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Abstract
The nearly dispersionless, so-called 'optical' vibrational modes observed by inelastic neutron scattering from icosahedral Al–Pd–Mn and Zn–Mg–Y quasicrystals are found to correspond well to modes of a continuum elastic sphere that has the same diameter as the corresponding icosahedral basic units of the quasicrystal. When the sphere is considered as free, most of the experimentally found modes can be accounted for, in both systems. Taking into account the mechanical connection between the clusters and the remainder of the quasicrystal allows a complete assignment of all optical modes in the case of Al–Pd–Mn. This approach provides support to the relevance of clusters in the vibrational properties of quasicrystals.

1. Introduction

Quasicrystals are long range ordered materials whose diffraction patterns present symmetries incompatible with translational invariance [1, 2]. Most structural analyses of icosahedral phases have shown that they can be described as a quasiperiodic packing of groups of atoms or 'clusters' with a local icosahedral symmetry (e.g. pseudo-Mackay icosahedra).

Experimental electron density maps of crystal approximants have shown that more electrons are localized on clusters than between clusters [3], supporting this idea of cluster building blocks. From the vibrational point of view, the experimental evidence for the resulting expected phonon confinement is less clear. Inelastic neutron scattering (as well as inelastic x-ray scattering [4]) on several icosahedral phases revealed that the excitation spectrum can be split into two regimes: acoustic and optical [5–7]. The acoustic regime is characterized by well defined longitudinal and transverse modes which display a linear dispersion in the low wavevector q range. The high energy part of the excitation spectrum displays somewhat

broadened bands ($\sim$4 meV width) of dispersionless excitations or optical modes. The cross-over between the two regimes is abrupt and occurs for wavevectors q between 3.5 and 6 nm^{-1}, i.e. for a wavelength of the order of D_{cl} (D_{cl}: cluster diameter). This shows up as a rapid broadening of the acoustic modes and an intermixing of phonon modes in the different branches. Although no gap opening has been observed, the energy position of the optical bands matches the crossing of the acoustic branch with pseudo-zone boundaries as defined by Niizeki [8]. These observations are in general agreement with the theoretical calculations of Hafner and Krajči for icosahedral quasicrystals [9] although these calculations do not provide a clear description of the optical modes.

The low lying energy range of the so-called optical modes, which features acoustic–optical crossing points in the dispersion curves, suggests some substantial interaction with the acoustic modes. Along these lines, a hybridization scheme between acoustic and optical modes has recently been proposed [10]. In this latter work, the so-called optical modes correspond to modes which are confined in the nanometric clusters.

Following the idea that the cluster-like nature of quasicrystals is crucial for both sound waves [10] and electronic properties, we propose a detailed identification of the so-called optical modes in quasicrystals, based on the approach of fundamental vibrational modes of nanospheres. The first kind of analysis that we apply (*free* sphere model, section 3) is to consider clusters as the elemental structural entities of quasicrystals. In this way, we can account for the low lying optical modes, since the model gives frequencies which compare well with those experimentally found both for *i*-Al–Pd–Mn and *i*-Zn–Mg–Y. These modes are spheroidal and/or torsional vibrations of the corresponding clusters. Although crude, this description turns out to already provide satisfactory estimates of the optical mode frequencies in a model without any freely adjustable parameters. In a second stage (sphere weakly coupled to a matrix, section 4), the cluster picture is given further realistic input by considering the vibrational coupling with a surrounding matrix, to tentatively account for cluster/cluster interactions and/or clusters overlapping. This latter model is found to match more completely with the experimental observations, particularly with respect to the damping parameters of the considered modes.

2. Vibrations of nanospheres and scattering of acoustic waves

For almost 20 years, studies have been carried out on the vibrational modes of approximately spherical nanometric clusters or nanocrystals embedded in glasses or in macroscopic crystals using Raman or Brillouin light scattering [11–16]. For these embedded nanocrystal systems, the observed low lying modes correspond well to those of a free continuous-medium nanosphere of density ρ_{cl}, longitudinal speed of sound v_{cl}^{L}, transverse speed of sound v_{cl}^{T} and diameter D_{cl}. The vibrational modes of such a sphere were studied for the first time by Lamb [17]. The modes of a free sphere are characterized by a polarization index p that denotes either spheroidal (SPH) or torsional (TOR) modes, the usual quantum numbers ℓ and m of spherical harmonics and the harmonic index n. Among the spheroidal modes the simplest are the spherical ($\ell = 0$), dipolar ($\ell = 1$) and quadrupolar ($\ell = 2$) modes. The mode frequency $\nu_{p\ell mn}$ is inversely proportional to the diameter D_{cl} and proportional to the (longitudinal or transverse) sound speed v_p in the material of the nanosphere:

$$\nu_{p\ell mn} = \frac{S_{p\ell n} v_p}{D_{cl}} \tag{1}$$

where $v_{TOR} = v_{cl}^{T}$, $v_{SPH} = v_{cl}^{L}$ and $S_{p\ell n}$ is a constant for modes of type (p, ℓ, n). The numerical values of $S_{p\ell n}$ were found long ago [17] for a free vibrating sphere.

Table 1. Calculated vibrational energies for a free cluster of Al–Pd–Mn of diameter $D_{cl} = 1.0$ nm. Corresponding experimentally observed optical modes are indicated in superscripts.

		Spheroidal E (meV)	Torsional E (meV)
$\ell = 0$	$n = 0$	22.8[O4]	
	$n = 1$	52.2	
$\ell = 1$	$n = 0$	16.3[O3]	26.6
	$n = 1$	32.7	42.0
$\ell = 2$	$n = 0$	12.2[O2]	11.5[O2]
	$n = 1$	23.1[O4]	32.9

In a recent work [18, 19], it was shown that a sphere embedded inside a matrix scatters acoustic waves more efficiently when their frequencies match certain values which turn out to be generally very close to the free sphere eigenfrequencies. More precisely, it is possible to calculate the position and width of these resonances using the so-called complex frequency model (CFM). The interesting point is that these resonances do not depend on the nature of the incident acoustic waves (plane waves, spherical waves, longitudinal, transverse, . . .). Therefore, we can expect these resonances to be important even when many spheres are involved. This is similar to the 'hard' and 'soft' scatterer picture invoked to interpret sound mode broadening in quasicrystals [10].

In the following, we will apply this continuum mechanical model to very small clusters (<2 nm diameter). Also, the application of continuum type boundary conditions at the interface between the icosahedral cluster and the rest of the quasicrystal is an idealization. A more accurate treatment would need to consider an atomic level description of the cluster and its interface [20]. However, despite these limitations, our numerical results are in good agreement with experiments.

In order to illustrate the applicability of nanosphere mode analysis to quasicrystals, we first consider the results of the free sphere model (because it requires fewer parameters) for Al–Pd–Mn and Zn–Mg–Y. Then, in order to account for a more realistic situation and a more complete vibrational pattern, we examine the case where Al–Pd–Mn clusters are weakly coupled to a surrounding matrix.

3. Free sphere model

3.1. Al–Pd–Mn

The shape of the icosahedral clusters in Al–Pd–Mn is nearly spherical. The number of atoms per cluster ($\simeq 51$) can be considered as sufficient to approximate the lowest-energy confined modes by those of a continuum sphere. Using the approach described in [18], the frequencies of the vibrational modes were calculated for a continuous-medium free nanosphere with a diameter equal to the size of the cluster, i.e. $D_{cl} = 1.0$ nm [21–23]. Both longitudinal and transverse sound speeds in the clusters were approximated with the bulk sound speeds in the Al–Pd–Mn quasicrystal, i.e. $v_{cl}^{L} = 6500$ m s^{-1} and $v_{cl}^{T} = 3500$ m s^{-1} [24]. Table 1 displays the thus-obtained frequency values for the fundamental ($n = 0$) and the first harmonic ($n = 1$) of each type of mode (SPH or TOR) and angular momentum ℓ.

The optical modes of Al–Pd–Mn quasicrystals observed by inelastic neutron scattering [6] have the following approximate energies: $E_{O1} \simeq 7$ meV, $E_{O2} \simeq 12$ meV, $E_{O3} \simeq 16$ meV and $E_{O4} \simeq 24$ meV, with hardly any dependence on wavevector q. The results of the free sphere

Table 2. Calculation of vibrational energies for a free sphere of Zn–Mg–Y of diameter $D_{cl} = 1.2$ nm.

		Spheroidal E (meV)	Torsional E (meV)
$\ell = 0$	$n = 0$	12.4[O2]	
	$n = 1$	31.6	
$\ell = 1$	$n = 0$	10.8[O2]	19.6[O3]
	$n = 1$	20.7	31.0
$\ell = 2$	$n = 0$	8.9[O1]	8.5[O1]
	$n = 1$	15.5[O3]	24.3

model calculations presented in table 1 permit the following assignments.

O2: the $E_{O2} \simeq 12$ meV mode corresponds to the spheroidal and torsional $\ell = 2$ fundamental modes. Both of these modes are fivefold degenerate.

O3: the $E_{O3} \simeq 16$ meV mode corresponds to the triply degenerate dipolar $\ell = 1$ spheroidal mode.

O4: the $E_{O4} \simeq 24$ meV mode corresponds to the spherical $\ell = 0$ mode and also to the fivefold degenerate quadrupolar $\ell = 2$, $n = 1$ spheroidal mode.

It turns out that the *free* sphere calculations are able to provide an accurate assignment for all of the optical mode energies except for the lowest one (O1) (as described in section 4, calculations taking into account the cluster–matrix interaction allow the 'missing' mode O1 to be accounted for). For each of these modes, we might expect the inelastically scattered intensities to scale with the corresponding total number of modes, taking into account their degeneracy. Such tentatively appears to be the case when examining the reported lineshapes [6]. However, to make a detailed comparison would require a quantitative analysis of the inelastic scattering intensities of individual modes, which is beyond the scope of this work.

In order to further assess the relevance of the *free* sphere description to the low energy optical modes in quasicrystalline structures, we now examine the case of Zn–Mg–Y.

3.2. Zn–Mg–Y

The icosahedral quasicrystal Zn–Mg–Y has clusters of diameter $D_{cl} = 1.2$ nm [7]. We calculated the energies of a free spherical cluster having the same diameter ($D_{cl} = 1.2$ nm) as the Zn–Mg–Y clusters and the same sound speeds as bulk Zn–Mg–Y: $v_{cl}^L = 4800$ and $v_{cl}^T = 3100$ m s^{-1} [7]. The results are given in table 2.

Once again, the calculated vibrational energies are found to compare well with those of the optical modes measured through inelastic neutron scattering, i.e. $E_{O1} \simeq 8$ meV, $E_{O2} \simeq 12$ meV and $E_{O3} \simeq 17$ meV [7]:

O1: the $E_{O1} \simeq 8$ meV mode corresponds to the fivefold degenerate spheroidal and torsional $\ell = 2$ modes (whose frequencies are usually almost the same),

O2: the $E_{O2} \simeq 12$ meV mode corresponds to the spherical $\ell = 0$ and the spheroidal dipolar $\ell = 1$ modes,

O3: the $E_{O3} \simeq 17$ meV mode corresponds to the fivefold degenerate quadrupolar $\ell = 2$, $n = 1$ and the triply degenerate torsional $\ell = 1$ modes.

Much like the results obtained for Al–Pd–Mn, the *free* sphere model is found to provide a sound description of all the optical modes in Zn–Mg–Y. The above assignments are restricted

to the low energy range ($E < 30$ meV) where modes were unambiguously identified experimentally.

It is worth noting that from group theoretical selection rules [25] only the spherical and spheroidal quadrupolar modes can be observed by Raman scattering, as experiments confirm (these selection rules can be broken for anisotropic materials or under resonant excitation). No such selection rules exist for inelastic neutron scattering. Besides, it should be noted that the degeneracies of the aforementioned modes (in any case for $\ell \leqslant 2$) are not lifted by lowering the symmetry from spherical to icosahedral. This provides a supplementary justification for using spheres to approximate the icosahedral clusters.

The present calculation predicts undamped vibrational modes whereas the observed excitations are somewhat broadened (~ 4 meV). This may be at least partly attributed to a variation of actual quasicrystal cluster masses, since structural studies have shown that there are several chemical decorations on the same cluster skeleton or by introducing a cluster matrix interaction. Moreover, as evidenced in the Al–Pd–Mn case with the O1 mode, the free sphere model does not account for all vibrational modes when the clusters are embedded in a matrix, even if the cluster/matrix coupling is weak. In the following section, it is shown that calculations taking into account the cluster/matrix interaction can account for the 'missing' O1 mode and for the finite width of the modes.

4. Sphere weakly coupled to a matrix: the Al–Pd–Mn case

The mode frequencies of embedded clusters can be calculated knowing the elastic properties of both the clusters (ρ_{cl}, v_{cl}^L and v_{cl}^T) and the neighbouring matrix (ρ_m, v_m^L and v_m^T) and by assuming the continuity of the stresses and of the atomic displacements upon crossing the cluster/matrix interface [18]. From Murray and Saviot [18], it is possible to determine the spectral width of a confined mode as a function of the elastic constants and densities of both the cluster and the matrix. As expected, the weaker the contrast of elastic constants and densities between cluster and matrix, the stronger the delocalization of the cluster mode in the matrix and the larger its spectral width. Furthermore, from the same authors [18], taking into account the cluster/matrix interaction leads to 'extra modes' that involve the coupled motions of the cluster and the surrounding matrix. These modes will be referred to as mixed cluster–matrix modes.

Similarly to the *free* sphere modes, the frequencies of the cluster–matrix modes are inversely proportional to the cluster diameter. The more notable modes of this type are the *librational* torsional (TOR, $\ell = 1$) mode and the *rattling* spheroidal dipolar (SPH, $\ell = 1$) mode. Both of these modes correspond to semi-rigid oscillations of the cluster linked to its surroundings. The frequencies of these last two kinds of modes are zero for a free cluster.

To *phenomenologically* model the weakness (i.e. mechanical flexibility) of the joint between the nanosphere representing the nanometric clusters and the matrix, we introduce an additional 'x-layer' consisting of a softer (in terms of elastic constants) and lighter medium, as in a previous work [26]. Note at this point that such a simplified model only aims to account for a possible partial delocalization of the cluster vibrational wavefunction, due to its interaction with an environment. The calculation of the cluster eigenmodes requires the knowledge of the x-layer parameters (density ρ_X, longitudinal speed of sound v_X^L, transverse speed of sound v_X^T and thickness d_X). Since these parameters are *a priori* unknown, they were numerically adjusted so that both librational and rattling mode energies fit with that of the lowest energy optical mode ($E_{O1} \simeq 7$ meV).

In table 3 the calculated x-layer model vibrational energies and the phonon full widths at half maximum (FWHM) are given using the same cluster as before with an intermediate

Table 3. Calculated energies for a Al–Pd–Mn cluster, diameter $D_{cl} = 1.0$ nm, weakly bonded to the rest of the quasicrystal by a soft x-layer.

		Spheroidal		Torsional	
		E (meV)	FWHM (meV)	E (meV)	FWHM (meV)
$\ell = 0$	$n = 0$	24.5^{O4}	1.4		
	$n = 1$	51.4	0.8		
$\ell = 1$	$n = 0$	6.6^{O1}	2.4	7.0^{O1}	0.6
	$n = 1$	16.9^{O3}	0.4	26.2^{O4}	0.4
	$n = 2$	32.1	0.6		
$\ell = 2$	$n = 0$	14.6^{O2}	1.6	13.2^{O2}	0.6
	$n = 1$	22.8^{O4}	0.6	31.9	0.6

x-layer. The parameters of the x-layer giving rise to a lowest optical mode energy of 7 meV are sound speeds $v_X^L = 2000$ m s^{-1} and $v_X^T = 1000$ m s^{-1}, mass density $\rho_X = 3.4$ g cm^{-3} and thickness $d_X = 0.05$ nm. Although the x-layer may be viewed as the so-called 'glue' regions interconnecting the clusters [1–3], the thus-obtained x-layer parameter values are only meant to model a weak linking between the cluster and its surroundings; they cannot be given a firm physical meaning. The surrounding matrix was modelled as a thick shell surrounding the x-layer with an infinite radius. The sound speeds and mass density of the surrounding matrix were set equal to those of the cluster, hence of the bulk quasicrystal. Note that the so-called 'matrix modes' [18] are not given here because of their huge damping; they are irrelevant to the present investigation.

The comparison of the free cluster vibrational energies (table 1) with those of the cluster linked to the surroundings (table 3) shows that the cluster/matrix interaction does not significantly change the vibrational frequencies (the parameters of the x-layer and of the matrix have only a weak effect on most of the optical mode energy positions). The main differences originate from non-zero FWHMs and the appearance of cluster–matrix mixed modes (rattling and librational ones) in the latter case. These mixed modes are relatively strongly localized on the cluster. Thanks to the x-layer model, the lowest energy optical mode O1 can now be assigned to the triply degenerate librational mode (TOR, $\ell = 1, n = 0$) and also to the triply degenerate spheroidal rattling mode. The assignment of the other modes, O2 and O4, remains unchanged, while the O3 mode now corresponds to the first harmonic ($n = 1$) of the triply degenerate dipolar $\ell = 1$ spheroidal mode. Obviously, the lowest energy mode depends relatively strongly on the cluster–surroundings bonding, the properties of which are not well known. Therefore, at the present stage, it should be considered cautiously.

The approach we have proposed in this article relies on no further assumption than a cluster based structure that has widely been reported for both *i*-AlPdMn and *i*-ZnMgY. Cluster modes are a *natural* consequence of a structure having a nanometric relief. In that sense, equivalent modes are expected to occur for non-icosahedral cluster structures (for instance cylinders exhibit radial breathing modes like those observed in carbon nanotubes). So far, most inelastic neutron studies and computer simulation studies have assigned the low energy optical modes to the dynamics of single atoms. Such assignment derives from the ability of both techniques to probe the dynamics inherent to a particular species, yet they do not provide information about the precise nature of the modes which involve the considered atom. The cluster origin of the optical modes is not necessarily in contradiction with single-atom dynamics: the participating ratio of a single atom to a cluster mode is expected to depend on the nature of the atom and its location within the cluster as well as on the type of cluster mode.

5. Conclusion

The optical modes observed by inelastic neutron scattering in icosahedral Al–Pd–Mn and Zn–Mg–Y quasicrystals correspond well to the modes of free continuous-medium nanospheres having the same diameter as their building clusters and the same sound speeds as in the bulk quasicrystal.

The model of the nanosphere is expected to be valid only for the lowest energy modes corresponding to the fundamental modes or, at most, to their first harmonics, i.e. modes for which the separation between maxima and minima of the vibrational wavefunction is much larger than the interatomic distance.

The linking of the clusters with their surroundings (as phenomenologically modelled by the x-layer model) partially delocalizes the confined modes in the matrix. Due to the interaction, through the 'glue' regions, between neighbouring clusters, cluster modes of same symmetry are expected to couple, thereby establishing a coherence among them.

Acknowledgments

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