistive quasicrystals, is consistent with our observations.

Yvonne Calvayrac, Claire Berger and Joseph Poon are warmly thanked for giving samples of very high structural quality. Anne Sadoc and Zoltan Dankházi are acknowledged for their contribution to experiments.

References

- Audier M and Guyot P 1990 *Quasicrystals* ed M V E Jaric and S Lundqvist (Singapore: World Scientific)
- Belin E, Dankházi Z, Sadoc A and Dubois J M 1994a *J. Phys.: Condens. Matter* **6** 8771
- Belin E, Dankházi Z, Sadoc A, Dubois J M and Calvayrac Y 1994b *Europhys. Lett.* **26** 677
- Belin E, Dankházi Z, Sadoc A, Flank A M, Poon J S, Müller H and Kirchmayr H 1996 *Proc. 5th Int. Conf. on Quasicrystals (Avignon, 1995)* ed C Janot and R Mosseri (Singapore: World Scientific) p 435
- Belin-Ferré E, Dankházi Z, Sadoc A, Berger C, Müller H and Kirchmayr H 1996 *J. Phys.: Condens. Matter* **8** 3513
- Berger C 1994 *Lectures on Quasicrystals* ed F Hippert and D Gratias (Les Ulis: Editions de Physique)

- Black P J 1955 *Acta Crystallogr.* **8** 43
Bown M G and Brown P J 1956 *Acta Crystallogr.* **9** 911
Dong C, Perrot A, Dubois J M and Belin E 1994 *Mater. Sci. Forum* **150 & 151** 403
Friedel J and Dénoyer F 1987 *C. R. Acad. Sci., Paris II* **305** 171
Fujiwara T 1993 *J. Non-Cryst. Solids* **153 & 154** 390
Fujiwara T and Yokokawa T 1991 *Phys. Rev. Lett.* **63** 333
Hafner J and Krajci M 1992 *Phys. Rev. Lett.* **68** 2321
———1993 *Phys. Rev. B* **47** 11 795
Janot C 1992 *Quasicrystals: a Primer* (Oxford Scientific)
———1996 *Phys. Rev.* **5** 181
Janot C and de Boissieu M 1994 *Phys. Rev. Lett.* **72** 1674
Klein T, Berger C, Mayou D and Cyrot-Lackmann F 1991 *Phys. Rev. Lett.* **66** 2907
Krajci M, Hafner J and Mihalkovic M 1996 *Europhys. Lett.* **34** 207
Krajci M, Windisch M, Hafner J, Kresse G and Mihalkovic M 1995 *Phys. Rev. B* **51** 17 355
Krause M O and Oliver J H 1979 *J. Phys. Ref. Data* **8** 329
Lanco P, Berger C, Cyrot-Lackmann F, Fourcaudot G and Sulpice A 1992 *Europhys. Lett.* **18** 227
Mayou D 1994 *Lectures on Quasicrystals* ed F Hippert and D Gratias (Les Ulis: Editions de Physique)
Mori M, Matsuo S, Ishimasa T, Matsuura T, Kamiya K, Inokuchi H and Matsukawa T 1991 *J. Phys.: Condens. Matter* **3** 767
Pierce F S, Guo Q and Poon S J 1994 *Phys. Rev. Lett.* **73** 2220
Pierce F S, Poon S J and Guo Q 1993 *Science* **261** 737
Poon S J 1992 *Adv. Phys.* **41** 303
Sabiryanov R F, Bose S K and Burkov S E 1995 *J. Phys.: Condens. Matter* **7** 5437
Stadnik M Z and Stroink G 1993 *Phys. Rev.* **47** 100
Trambly de Laissardière G and Fujiwara T 1994 *Phys. Rev. B* **50** 5999