Quasicrystals / Quasicristaux

Dynamics of quasicrystals

Dynamique des quasicristaux

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A R T I C L E   I N F O

A B S T R A C T

The (lattice) dynamics of quasicrystals differs in many aspects from that of lattice periodic systems. This they have in common with other aperiodic crystals. The dynamics of quasicrystals is discussed here in the context of these general aperiodic crystals, but the special features of quasicrystals are stressed. The lattice dynamics is now fairly well understood. Especially for aperiodic crystals, there are excitations related to the possibility to describe the systems in superspace. These 'phasons' are discussed in particular.

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R É S U M É

La dynamique de réseau des quasicristaux diffère de celle des structures avec periodicité de réseau sur un certain nombre de points. Ils partagent cette propriété avec d'autres structures apériodiques. La dynamique des quasicristaux est discutée dans le contexte de ces structures apériodiques en général, mais les aspects spécifiques des quasicristaux sont soulignés. La dynamique de réseau est assez bien comprise maintenant. Un aspect particulier des excitations des structures apériodiques est lié à la possibilité de décrire ces systèmes dans un superespace. Ces excitations « phasons » sont discutées spécifiquement.

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1. Introduction

Since Laue showed in 1912 that the atoms in a crystal are arranged with lattice periodicity, it was assumed for a long time that this property was the most important characteristic of a crystal. The symmetry groups for such periodic arrays, the space groups, had been known already from the 19th century onwards. These groups turned out to be very important for the study of the physical properties of solids, because the states of electrons and lattice vibrations in such systems could be characterised by irreducible representations of these groups, and the determination of these states could be greatly simplified using them. The lattice periodicity can be seen in the diffraction pattern: this consists of sharp peaks on a three-dimensional lattice, besides a diffuse component.

However, 70 years later it became clear to a larger audience that the assumed lattice periodicity was not the property of all solids, when Shechtman discovered quasicrystals in 1982. The definition of 'crystal' had to be adapted to the new situation. The fact that quasicrystals are not lattice periodic follows from the symmetry of the diffraction pattern, which contains five-fold symmetry axes, which is incompatible with lattice periodicity. The discovery led to strong objections from a number of crystallographers, but was welcomed by another group of scientists working also on ordered compounds

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without lattice periodicity: the crystallographers of incommensurate phases, which were known already from the early sixties. All these structures share the property that they have a three-dimensional set of sharp diffraction peaks, but lack lattice periodicity, for which reason they are called aperiodic crystals.

Physical properties of solids are, to a large extent, determined by their structure and symmetry. In particular, for linear problems, this relies on the representations of the symmetry group. Therefore, electrons and small oscillations around the equilibrium positions can for lattice periodic structures be characterised by wave vectors from the Brillouin zone and representations of the space group. For aperiodic crystals, the way to proceed is not so obvious. Because quasicrystals form a subclass of the class of aperiodic crystals, we start with a discussion of the problem for general aperiodic crystals and come back to quasicrystals later. Dynamics in solids, however, is not restricted to small oscillations. One may consider also phase transitions and non-linear excitations for aperiodic crystals in general, and for quasicrystals in particular, because these may also differ in character from those in lattice periodic crystals. However, we start with the small oscillations around the equilibrium positions, and call this *par abus de langage* lattice dynamics, even for the systems without lattice periodicity.

In aperiodic crystals the diffraction pattern shows sharp peaks $\mathbf{k}$ at positions given by:

$$\mathbf{H} = \sum_{i=1}^{n} h_i \mathbf{a}_i^* \tag{1}$$

This formula holds also for lattice periodic systems, and then n is equal to the dimension of space, but for aperiodic crystals n is larger than that. The smallest number of basis vectors $\mathbf{a}_i^*$ in Eq. (1) is the rank of the diffraction pattern, and this is 3 for a lattice periodic crystal. The set of vectors $\mathbf{H}$ of the form of Eq. (1) is called the Fourier module of the aperiodic system.

If n is larger than the dimension, the system is not lattice periodic, which means that the usual techniques to study states in these systems fail. One may, however, define a lattice periodic structure that completely defines the aperiodic one as follows. The n basis vectors in Eq. (1) can be viewed as the projection of n independent vectors $\mathbf{a}_i^{*s} = (\mathbf{a}_i^*, \mathbf{b}_i^*)$ in an n-dimensional space, and consequently the vectors $\mathbf{H}$ are the projection of vectors $(\mathbf{H}, \mathbf{H}_I)$. The embedding of the aperiodic structure into the higher-dimensional space then goes as follows. Suppose the aperiodic structure is given by a density $\rho(\mathbf{r})$, then a lattice periodic system in n dimensions is given by:

$$\rho(\mathbf{r}) = \sum_{\mathbf{H}} \hat{\rho}(\mathbf{H}) \exp(i\mathbf{H}.\mathbf{r}) \rightarrow \rho(\mathbf{r}, \mathbf{r}_I) = \sum_{\mathbf{H}} \hat{\rho}(\mathbf{H}) \exp\big(i[\mathbf{H}.\mathbf{r} + \mathbf{H}_I.\mathbf{r}_I]\big) \tag{2}$$

The density $\rho(\mathbf{r}, \mathbf{r}_I)$ is by construction lattice periodic, its restriction to $\mathbf{r}_I = 0$ is just the density of the aperiodic structure and the lattice in n dimensions is spanned by the n vectors that are reciprocal to the n vectors $(\mathbf{a}_i^*, \mathbf{b}_i^*)$. Functions with diffraction spots as in Eq. (1) are called quasi-periodic, and the way to get a quasi-periodic function from a periodic function in more dimensions was known already in the 1920's. The embedding, however, of aperiodic crystals in this way and the determination of the proper space groups in more dimensions was developed in the 1960's [1]. This approach is the superspace approach. It may also be applied to a discrete quasi-periodic set of points. If the points in physical space are $\mathbf{r}_m$, and the direct lattice corresponding to the reciprocal vectors $\mathbf{a}_i^{*s}$ is spanned by $\mathbf{a}_i^s$ ($i = 1, \ldots, n$), the points in the n-dimensional unit cell have coordinates $(\mathbf{a}_i^*.\mathbf{r}_m)$ modulo integers. The closure of this set in the unit cell is formed by the so-called atomic surfaces, which may be continuous, or disconnected. They are the n-dimensional equivalent of the point atoms in a three-dimensional unit cell for a conventional crystal.

2. Lattice dynamics of periodic and aperiodic crystals

The lattice dynamics of a solid gives the small oscillations around stable equilibrium positions. If $\mathbf{n}_0$ gives the equilibrium positions and $\mathbf{u_n}$ the deviations from them, the potential energy is given in powers of the deviations as:

$$V = V(\mathbf{n}_0) + \frac{1}{2} \sum_{\mathbf{nn'}} s_{\mathbf{nn'}}^{ij} \mathbf{u_n}^i \mathbf{u_{n'}}^j + \text{terms of higher order} \tag{3}$$

For lattice periodic crystals, the vibration modes are characterised by a wave vector of the Brillouin zone and an arbitrary solution to the equations of motion is:

$$\mathbf{u}_{\mathbf{n}j}^{\alpha}(t) = \sum_{\mathbf{k}\nu} Q_{\mathbf{k}\nu} \mathbf{e}(\mathbf{k}\nu|j)^{\alpha} \exp\big(i(\mathbf{k} \cdot \mathbf{n} - \omega_{\mathbf{k}\nu} t)\big) \quad (\alpha = x, y, z) \tag{4}$$

where ν labels the modes with the same $\mathbf{k}$, their frequencies being denoted by $\omega_{\mathbf{k}\nu}$. For an aperiodic crystal with Fourier module as in Eq. (1), there is no Brillouin zone (BZ) if n is larger than the dimension. But there is, of course, a BZ in the superspace.

The modes may be measured with inelastic neutron or X-ray scattering. For a lattice periodic crystal, the measured intensity for energy transfer $\mathbf{q}$ and frequency ω is given by the absolute square of the scattering function [2]:

$$S(\mathbf{q}, \omega) = \sum_{\mathbf{k},\mathbf{K},\nu} \left| \sum_j \frac{b_j}{\sqrt{M_j}} e^{-W_j(\mathbf{q})} \mathbf{q} \cdot \mathbf{e}(\mathbf{k}\nu|j) e^{2\pi \mathbf{q}.\mathbf{r}_j} \right|^2 \delta(\mathbf{q} - \mathbf{k} - \mathbf{K})\delta(\omega - \omega_{\mathbf{k}\nu})/\omega \tag{5}$$

The sum runs for $\mathbf{k}$ over the BZ, for $\mathbf{K}$ over the reciprocal lattice, for ν over the branches, and for j over the atoms in the unit cell. $W_j(\mathbf{q})$ is the Debye–Waller factor. For aperiodic crystals, the same formula could be applied, but the size of the BZ is zero, and the number of particles in the unit cell is infinite, which is in agreement with the fact that all atom positions can be mapped into the unit cell in superspace, but then they give an infinite number too, the points of the atomic surfaces.

This has also consequences for the density of states. For lattice periodic crystals, the latter shows a finite number of jumps, the so-called Van Hove singularities [3]. In the derivation of the phenomenon, the lattice periodicity is crucial. For aperiodic crystals, it is not evident whether there are no or an infinite number of such singularities.

3. Incommensurate modulated phases

To understand the dynamics of aperiodic crystals, one has studied simple models. The simplest are those for incommensurate modulated phases. The peaks of the diffraction pattern (Eq. (1)) can be divided into two classes: the main reflections ($h_i = 0$ for $i > 3$) corresponding to a lattice periodic structure, the basic structure, and the others, the satellites, corresponding to (multi-)periodic displacements from the positions of the basis structure.

Incommensurate modulated phases occur frequently as intermediate phase between a high-temperature periodic phase and a low-temperature superstructure of the periodic phase. An early example is the γ-phase of Na_2CO_3. At high temperature, anhydrous Na_2CO_3 is hexagonal. It shows a phase transition to a monoclinic phase, and a second one where satellites appear with wave vector $\mathbf{q} = \alpha\mathbf{a}^* + \gamma\mathbf{c}^*$. The positions of the satellites shift with decreasing temperature until they 'lock in' at fixed values $\alpha = 1/6$ and $\gamma = 1/3$. Below the lowest phase transition, the values remain constant, and the now periodic structure has a unit cell that is six times the unit cell of the monoclinic phase. The phase transition towards the incommensurate phase is induced by a phonon with wave vector $\mathbf{q}$ that becomes unstable. The second (lock-in) transition does not occur in all incommensurately modulated materials. There are compounds where the incommensurate phase remains to the lowest observed temperatures.

A simple model for the dynamics in the incommensurate phase is the *modulated spring model*, consisting of a one-dimensional chain with harmonic interactions between neighbours and spring constants that vary with the position in the chain:

$$V = \frac{1}{2} \sum_n \beta_n (x_n - x_{n-1} - a)^2, \quad \text{with } \beta_n = \beta\big(1 + \Delta \cos(2\pi nb + \phi)\big) \tag{6}$$

where a/b is an irrational number. The spectrum of small oscillations $u_n = x_n - na$ cannot be determined in the usual way, because the potential V is not periodic. Nevertheless, one may get an idea of the spectrum by calculating it for approximants: taking values $L/N \approx a/b$ for integers L and N. Especially for the case $\Delta = 1$, a plot of the spectrum for varying rational approximants shows an infinite number of gaps with a hierarchical structure (see Fig. 1a). Although this is a quite pathological model, it shows that spectra and states in aperiodic crystals may differ strongly from those in lattice periodic crystals. Strictly speaking, for these approximants the vibration states are extended: they differ just by a phase factor for positions differing by a lattice vector of the periodic lattice. However, inside the unit cell, which grows for growing approximants, the displacements may fall off almost exponentially (localised states) or with a power law. In the limit of the incommensurate phase, the latter states are called critical. For commensurate crystals, the spectrum consists of bands and the states are extended, but for incommensurate crystals the spectrum may have a fractal structure and the states may be localised or critical (cf. Section 10).

A similar model is the Frank–Van de Merwe model (usually called Frenkel–Kontorova model (FK)), which consists of a harmonic linear chain in an external sinusoidal potential with periodicity incommensurate with the lattice constant of the chain. The potential is given by:

$$V = \sum_n \left[\frac{\alpha}{2}(x_n - x_{n-1} - b)^2 + \frac{\lambda}{2\pi}\big[1 - \cos(2\pi x_n/a + \phi)\big] \right] \tag{7}$$

with lattice constant b for the chain, and periodicity a for the external potential, a/b being irrational. The equation of motion for the particles is, in terms of displacements $u_n = x_n - nb$:

$$m\omega^2 u_n = \alpha(2u_n - u_{n+1} - u_{n-1}) + (2\pi\lambda/b)\cos(2\pi\bar{x}_n/a)u_n \tag{8}$$

where the $\bar{x}_n$ are the equilibrium positions of the chain in the external potential. Also in this case, the vibration spectra have been calculated. The basic structure is a chain modulated by the external potential. As Aubry has shown [4], for small values of λ, the modulation is sinusoidal, but there is a critical value λ_c above which the modulation function is no longer continuous. The vibration eigenvectors differ qualitatively in the two regimes. In contrast with the modulated spring model, the FvdM model does not have a $q = 0$ mode with frequency $\omega = 0$ due to the non-translational invariance of the background potential. A rigid shift of the chain does not leave the energy invariant. However, for small values of λ, when
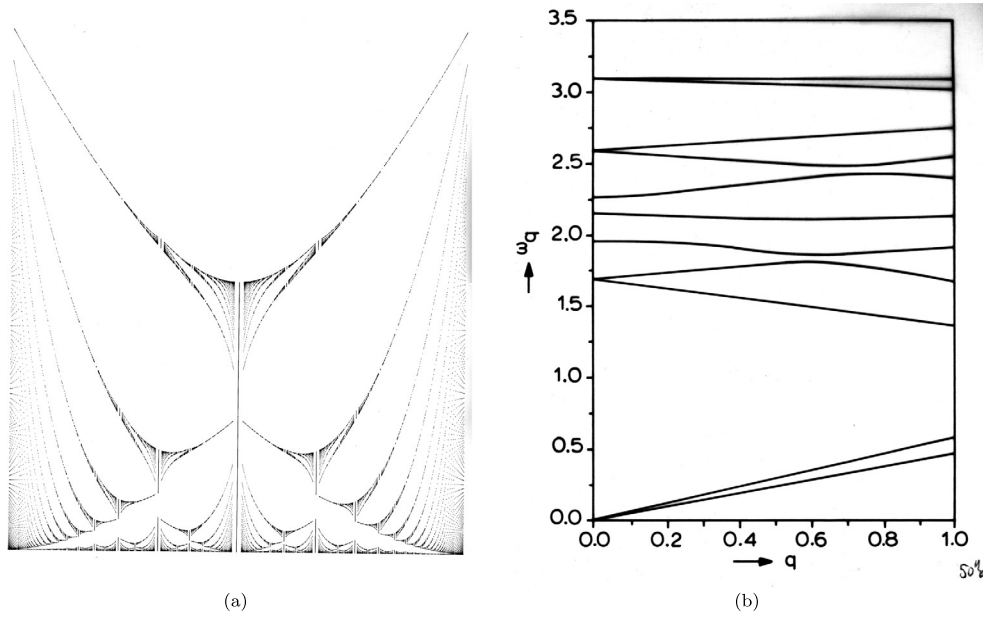
Fig. 1. (a) Vibration spectra for values of L/N between 0 and 1 in the modulated spring model. (b) Dispersion curves in the DIFFFOUR model with potential energy given in Eq. (9), for an 11-fold approximant.

the chain is sinusoidally modulated, an arbitrary shift of one atom followed by a relaxation of the whole chain does not change the energy. In this case, the modulation is shifted with respect to the basic lattice and this gives an $\omega = 0$ mode. It is called a sliding mode.

In these two models, the aperiodicity is already built in the mutual interactions. A third model gives a first explanation of the occurrence of modulated phases and makes it possible to compare the vibration properties of the periodic and aperiodic structures. It is the discrete frustrated Φ^4 (DIFFFOUR) model [5]. It is a one-dimensional chain with up to second-neighbour interactions, with potential energy expressed in the displacements u_n from the equidistant array as:

$$V = \sum_n \left(\frac{\alpha}{2}(u_n - u_{n-1})^2 + \frac{1}{4}(u_n - u_{n-1})^4 + \frac{\beta}{2}(u_n - u_{n-2})^2 + \frac{\delta}{2}(u_n - u_{n-3})^2 \right) \qquad (9)$$

If one assumes that α, β and δ depend on temperature as a consequence of non-linear terms, there are various phases in the α–β–δ phase diagram. Among them are incommensurate modulated phases. Normalising to $\beta = -1$, the modulation wave vector q is given by the expression $\cos(q) = (1 - \sqrt{1 - 3\alpha\delta + 9\delta^2})/6\delta$. There is also a phase with $x_n = 0$ (all n). This is just a periodic chain. This chain becomes unstable at the phase boundary, where the frequency of two modes with wave vectors $\pm q$ go to zero (see Fig. 3). In this case, the aperiodicity stems from the frustration between first- and second-neighbour interactions.

Close to the transition line between basic structure and modulated phase, the modulation vector in the latter changes continuously, but there is, like for the FvdM model, a transition line between this area with continuously varying modulation vector and an area where only rational values of the modulation vector are taken. On the borderline, the integrated density of states is a non-decreasing function with an almost everywhere vanishing derivative. This is called a devil's staircase.

In the temperature region where the atomic surfaces are continuous, there are two branches for which the frequency goes to zero when the wave vector tends to zero (Fig. 1). One is the usual acoustic branch. The other can be described as a shift of the modulation with respect to the atoms. It is a combination of the two soft modes at $\pm q$ and it is called a phason. Its frequency remains zero in the modulated phase, but it is an overdamped mode, as will be discussed later. The other combination of the two modes at $\pm q$ describes an oscillation of the amplitude of the modulation function, and is called amplitudon. After the phase transition, its frequency rises steeply.

4. Incommensurate composites

A different class of aperiodic crystals is that of incommensurate composites. They consist of two or more subsystems that have the structure of an incommensurate modulated crystal each with a lattice periodic basis structure and a modulation that is usually determined by the interaction with the other subsystems, while the subsystems are mutually incommensurate. Distinguishing the subsystems by a label ν, the reciprocal bases for the subsystems have vectors $\mathbf{a}_i^{*\nu}$ ($i = 1, 2, 3$). Then the total diffraction pattern has vectors $\mathbf{a}_j^*$ (Eq. (1)) such that:

$$\mathbf{a}_i^{*\nu} = \sum_{j=1}^{n} Z_{ij}^{\nu} \mathbf{a}_j^* \tag{10}$$

A simple model, also for the dynamics, is the double-chain model (DCM). It consists of two different chains with first-neighbour harmonic interaction in the chains and a long-range interaction between atoms of different chains. This leads to two modulated chains: one is modulated with the periodicity of the other. Just as for the FK-model, the modulation is sinusoidal for small interchain interactions, but becomes discontinuous for stronger interactions.

Without interaction, the two subsystems have their proper lattice dynamics. One can distinguish two Brillouin zones, one for each subsystem. With interaction, there is no longer a finite Brillouin zone and the dispersion curves become mixed, especially at the crossing points of these curves. A mode then has non-zero displacements of all the atoms in both chains, although the participation of the two chains may vary quickly with wave vector. In the case of small interaction, the modulation functions are smooth, but beyond a certain limit, these become discontinuous, another example of 'breaking of analyticity' [4]. In the superspace description, this means that the atomic surfaces become discontinuous.

In the case of continuous modulation, there are two phonon branches with frequency tending to zero when the wave vector goes to zero. One is related to the fact that the system is translation invariant. These vibrations correspond to acoustic waves in both chains. The other branch corresponds to a movement of one chain with respect to the other. Because of the incommensurability, a relative shift of the two chains gives a situation with the same energy. The motion in the case of these vibrations is called a sliding mode, and is similar to the situation for the FvdM model.

The models discussed here are essentially one-dimensional. However, considering models in more dimensions is essential. Otherwise, a phase transition would not be possible. Going to higher dimensions could also wipe out some of the peculiar properties found for one-dimensional models, like the types of spectra and vibration states, which are not found for periodic crystals. A possible way to investigate this is considering coupled chains in more dimensions. Here we shall consider another type of systems, directly related to quasicrystals, the tiling models.

5. Lattice dynamics in tiling model systems with non-crystallographic symmetry

Before the discovery of quasicrystals, aperiodic structures were already studied by mathematicians. The best known example is the Penrose tiling, with decagonal symmetry. Other examples are the 2D Ammann–Benker tiling or a 3D generalisation of the 2D Penrose tiling. These have octagonal and icosahedral symmetry, respectively, and for that reason they are necessarily aperiodic. Soon there were speculations that similar crystal structures could occur in nature, and would have perhaps interesting physical properties. Simple models for the vibrations in quasicrystals are obtained by considering a 2- or 3-dimensional tiling with atoms at the vertices and an interaction between these, which minimises the energy for zero displacements.

The simplest model is to take such a tiling, put atoms at the vertices and connect close neighbours with harmonic springs [6,7]. The problem of the aperiodicity can be attacked via a choice of approximants. For example, the Ammann–Benker tiling, with eight-fold symmetry, is a tiling with tiles of two types; a square and a rhomb with angle of 45°. It may be obtained from a four-dimensional periodic structure. This has a lattice with 4 basis vectors:

$$a(1, 0, 1, 0), \quad a(c, c, -c, c), \quad a(0, 1, 0, -1), \quad a(-c, c, c, c), \quad \text{with } c = \sqrt{1/2} \tag{11}$$

and in each lattice point an atomic surface, which is an octagon, the projection of the unit cell on the internal space. An approximant is then obtained by replacing c in the two last coordinates by a rational number L/N. This gives a lattice periodic square structure in physical space, for which the eigenvibrations can be calculated in the standard way. One may expect to learn about the aperiodic system by looking at a series of approximants: $\sqrt{1/2} \approx \frac{2}{3}, \frac{3}{4}, \frac{29}{41}, \frac{70}{99}, \ldots$. In Fig. 2 are given for the analogous case of the 3D icosahedral tiling the density of states, dispersion curves in the Brillouin zone of the approximant and the dispersion curve for low energy for two different approximants. In the first the pointed line gives the result for a simple square lattice, where the Van Hove singularities are clearly visible. But also the approximant has similar features and this remains so for higher approximants. The second figure shows that there are two curves going to zero, the two acoustic branches. There is no sliding mode, because the atomic surfaces are disjunct. In the third figure it is shown hat there is rapid convergence for the dispersion for higher approximants.

6. Tensorial properties of quasicrystals

Sound waves and other long-wavelength lattice vibrations can also be described in terms of tensors, in particular, the elastic tensor. For lattice periodic crystals, this tensor is a rank-four tensor, and for the general case this has 21 independent components. It gives the relation between strain and stress. For aperiodic crystals, the displacements from a basic structure may have components in the physical space as well as in the internal space. For that reason, one has to distinguish phonon strain $e_{ij} = (\partial_i u_j + \partial_j u_i)/2$ ($i \leqslant j = 1, 2, 3$) and phason strain $f_{ij} = \partial_i u_j$ ($i = 1, \ldots, 3; j > 3$). The elasticity tensor then has 3 components: the phonon–phonon, the phason–phonon and the phason–phason parts. The elastic energy then may be expressed as:
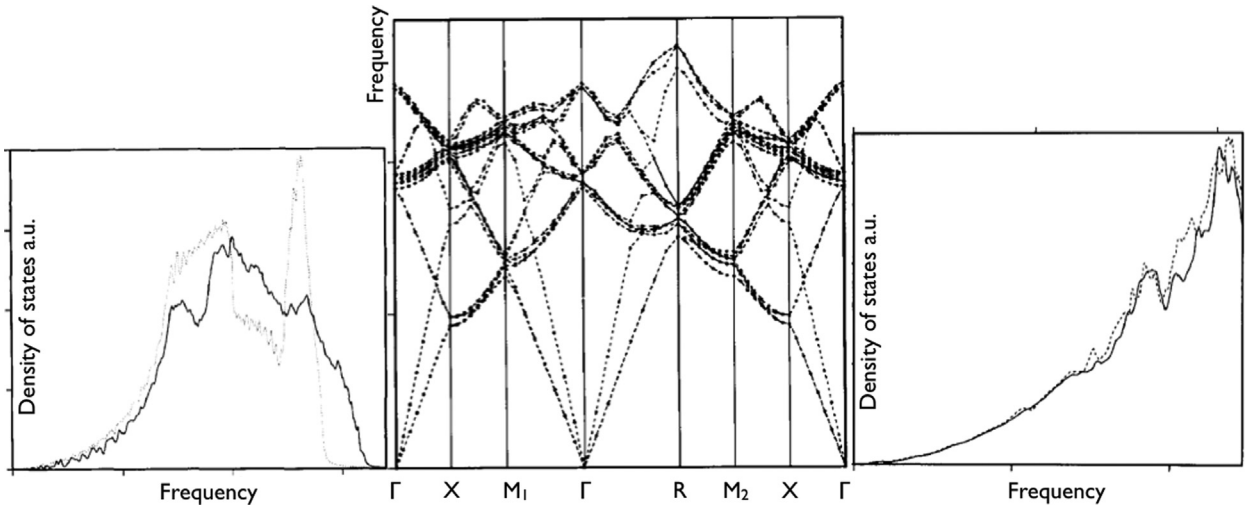
Fig. 2. 3D icosahedral tiling: density of states, dispersion curves, scaling properties [6,7].

$$F = \int d\mathbf{r} \left(\frac{1}{2} \sum_{ijk\ell} c_{ijl\ell}^E e_{ij} e_{k\ell} + \frac{1}{2} \sum_{ijk\ell} c_{ijk\ell}^I f_{ij} f_{k\ell} + \sum_{ijk\ell} c_{ijk\ell|}^{EI} e_{ij} f_{k\ell} \right) \tag{12}$$

The number of independent components is determined by the point symmetry of the crystals. For icosahedral quasicrystals, for example, there are two independent components for c^E, 2 for c^I and 1 for c^{EI}, called the phonon–phonon, the phonon–phason, and the phason–phason elastic constants, respectively. With this expression, one may determine the elastic waves in the crystal.

7. Hydrodynamic modes and phasons

When in a crystal a mode with wave vector $\mathbf{q}$ becomes soft and leads to an instability, the two modes at $\pm\mathbf{q}$ lead to two new modes in the structure after the phase transition. One describes a motion of the modulation function with respect to the crystal, the other one corresponds to an oscillation of the amplitude of the modulation function. They are called phason and amplitudon, respectively. For an incommensurate wave vector, the energy of the system does not change if the phase of the modulation function is varied. Therefore, this mode has zero frequency. In fact, there is a branch of such excitations, because the modes $\mathbf{q} + \Delta\mathbf{q}$ are degenerate with those at $-\mathbf{q} + \Delta\mathbf{q}$ via a wave vector $2\mathbf{q}$. The frequencies are non-zero for non-zero $\Delta\mathbf{q}$. There are two branches, one for phasons and one for amplitudons. These excitations originate from phonons with wave vector around $\pm\mathbf{q}$. These go down in frequency when approaching the transition, and then the amplitudon frequencies go up steeply, whereas the phason modes keep a low frequency. This shows that the phasons are not additional degrees of freedom. They are actually phonons that can be described as long-wavelength oscillations of the phase.

In superspace a change in phase may be considered as a change in the internal space. Therefore, the phasons may be considered as oscillations of the crystal in superspace with polarisation in the perpendicular direction(s).

Similar dynamics can be found in incommensurate composites. Because of the incommensurate relation between the subsystems, one subsystem may be moved with respect to the other subsystem(s) without energy change. Also in this case, the change of relative position may be described as a shift of the whole system in internal space. The corresponding motion may, therefore, also be called 'phason'.

The argument, that a shift of the physical space in the direction of the internal space does not cost energy because the projection of the lattice points in superspace on the internal space is a dense set of points, is valid for all aperiodic crystals. Therefore, these phasons exist also for quasicrystals. The question then arises whether these motions are also elementary excitations of the aperiodic crystal. For that we can consider them in terms of hydrodynamics. Hydrodynamic modes are slowly decaying modes, in contrast to the variables fast decaying towards thermal equilibrium. In general, these hydrodynamic modes are related to conserved quantities or to broken symmetries. One of the conserved quantities for aperiodic crystals is the energy connected with displacements in internal space. There is, however, a big difference with, for example, the situation in an isotropic anti-ferromagnet, where the energy does not depend on the orientation of the spins. Moreover, mode-counting arguments indicate that the phason modes cannot be propagating modes, but are diffusive modes; this argument, which has been mainly used for quasicrystals [8–10], is in fact also true for all aperiodic crystals and in particular incommensurately modulated phases, as was shown in [11]. This apparent contradiction with experiment is in fact reconciled once the damping of the modes is properly taken into account. Therefore, a long-wavelength disturbance in the orientation will decay slowly. For aperiodic crystals, a uniform displacement in internal space does not change the
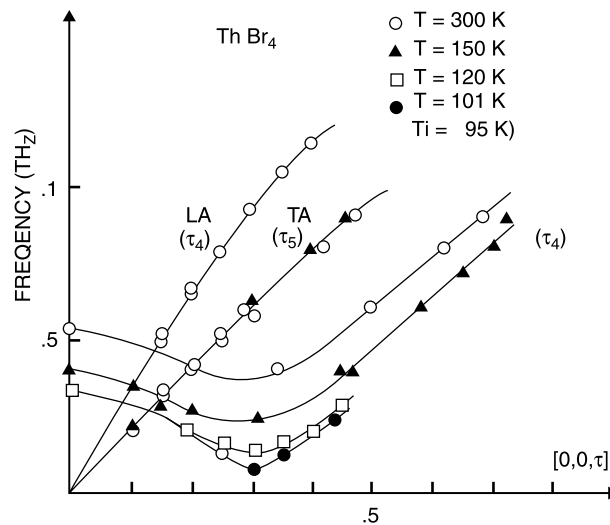
Fig. 3. Soft mode in ThBr$_4$ [12].

energy globally, but energy loss in one point will be compensated by energy gain in another. Especially with discontinuous atomic surfaces, the local energy change may be substantial. Therefore, it is not clear whether such modes may be called hydrodynamic. Anyway, these modes may have an additional damping because of the energy cost of the phason jumps. But even in the case of continuous atomic surfaces, phasons are expected to be overdamped. In simple models, the quadratic and the higher-order terms for acoustic modes go to zero, but for phasons the latter tend to a constant. A phenomenological argument for the damping of phasons in incommensurate phases has been given by Strukhov and Levanyuk [13]. The fact that phason modes in incommensurately modulated phases have a width which remains constant as **q** goes to zero (unlike phonon excitations) means in the long-wavelength limit that phason modes are diffusive excitations. In this long-wavelength hydrodynamic limit the 'dispersion relation' of a phason mode with wave vector **q** comports only a purely imaginary part and writes: $\omega = -iD_{phason}\mathbf{q}^2$, where D_{phason} is the phason diffusion constant. Whereas in the case of incommensurately modulated phases, one can expect a higher wavevector region for which phason modes have the characteristic signature of a damped harmonic oscillator, this is certainly no longer true for quasicrystals. The question remains open in the case of composite crystals (see [14] for a discussion on this point). The fact that the phason modes are overdamped means that there are no oscillations. Use of the term 'lattice vibrations' then becomes actually misplaced.

Phasons as extended excitations, comparable with acoustic phonons, but with an overdamped character, correspond with large-scale oscillation of the crystal positions in superspace with respect to the physical space. Another dynamic phenomenon is a local oscillation describing a jump between two positions in the quasicrystal. This happens if a gap between atomic surfaces passes through the physical space when the aperiodic systems moves in internal space. Sometimes this is also called a phason, but in order to avoid confusion with the collective mode, it would be better to call them 'phason jumps'. Such phason jumps have been observed in experiments, and they have a rather well-defined frequency [15,16].

Phasons have three consequences for scattering. In the first place, the phason oscillations will affect the Debye–Waller factor in the same way as phonons do. In the second place, they will contribute to the diffuse scattering. In a simple approximation, which neglects phason–phonon coupling, for icosahedral crystals one may calculate this scattering using the four elastic constants for the materials: the usual two Lamé coefficients and the two phason elastic constants K_1 and K_2 [17–19]. The shape of the so-called phason diffuse scattering depends only on the ratio K_2/K_1. It can reproduce nicely the observed diffuse scattering in the i-AlPdMn phase, as shown in Fig. 4 [20]. In fact, all icosahedral phases studied up to now do present a diffraction pattern with a 'phason' diffuse scattering, which is most likely quenched in. This phason diffuse scattering does not show up for a periodic approximant, in agreement with the unique 'aperiodic' character of those 'excitations'. And finally, phasons produce new branches in $S(\mathbf{q}, \omega)$ when they are not overdamped. The diffusive character of long-wavelength phason modes has been shown experimentally in the case of the i-AlPdMn icosahedral quasicrystal [21]. Using coherent X-ray photon correlation spectroscopy, it was shown that indeed phason fluctuations decay exponentially with time above 500 °C. At 700 °C, the characteristic time is smaller for longer wavevector and goes like $1/q^2$ as expected for a diffusive mode [22,21] (see Fig. 6).

8. Dynamics of decagonal and ternary icosahedral quasicrystals

Decagonal quasicrystals are periodic in one direction and are stackings of (puckered) layers that are quasi-periodic and have a ten- or five-fold axis. The diffraction pattern is 5-dimensional with four basis vectors in a plane perpendicular to the fifth. In that plane, five-fold symmetry is observed. The structure implies an anisotropy in the dispersion: sound velocities are expected to be different along the axis or perpendicular to the axis. This has been found, but the effect is not so strong
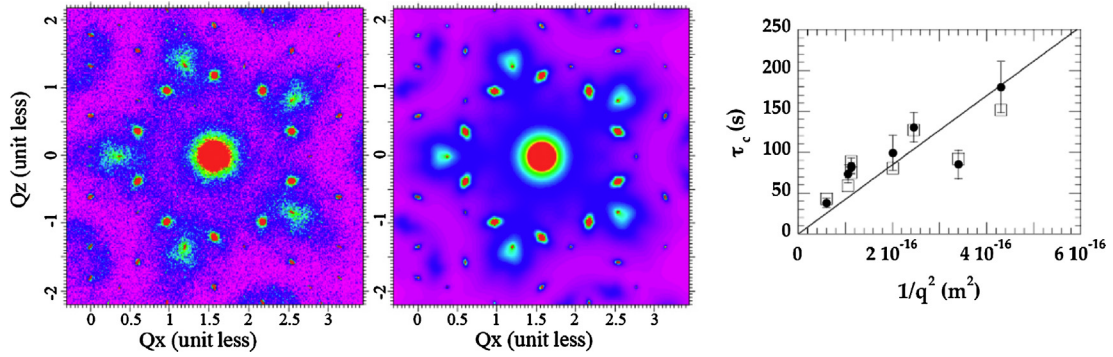
Fig. 4. (Color online.) Left two panels: Diffuse scattering measured in a plane perpendicular to a 5-fold axis as measured and simulated using the hydrodynamic theory. Right panel: evolution of the phason characteristic time decay as a function of **q**, as measured at 700 °C.
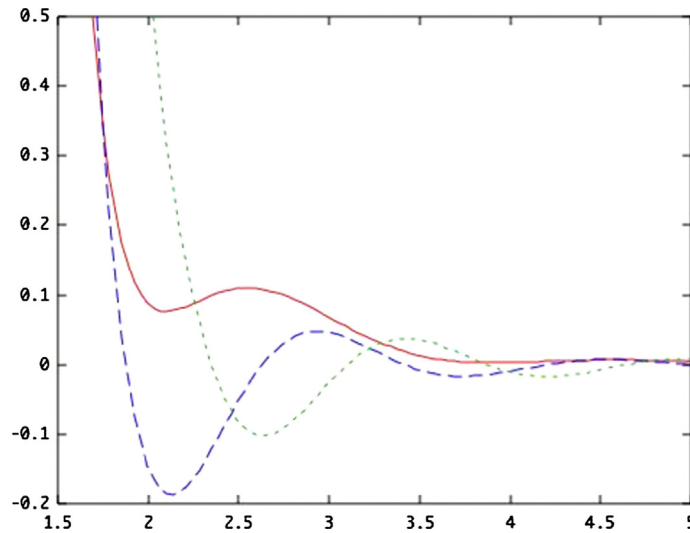

Fig. 5. (Color online.) Oscillating potentials between B–B, B–Fe and Fe–Fe pairs according to Mihalkovič et al. [26].

as theoretical models predict [23,24]. Because decagonal quasicrystals are simpler than icosahedral ones, and their structure was earlier understood, the study of their dynamics is quite natural [25].

In the years after the discovery of quasicrystals, the quality and size of the samples were not high enough to allow the use of inelastic neutron scattering for the study of lattice dynamics. The first quasicrystals of high enough quality to permit such experiments were ternary compounds like AlPdMn and AlCuFe [27,28]. For these compounds, rather realistic models for the structure were developed [29]. These were, however, not realistic enough to allow model calculations of the vibration modes. In particular, chemical ordering was found to be difficult to model.

The first results obtained in the study of the i-AlCuFe [30,31] and i-AlPdMn icosahedral phases [32] have demonstrated that well-defined acoustic modes can be observed close to strong Bragg peaks. Then the signal broadens rapidly as the phonon wave vectors become larger than 0.3 Å^{-1}, i.e. for wavelengths of the order of 2 nm, while the dispersion relation departs from a linear dispersion. This abrupt broadening occurs when the acoustic branch crosses low-lying dispersionless optical modes and pseudo-Brillouin zone boundaries (PBZB, as proposed by Niizeki [33,34]). The broadening rate is much larger than the expected $\mathbf{q}^2$, and goes as $\mathbf{q}^4$. It is interpreted as resulting from a mode mixing between the acoustic excitation and the broad energy distribution (about 4 meV FWHM) of the optical excitation located at about 6.5 meV. This mode mixing occurs over a rather limited **q**-range, after which what is measured is a broad distribution of modes centered at energies corresponding to the crossing of the acoustic branch with the pseudo-Brillouin zone boundaries and has been observed for other icosahedral phases [32], Zn–Mg–Y [35] and the decagonal Al–Ni–Co phase [24]. In this higher energy range, the plane wave expansion is certainly questionable, and the very notion of a well-defined phonon excitation needs, most likely, to be revisited.
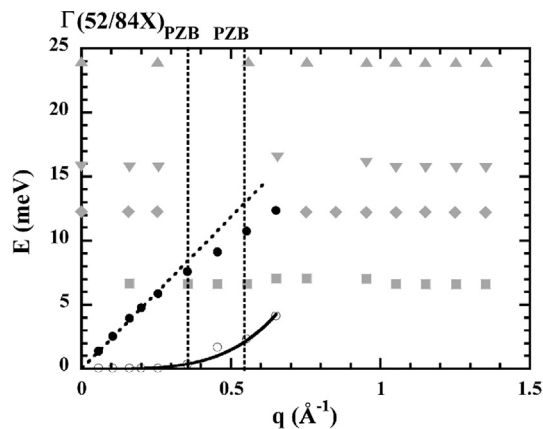
Fig. 6. i-AlPdMn dispersion relation extracted from different measurements. Filled black symbols are for the TA acoustic modes, grey symbols for optic-like excitations. The open circle stands for the FWHM of the acoustic excitations, the solid line is a $\mathbf{q}^4$ fit. The vertical dashed lines indicate the first pseudo-Brillouin zone boundaries.

(a)   (b)
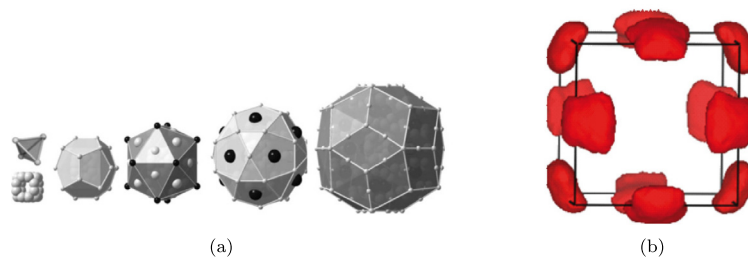
Fig. 7. (Color online.) (a) Successive shells in the structure of ZnSc. (b) Simulated motion of the central tetrahedron.

9. Dynamics of binary quasicrystals

A crucial step toward the understanding of the lattice dynamics in quasicrystals was the discovery of binary systems of high quality by A.P. Tsai [36]. They are of high quality and their structure could be determined on the basis of the clusters constituting the 1/1 approximant ZnSc [37]. This made it possible to start more refined calculations of the dynamics. The structure in the approximant consists of a series of successive shells (Fig. 7a). In the center, a tetrahedron is situated. Its presence would break the icosahedral symmetry, but this is restored by the dynamics. Simulations show jumps between various positions (Fig. 7b).

Using potentials between the atoms derived from *ab initio* calculations [26], as given in Fig. 5, the modes could be calculated for the 1/1 approximant in the standard way. Because of the lack of a Brillouin zone, this was not possible for the quasicrystal. Instead one has compared the 1/1 with the 3/2 approximant calculations with inelastic neutron scattering experimental data for ZnSc and the icosahedral phase of ZnMgSc [38]. The results are shown in Fig. 8. The observed dispersion relation is perfectly reproduced by the simulation. As for other quasicrystals, well-defined acoustic modes are seen in the low-**q** region for both the 1/1 approximant and the quasicrystal, whereas at higher energy broad dispersionless excitations are observed. Besides the overall similarity of the dispersion relation, distinct differences are observed [38]. In particular, the pseudo-gap between the acoustic branch and the optical one is larger and better defined in the 1/1 approximant than in the quasicrystal. This can be explained by the occurrence of two PBZB in the quasicrystal as opposed to a single one in the approximant, shown as vertical dashed lines in Fig. 8. The simulation reproduces not only the dispersion relation but also the overall intensity distribution, which validates both the model and the pair interaction used. The first analysis has shown that some particular cluster, and in particular the central tetrahedron, plays a crucial role [39]. Indeed recent experiments have shown that the central tetrahedron behaves as a single 'molecule' and jumps between different configurations at high temperature, whereas at low temperature a libration motion of this entity is observed [40,41]. When the tetrahedron jumps takes places, it induces a strong distortion of the successive shells conferring to the system an exceptional dynamical flexibility.

10. Dynamics of aperiodic crystals from a mathematical point of view

The determination of the diffraction by quasi-periodic structures as introduced by de Wolff [42] was put in a mathematically rigorous setting by Hof [43]. At least partially, because there are strong results for the scattering function as Fourier transform of the autocorrelation function of systems 'with finite local complexity'. That means that incommensurate
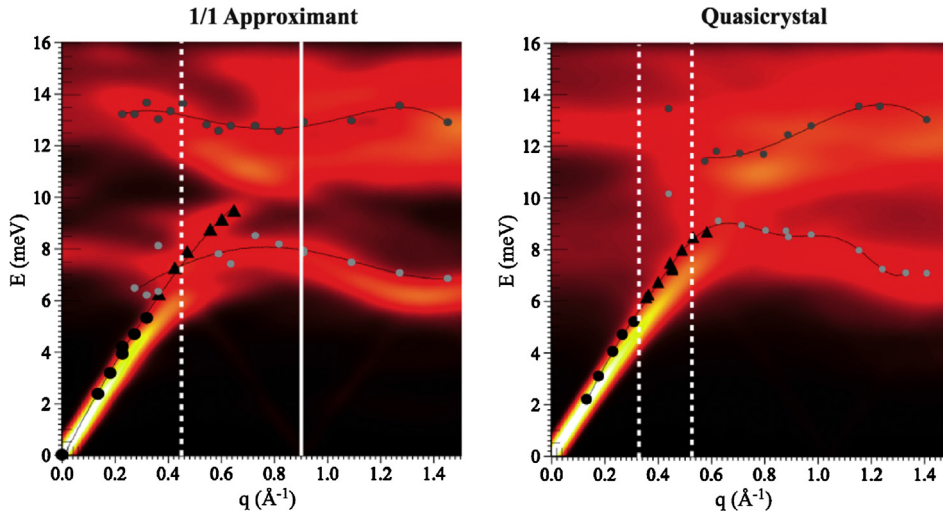
Fig. 8. (Color online.) $S(\mathbf{q}, \omega)$ for an approximant ZnSc and the quasicrystal ZnMgSc [38]. Solid symbols: dispersion relation measured in the Zn–Sc 1/1 periodic approximant and in the icosahedral Zn–Mg–Sc quasicrystal. The vertical dashed lines stand for the ZB and PZB. The plain vertical line is a zone center. The filled circles and triangle stand for the acoustic excitations, whereas the grey one's correspond to broad optical excitations. The lines are guide for the eyes. The colored background correspond to the simulation carried out using the oscillating pair.

phases with smoothly varying modulation function do not belong to this class, but tiling models (which are cut-and-project systems) do. Also the mathematical theory does not include multiple scattering effects on the diffraction intensity. For the dynamical structure factor, such a rigorous treatment has not yet been given at all. However, for physical properties there are rigorous results for the spectra and electron states in simple, mostly one-dimensional, aperiodic potentials.

The Bloch theorem, which says that eigenstates in a periodic potential can be written as the product of a plane wave phase factor and a function with the periodicity of the potential ($\Psi(\mathbf{r}) = \exp(i\mathbf{k}.\mathbf{r})U(\mathbf{r})$) is essentially a group theoretical result. As such, it is also valid in the superspace. The reason that this is not as useful as in crystals with 3D periodicity is that the function $U(\mathbf{r})$ may become very complicated.

The character of this function $U(\mathbf{r})$ is still an open question. There are very few mathematically rigorous results. Numerical calculations on, mainly one-dimensional, models suggest that eigenstates (or phonon eigenvectors in the case of lattice dynamics) are either extended, or localised or critical. Roughly speaking, these states are not decaying spatially, are exponentially localised or 'something else' (for example, decaying with a power law), respectively. For two and three dimensions, these indications are less clear. There are numerical calculations showing a concentration of an eigenstate on very specific lattice points. But mathematically the question is open.

The same holds for the spectra. In one dimension, there are examples (e.g., the modulated chain) where the spectrum is fractal. In structures with aperiodicity in one direction, this fractal property is washed out, and for quasicrystals with aperiodicity in all directions, calculations show a delicate fine structure, that is, however, not seen in the present experimental results.

Even for a fundamental expression, as for the dynamic structure factor, one uses the expression derived for phonons in lattice periodic structures. Strictly speaking, its derivation for aperiodic crystals has not yet been given.

11. Soft modes and phase transitions

Phase transitions in crystals are usually intimately connected with dynamical effects. An example is the second-order phase transition from an unmodulated to an incommensurate modulated crystal (see Fig. 3). The standard picture here is that a phonon branch becomes soft, which leads to the phase transition. In principle, such dynamic phenomena may occur in aperiodic crystals as well. A theoretical example is here the softening of a phason in an icosahedral quasicrystal [44]. Such phason softening has been observed experimentally in the i-AlPdMn phase, where the diffuse scattering increases as the temperature is decreased, a very counterintuitive behaviour that can fully be explained by a softening of one of the phason elastic constants, which points to a 3-fold instability [45]. In this case the phase transition is not realised, most likely for kinetic reasons.

Other examples have been found in incommensurate composites. In general, one has to distinguish for aperiodic crystals between phase transitions where the rank does not change and those where the rank is increased. An example of the former is the centering transition from a primitive to a face-centered icosahedral phase. An example of the latter is the transition from the unmodulated to the incommensurate modulated structure. Another example has been found for *n*-nonadecane-urea, where a rank-four to rank-five transition has been found. This transition goes together with critical phenomena, which is an indication that the transition is induced by a dynamical effect [46], possibly a soft (phason) excitation.

12. Summary

The dynamics of aperiodic crystals is an interesting topic in solid-state physics. For these materials, the standard experimental and theoretical techniques are not directly applicable. New ones had to be developed. In the early stages, the quality of the samples was a major problem. Now high-quality samples are available. Due to progress in computational techniques, one now has a fairly good understanding of the phenomena. However, especially from the fundamental point of view, a number of questions are still open. The precise character of spectra and vibration states is unknown. Also the problem of characterising states and eigenmodes with representations of the symmetry group remains unsolved. And the expression for the scattering amplitude (Eq. (5)) for aperiodic crystals needs also a renewed study. Other questions are concerned with applications. Aperiodic crystals, and in particular quasicrystals, have special properties that possibly offer new applications. But it is not clear in how far the aperiodicity here is essential. Some of the periodic materials, like (lattice periodic) complex metallic alloys, seem to have similar properties.

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