The vibrational density of states of three-dimensional quasicrystals

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Abstract. We have computed the vibrational densities of states (DOS) both of several ideal approximants of icosahedral quasicrystals, up to 13/8, and of an actual $Al_{70}Pd_{21}Mn_9$ icosahedral alloy, in the framework of the harmonic approximation.

The dynamic matrix has been constructed for a spring potential in the cluster approximation. In order to compute the DOS we have used the continued-fraction expansion of the Green's function and the coefficients of this expansion have been obtained with the recursive technique.

The DOS of the 13/8 approximant is in agreement with the one already obtained in the literature, by using the commensurate approximation and the direct diagonalization. This strongly suggests that, provided the size of the cluster is large enough, the two methods are equivalent. On the other hand, recursive technique algorithms are much more convenient from the point of view of computing time.

The DOS computed for the actual case of AlPdMn shows a satisfactory qualitative agreement with the neutron-weighted DOS, measured for the same compound. This is an interesting result, since it indicates that, in spite of the simple assumption adopted for the potential, the model describes quite well the main features of the vibrational spectrum of this quasicrystal. Further improvements in this direction can then be made.

1. Introduction

In the last decade several works have been devoted to the study of the vibrational properties of one-dimensional quasicrystals. In contrast, very few works concerning two- and three-dimensional quasicrystals have been performed so far.

This striking difference is due to the fact that, in the one-dimensional case, it is possible to obtain the exact solution by using the renormalization-group analysis, while the same method cannot be straightforwardly applied to two- and three-dimensional cases. Beyond that, since this new class of ordered structures does not possess translational invariance, the direct diagonalization of the dynamic matrix, in the framework of a perfect harmonic theory, presents obvious difficulties of computation. For these reasons, other approaches than the direct diagonalization have been recently used to study such properties [1–4].

In the last few years, the interest in this subject has been also enhanced by the availability of new experimental measurements, performed on single grains of stable quasicrystals, like for example $Al_{70}Pd_{21}Mn_9$ [5, 6]. Thus a comparison between experimental and numerical results allows a significant check on the validity of the approximations introduced in the phenomenological models. This comparison will be carried out also in the present work.

In this paper we present a study of the total vibrational density of states (DOS) of icosahedral quasicrystals. For these structures, the standard method of direct diagonalization of the dynamic matrix requires a considerable amount of computer memory, even when one applies symmetry considerations [7]. To overcome this problem, we have used the continued-fraction expansion of the Green function with the recursion method [8]. This method allows us in fact to calculate the Green's function matrix elements without passing through the diagonalization of the dynamic matrix.

The recursion method is a very general mathematical tool, especially suitable for application when one has to deal with large sparse matrices. It has the advantage that no additional hypotheses (such as spatial periodicity) have to be satisfied by the operator to be tridiagonalized, so the procedure is strongly indicated in general cases in which traditional techniques are not applicable. In literature it has been already successfully employed in the calculation of electronic and vibrational properties of solids, either ordered or disordered [1–3], [9–11].

In this paper we apply the recursion method to the calculation of the DOS, in the cluster approximation, of both several approximants of an ideal quasicrystal and an actual $Al_{70}Pd_{21}Mn_9$ icosahedral alloy.

The atomic positions of the ideal approximants have been computed with the section method. We have performed the DOS calculation for the ideal approximants up to a cell of about 45 000 atoms. The results agree with those of [7, 12], obtained by using the direct diagonalization and the commensurate approximation. This strongly suggests that, provided the size of the cluster is large enough, the recursive technique is a very good approximation of the direct diagonalization. On the other hand, by using the recursive technique, we have been able to study much larger systems.

We also present results for the DOS, computed with the same technique, of a cluster of about 23 500 atoms, belonging to an actual $Al_{70}Pd_{21}Mn_9$ icosahedral quasicrystal. The atomic positions of the actual quasicrystal have been extracted by the authors of [5], by using the experimental data obtained by neutron and x-ray diffraction on a single grain of the perfect AlPdMn icosahedral phase. A satisfactory qualitative agreement is found between our result and the experimental DOS measured on the same icosahedral quasicrystal [6]. In this case, since the experimental data are neutron weighted, no quantitative comparison can be performed. However, all the features of the experimental spectrum are reproduced. We conclude that the theoretical model describes quite well the real quasicrystal behaviour, in spite of the simple form considered for the potential.

In the following section the method used to generate the 3DPT and the construction of the dynamic matrix are briefly discussed. The third section describes the recursive technique used to obtain the coefficients of the continued-fraction expansion of the Green's function. In the fourth section the results for the ideal quasicrystal approximants are shown and commented on. In the fifth section the recursive technique is applied to the case of an actual icosahedral quasicrystal, namely AlPdMn, and a comparison of the results with the experimental DOS for the same compound is carried out.

2. Structure and dynamics

In this section we briefly describe the main features of the 'section method' and the construction of the dynamic matrix. Since this method has already been used in the literature (see for example [7]) we will not enter into details.

To construct an ideal icosahedral quasicrystal, we consider a six-dimensional (6D) space

V divided into an 'internal' space V_i and an 'external' space V_e:

$$V = V_i \oplus V_e. \tag{1}$$

In the space V we choose a simple hypercubic lattice with basis vectors†

$$
\begin{aligned}
a_1 &= (n, m, 0, n, m, 0)/(\sqrt{m^2 + n^2}\sqrt{2}) \\
a_2 &= (-n, m, 0, n, -m, 0)/(\sqrt{m^2 + n^2}\sqrt{2}) \\
a_3 &= (0, n, m, m, 0, -n)/(\sqrt{m^2 + n^2}\sqrt{2}) \\
a_4 &= (m, 0, n, 0, -n, m)/(\sqrt{m^2 + n^2}\sqrt{2}) \\
a_5 &= (m, 0, -n, 0, -n, -m)/(\sqrt{m^2 + n^2}\sqrt{2}) \\
a_6 &= (0, n, -m, -m, 0, n)/(\sqrt{m^2 + n^2}\sqrt{2}).
\end{aligned}
\tag{2}
$$

The projection of the elementary cell of this lattice on the space V_i is a three-dimensional (3D) polyhedron, called a triacontahedron. On every point of the 6D hypercubic lattice we then place a triacontahedron, thus obtaining a 6D periodic structure (6DPS). If we now intersect this 6DPS with the subspace V_e we obtain a particular geometrical array. By taking m and n as integers, this array can be shown to be periodic with a cubic cell edge T given by

$$T = \sqrt{2(n^2 + m^2)}. \tag{3}$$

In particular, if m/n belongs to the Fibonacci sequence, then the array is called the m/n cubic approximant of the ideal quasicrystal. In the limit in which m/n goes to $\phi_{Au} = (1 + \sqrt{5})/2$, then an ideal quasicrystal with icosahedral symmetry and no periodicity is generated.

In the ideal quasicrystal only two tiles occur: a prolate and an oblate rhombohedron. In the periodic approximation, more than two tiles occur, due to the deformation of the triacontahedron [7].

Table 1. In the first row the number of atoms N belonging to the elementary cell are reported for various approximants of the ideal icosahedral quasicrystal, in the second row the corresponding number densities are shown.

ϕ_k	2/1	3/2	5/3	8/5	13/8
N	167	631	2530	10595	44427
ρ	5.281	4.760	4.512	4.461	4.416

In table 1 we give the values of the numbers of atoms N belonging to the elementary cell and the corresponding number densities for various ϕ_k-approximants. The values of N are obtained by including all the opposite boundaries of the triacontahedron, to restore the tetrahedral plus inversion symmetry for the approximants. This procedure has been already adopted by the authors of [7]. In the case of the ideal icosahedral quasicrystals the density is

$$\rho = \frac{4\Phi_{Au}(2\Phi_{Au}^2 + 3\Phi_{Au} + 3)}{\sqrt{8(1 + \Phi_{Au}^2)^3}} = 4.3525\ldots \tag{4}$$

† All the distances between the atoms of the approximants are expressed in units of the hypercubic lattice spacing $a = 1$.

As can be seen from table 1, the density of the approximants is converging to the ideal density.

Once we have obtained the quasilattice, the construction of the dynamic matrix is straightforward.

A spring constant model has been used for the forces [13]. In the following section we show how the dynamic matrix has been used in the framework of the recursive technique.

3. Calculation of vibrational spectra of solids with the continued-fraction technique

It can be shown [14] that the total DOS is related to the Green's function of the system by the equation

$$\rho(\omega) \equiv \sum_s \delta(\omega - \omega_s) = -\frac{1}{\pi} \lim_{\eta \to 0^+} \frac{1}{N} \mathrm{Im}\Big(\omega \ \mathrm{Tr}[\mathbf{G}(\omega + i\eta)]\Big) \tag{5}$$

where N is the number of states in the system and the ω_s^2 are the eigenvalues of the dynamic matrix. By using equation (5) the problem of computing the total DOS can be then reduced to the evaluation of the trace of the Green's function.

Let us then consider a diagonal matrix element for $\mathbf{G}$, given by

$$G_{00}(\omega^2) = \langle u_0|(\omega^2 \mathbf{I} - \mathbf{D})^{-1}|u_0\rangle \tag{6}$$

where $|u_0\rangle$ is a state of interest for the dynamic matrix $\mathbf{D}$. To evaluate the diagonal element of equation (6) we use the standard three-term recurrence relations [8, 15], that reduce the dynamic matrix $\mathbf{D}$ into a tridiagonal form. Starting from the initial state $|u_0\rangle$ we generate a new basis $\{|u_n\rangle\}$ and two sets of coefficients $\{a_n\}$ and $\{b_n^2\}$, with the following prescription:

$$a_n = \langle u_n|\mathbf{D}|u_n\rangle \qquad |U_{n+1}\rangle = (\mathbf{D} - a_n\mathbf{I})|u_n\rangle - b_n|u_{n-1}\rangle$$

$$b_{n+1}^2 = \langle U_{n+1}|U_{n+1}\rangle \qquad |u_{n+1}\rangle = \frac{1}{b_{n+1}}|U_{n+1}\rangle.$$

It is easy to show that, in terms of the $\{a_n\}$ and $\{b_n^2\}$, the expression for the Green's function matrix element, $G_{00}(\omega^2)$, is given by

$$G_{00}(\omega^2) = \cfrac{1}{\omega^2 - a_0 - \cfrac{b_1^2}{\omega^2 - a_1 - \cfrac{b_2^2}{\omega^2 - a_2 - \cdots}}} \tag{7}$$

where the number of coefficients of the continued-fraction expansion is equal to rank of the matrix $\mathbf{G}$. The idea of the recursive technique is that, by using only a small number of these coefficients, it is possible to reconstruct the matrix element G_{00} with a good precision.

The application of the recursion method to the study of vibrational properties of disordered or partially ordered systems [1–3] presents a number of advantages. A high degree of numerical accuracy can be achieved and directly controlled by appropriate stability tests. Furthermore, there is great improvement as regards computational speed and memory occupation over traditional methods which require direct diagonalization of the dynamic matrix.

In order to obtain the total DOS the choice of the initial state of the recursion must be done carefully. The expression for the DOS, equation (5), contains in fact the trace of the Green's function. Every term of the form

$$-\frac{1}{\pi} \mathrm{Im}[\omega G_{nn}(\omega + i0^+)] \tag{8}$$

is the projected DOS on a given state of interest for **D**. The trace of the Green's function can be computed by using the following procedure [16]: let us choose as initial state of the recurrence

$$|u_0\rangle \equiv \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \lambda_i |\psi_i\rangle \qquad (9)$$

where $\{|\psi_i\rangle\}$ is a given set of basis functions and λ_i are real random phases, i.e. they can assume, with the same probability, the values $+1$ or -1. With this choice, the matrix element of **G** diagonal on $|u_0\rangle$ is the sum of two contributions:

$$\langle u_0|G|u_0\rangle = \frac{1}{N} \sum_i G_{ii} + \frac{1}{N} \sum_{i \neq j} \lambda_i \lambda_j G_{ij}. \qquad (10)$$

Now, we see that the first term is just the average Green's function of equation (5) that we want to compute, while the second one becomes vanishingly small as the number of states N increases, due to the product of uncorrelated phases.

4. Total density of states for a 3DPT

Let us now analyse the results obtained for the ideal quasicrystal approximants. In order to obtain the results presented in this section, we have used the same model as in [7], except for the fact that there a direct diagonalization of the dynamic matrix was performed to compute the DOS up to the 5/3 approximant, while we used the recursive technique to compute the DOS up to the 13/8 approximant. The results shown in this section are important to the understanding of to what extent the recursive technique is able to reproduce the results of the direct diagonalization.
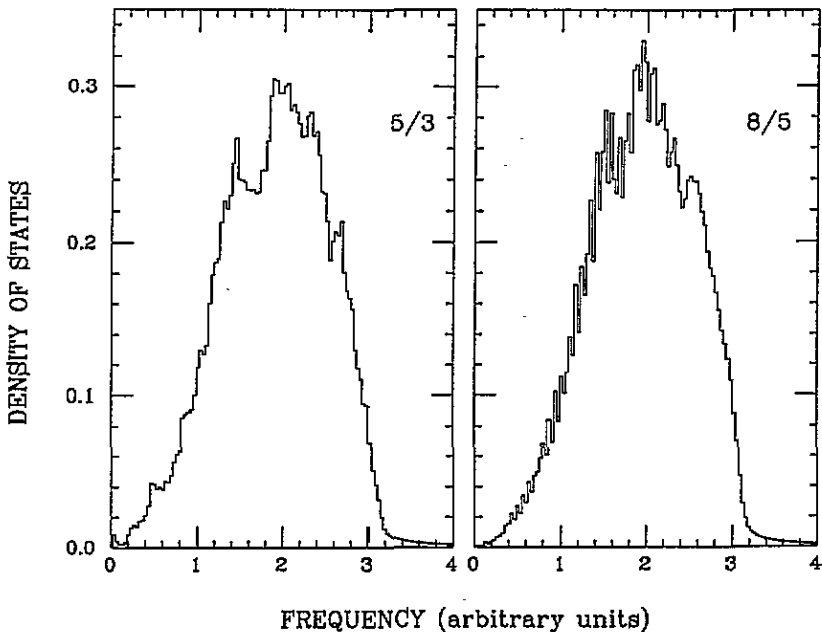

Figure 1. The vibrational density of states obtained with the recursive technique for $\phi_3 = 5/3$ (left) and for $\phi_4 = 8/5$ (right) approximants.

The calculations were performed on a Vax 6000/410, a Vax 4000/200 and on an IBM-3090. On the IBM-3090 about two hours of CPU time have been used for computing the DOS for the biggest cluster. For the DOS presented in this section we used a spring potential with an atom placed at each vertex of the ideal lattice, with all the masses equal, all the spring constants equal and a cut-off radius of 0.8 units of hypercubic lattice spacing for the interactions. This distance represents the shortest cut-off distance, on the three-dimensional lattice, necessary to have all the atoms linked to at least one neighbour. This particular choice reproduces the same results as were obtained in [7] (figures 2 and 3) with the direct diagonalization.
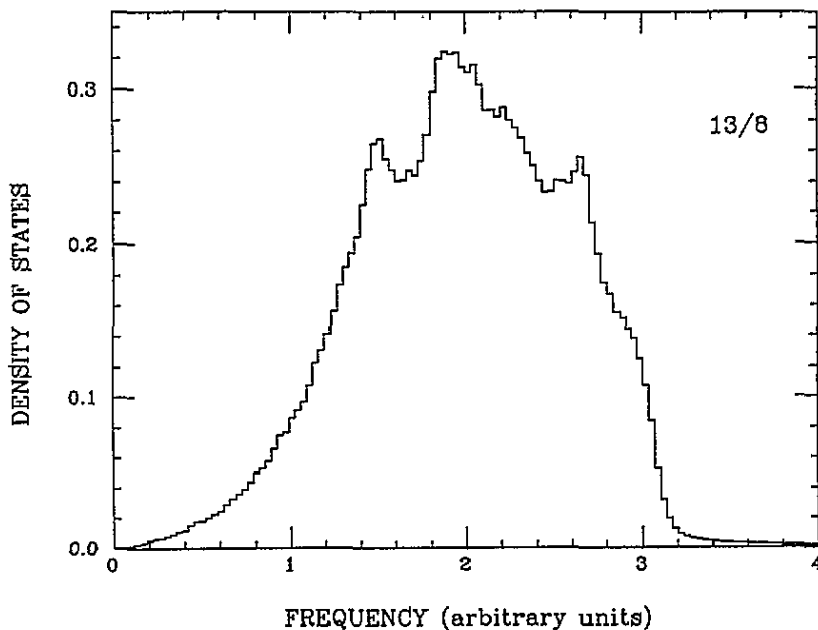

Figure 2. The vibrational density of states obtained for the $\phi_5 = 13/8$ approximant. For this result 150 coefficients of the continued-fraction expansion and an imaginary part of 0.02 have been used.

The dynamic matrix has been stored with a sparse-matrix storage algorithm. To test the accuracy of the calculation we have monitored the scalar product between the nth state of the recursion and the initial state [17]. The continued-fraction expansion has been simply truncated when this orthogonality is no longer satisfied.

No difference has been found between the double- and the quadruple-precision calculations. Moreover, a comparison between calculations performed with different numbers of continued-fraction coefficients shows that the asymptotic region has been reached.

In figures 1 and 2 the DOS obtained for $\phi_3 = 5/3$, $\phi_4 = 8/5$ and $\phi_5 = 13/8$ respectively are shown. The corresponding numbers of atoms of the elementary cell are those reported in table 1. Before losing numerical stability it has been possible to calculate with the recursive technique 150 coefficients of the continued-fraction expansion for the 13/8 approximant. We notice that the DOS with $\phi_3 = 5/3$, figure 1, already looks quite similar to that of figure 2, with $\phi_5 = 13/8$. In the case of AlMn it has been shown [4] that no substantial difference arises between the DOS of the $\phi_5 = 13/8$ approximant and the DOS of the further
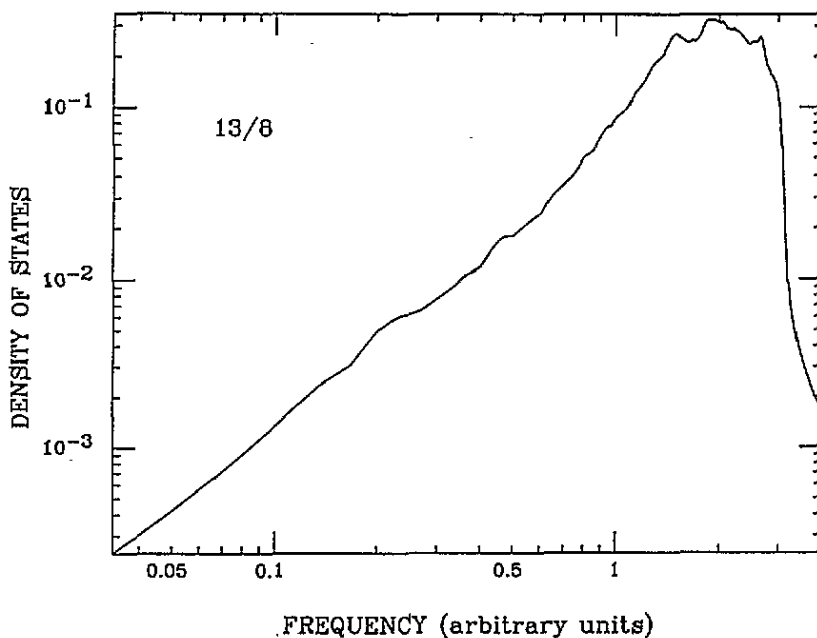
Figure 3. As in figure 4, but with a log–log scale to display the low-ω^2 behaviour. A linear interpolation has given a coefficient of 2.0 for the lower frequencies (from 0.15 up to the value 1.85 of the arbitrary scale).

approximant, i.e. $\phi_6 = 21/13$.

In figure 3 the same DOS as in figure 2 is shown in a log–log scale, to display better the low-ω behaviour. A quite good ω^2-behaviour is found, except for in the very low part of the spectrum. A linear interpolation has been done for the log–log data of the 13/8 approximant of figure 3. For the lower frequencies, up to the value 0.15 of the arbitrary scale, a coefficient of 1.6 has been found. For the frequencies in the range extending from 0.15 to 1.85 a coefficient of 2.0 has been found. This is in agreement with the results of [18].

It is noticeable that in the cluster approximation further sparing of memory is obtained with respect to the commensurate approximation (the dynamic matrix being real instead of complex), and the DOS that we obtained is identical to the one obtained, within the latter approximation, by Los and Janssen for the 5/3 approximant as a pioneering result [7]. The results presented so far, though they do not add anything new to the knowledge of the total DOS of an ideal quasicrystal, are still important because they show that the recursive technique is capable of reproducing well the results of an exact calculation.

In the next section we present the results obtained in the framework of the cluster approximation, with the same technique, for a real quasicrystalline sample.

5. Total density of states for AlPdMn

In this section we present the results obtained for the $Al_{70}Pd_{21}Mn_9$ icosahedral phase. The atomic positions that we used have been determined with x-ray and neutron diffraction investigation performed on a perfect single grain [5]. For the calculation of the DOS we used a spring potential with all the springs equal. A cut-off distance of 4.6 Å for the interactions

has been also introduced. This distance corresponds to the radius of the first-order pseudo-Mackay icosahedron [5, 19]. In the calculation of the dynamic matrix we have used the physical values of the atomic masses. Thus, by applying the same method as illustrated in the previous sections, we obtained the DOS of figure 4, for a box of $100 \times 100 \times 100$ Å^3. The box contains 23 514 atoms, namely 16 478 Al, 4928 Pd and 2108 Mn. Also, in this case, the asymptotic region has been reached before the system loses numerical stability and the DOS of figure 4 has been obtained by using 300 coefficients in the continued-fraction expansion of equation (7).
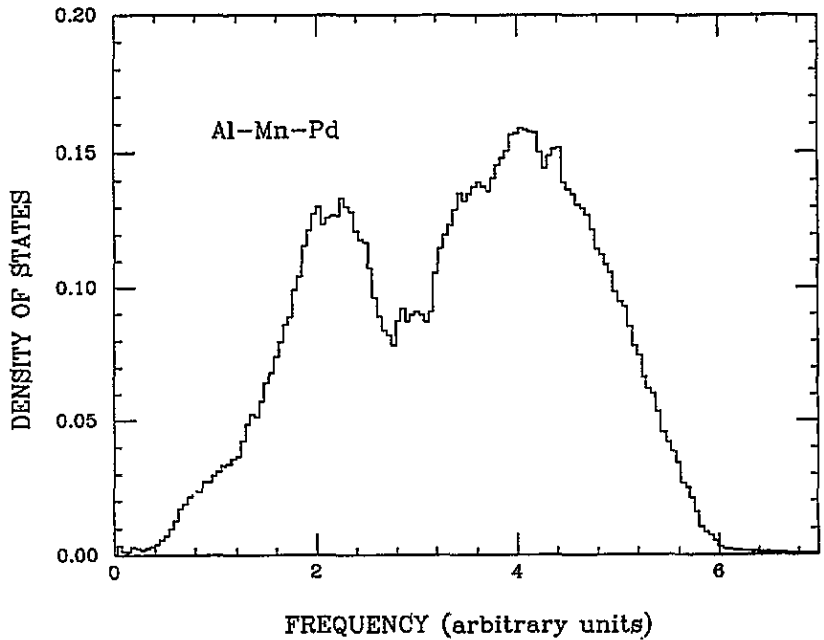

Figure 4. The vibrational density of states obtained with the recursive technique for an Al$_{70}$Pd$_{21}$Mn$_9$ quasicrystal. For this result 300 coefficients of the continued-fraction expansion and an imaginary part of 0.02 have been used.

The spectrum of figure 4 shows two main broad bands with a quite relevant depression in the middle. A third band might exist in this pseudogap. These features have been found experimentally for the same compound [6]. To compare theoretical and experimental results, we report in figure 5 the neutron measurements of the generalized vibrational density of states, published in [6]. The low-frequency part of the spectrum has not been experimentally investigated since the presence of Mn adds intensity in the quasielastic region. Thus, it is not possible to have an experimental counterpart for the shoulder appearing at low frequency. On the other hand, this rather peculiar behaviour of the low-frequency part of the spectrum needs a more realistic model to be definitively proved, since no direct physical interpretation has been available up to now. Further improvements of the calculation are in progress.

The two bands appearing in the DOS are likely to arise because of the presence of atoms with different masses. We observe, in fact, that the neutron-weighted DOS of the AlMn quasicrystal is single banded with no pseudogaps, as results from both theoretical calculations of [4] and the experimental measurements of [20]. Thus, the splitting of the band appearing in figure 4 and in figure 5 is likely generated by the presence of a very heavy species, namely the Pd, with lower concentration with respect to the lighter ones,
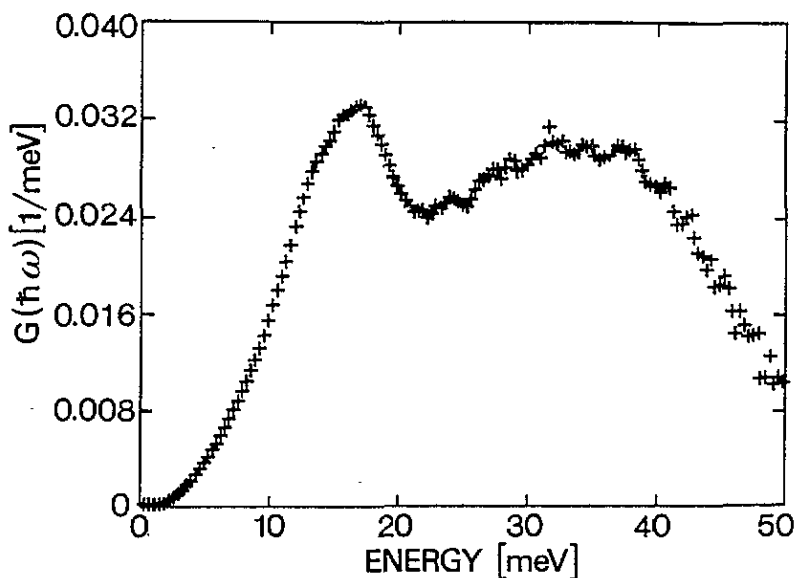
Figure 5. The experimental neutron-weighted vibrational density of states for an $Al_{70}Mn_{21}Pd_9$ icosahedral single grain.

the Al and the Mn. A similar behaviour can be found in random crystals, i.e. for perfect crystalline lattices where mass disorder has been introduced [21]. This consideration is also supported by the following argument: the ratio of the resonant frequencies of the harmonic oscillators of Al and Pd, provided that all the force constants are considered to be equal, is $\omega_{Al}^0/\omega_{Pd}^0 = \sqrt{M_{Pd}}/\sqrt{M_{Al}} = 1.99$. Now, we observe that the ratios of the frequencies corresponding to the two maxima of the experimental and the computed spectra (figures 4 and 5) are both approximately equal to 1.9. This can be interpreted as a signature of the independent oscillations of the two sublattices. If this assumption is correct, the introduction of a realistic force constant is not expected to modify the shape of the spectrum significantly.

6. Conclusions

In this paper we have studied the vibrational density of states of three-dimensional icosahedral quasicrystals, using the continued-fraction formalism and the cluster approximation. We have considered two kinds of lattice: in the first case a model system, i.e. commensurate approximants of an ideal icosahedral quasicrystal generated with the section method; in the second case an actual AlPdMn single grain in its icosahedral phase, for which the atomic positions have been extracted from experimental data [5].

The results we have obtained are very promising, though various approximations have been introduced. Our result for the DOS of the ideal approximants agree very well with those obtained in [7], by a direct diagonalization of the dynamic matrix. Moreover, there is a satisfactory qualitative agreement between the DOS we computed for the AlPdMn single grain and the neutron-weighted total density of states measured for the same compound [6].

Further improvements are in progress: in particular, for actual systems like AlPdMn the introduction of realistic force constants, or, even better, the choice of more appropriate interatomic potentials other than a simple spring model, may give more quantitative results.

Acknowledgments

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