Theory of the Raman Response in Fibonacci Superlattices

Chumin Wang and R. A. Barrio
Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,
04510 México, D. F., México

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A microscopic theory for obtaining the polarized Raman spectrum of Fibonacci chains is developed and applied to GaAs-AlAs heterostructures. The results of the theory, without adjustable parameters, are compared with experimental data, and remarkable agreement is attained. The treatment is performed in real space and, although this system is nonperiodic in a strict sense, it retains many properties usually associated with the translational invariance of crystals. Because of its computational efficiency, this theory is suitable to other finite-size systems.

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The interest that many physicists have shown in quasicrystals arises mainly from the fact that these present properties that were once associated with the translational invariance exclusive to crystalline structures. Real fivefold diffraction patterns[1] caused consternation amongst crystallographers. However, the existence of space-filling infinite structures in two dimensions with fivefold symmetries was familiar long before.[2] Quasicrystals in one dimension (1D) can be obtained from structures which are strictly periodic in a space with more dimensions.[3] Namely, the Fibonacci 1D system preserves somewhat the crystal properties of the 2D square lattice from which it is derived.[3] These ideal systems have acquired greater relevance because of the recent technical developments that have allowed the synthesis of real superlattices with a Fibonacci ordering.[4] Physical properties of these real systems can be tested experimentally; for instance, Raman scattering is ideal for vibrations, since the Raman activity of a given normal mode is governed by selection rules arising from conservation of the crystal momentum (**k**). In truly disordered systems,[5] the Raman spectrum (RS) is continuous, since the k conservation is relaxed.

Raman spectra taken from GaAs-AlAs heterostructures, built up in a Fibonacci sequence,[6] show discrete peaks at certain frequencies in the acoustic region (≤ 100 cm^{-1}) that follow a "golden section" progression. Furthermore, each peak is split into doublets, a fact that was explained[6] in terms of an incommensurate folding of a fictitious Brillouin zone, and of the conservation of the momentum **q** of the light. It is not clear why one should invoke zone folding, as in the case of periodic perturbations, to explain the phenomenon in this system.

The main purpose of this Letter is to present a theory without the assumption of any pseudoperiodicity in the direction of the Fibonacci stacking of planes.

Any microscopic theory, attempting to explain the Raman effect in solids, should take into account two fundamental physical quantities of the system: the dynamical correlation between the atomic motions, and the changes in the local polarizabilities of the atoms during vibration. The Raman cross section $R(\omega)$ can be thought of as proportional to[7,8]

$$-\frac{\omega}{\pi}\,\mathrm{Im}\sum_{l,m} e^{i\mathbf{q}\cdot(\mathbf{r}_l-\mathbf{r}_m)}[\nabla\alpha_l]\cdot\mathbf{G}(l,m)\cdot[\nabla\alpha_m], \tag{1}$$

where α_l is the polarizability tensor associated with the atom at site l with coordinates $\mathbf{r}_l$, and **G** is the displacement-displacement Green's function. The polarized part of the Raman tensor can be approximated by a model[7] which allows it to be written as a linear function of the bond stretching, and therefore the Raman activity of totally symmetric sites is nil.[9] In cases similar to GaAs-AlAs heterostructures, this means that the terms in square brackets select only the atoms that lie in the interfaces between the materials, which are the ones in nonsymmetric sites. Because not all the elements of **G** are needed, one can renormalize out the correlations between symmetric sites. This can be accomplished by our following the methods sketched in Fig. 1.

The structure in Fig. 1(a) consists of alternating blocks of GaAs and AlAs, containing N,N' atomic planes of the (001) type of GaAs and M planes of AlAs. The Fibonacci sequence is followed between blocks $A=M+N$ and $B=M+N'$. The first step consists of our mapping the 3D crystal onto a 1D linear chain, by defining a two-dimensional **k** vector lying on the (001) type planes that form the interfaces, as has been done for Si crystals.[10] This is shown as step (a)$\Longrightarrow$(b) in Fig. 1. Next, since only the As planes in the interfaces between the two materials are Raman active, one uses real-space renormalization techniques to eliminate the coordinates of the intermediate planes, which results in frequency-dependent effective force constants $\gamma(N,\omega)$, between the As renormalized planes i with frequency-dependent site energies $D(i,\omega)$. This is depicted in Fig. 1 as step (b)$\Longrightarrow$(c). After these steps, Eq. (1) can be written as

$$-C\frac{\omega}{\pi}\,\mathrm{Im}\sum_{i,j} e^{iq[r(i)-r(j)]}\mathbf{G}_{k=0}(i,j)(-1)^{i-j}, \tag{2}$$

where i and j are labels for the As selected planes; thus the distance between interfaces is $r(i)-r(j)$. The $\mathbf{G}_k$ is the Fourier transform of $\mathbf{G}$ with respect to the 2D $\mathbf{k}$ vector. The factor $(-1)^{i-j}$ arises from the change of phase between adjacent interfaces, which is noticeable in Fig. 1. The absolute value of the constant in square brackets in (1) is absorbed into the proportionality constant C.

We have devised a method to overcome the difficulty of the summation, which allows (2) to be calculated exactly, with very little computational effort. If one defines

$$\mathbf{g}(i,j)=\mathbf{G}_{k=0}(i,j)\exp\{iq[r(i)-r(j)]\},$$

the equations of motion for the Green's functions can be conveniently written as

$$[M\omega^2-D(1,\omega)]g(1,1)=1+\gamma(N,\omega)g(2,1)b_N^*,$$
$$[M\omega^2-D(2,\omega)]g(2,1)b_N^*=\gamma(N,\omega)g(1,1)+\gamma(M,\omega)g(3,1)b_M^*b_N^*,$$
$$\vdots$$
$$[M\omega^2-D(1,\omega)]g(1,2)b_N=\gamma(N,\omega)g(2,2),$$
$$[M\omega^2-D(2,\omega)]g(2,2)=1+\gamma(N,\omega)g(1,2)b_N+\gamma(M,\omega)g(3,2)b_M^*,$$
$$\vdots$$

$$[M\omega^2-D(1,\omega)]S(1)=1-\gamma(N,\omega)S(2)b_N^*,$$
$$[M\omega^2-D(2,\omega)]S(2)=1-\gamma(N,\omega)S(1)b_N-\gamma(M,\omega)S(3)b_M^*,$$
$$\vdots$$

where M is the As mass. The factor $b_N=\exp(iqd_N)$ takes into account the phase shift included in g, and the width d_N of a block with N planes can take only three values, depending on the nature of the block (N,M,N').

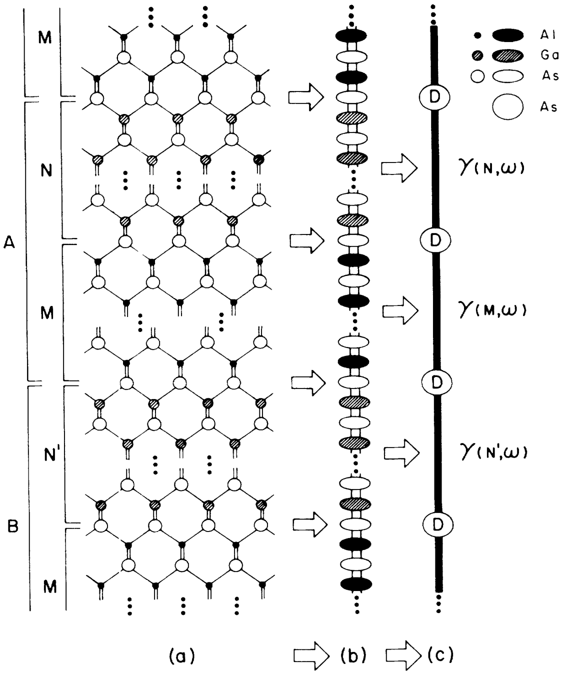

FIG. 1. Schematic representation of the two renormalization processes followed in the model. The real atoms are represented by circles, the renormalized planes are flat ellipses, and the final chain is formed by interface As sites with effective site energies D and force constants γ.

The partial summations $S(i)=\sum_j(-1)^{i-j}g(i,j)$ can be obtained by choosing all the equations with the same index i in $g(i,j)$. Notice that one can write "equations of motion" for the $S(i)$, which only differ from the original equations by a sign. These can be solved by the transfer-matrix method.[11] The final answer is $R(\omega)=(-C\omega/\pi)\,\mathrm{Im}\sum_i S(i)$. More details of this calculation will be given elsewhere.[11]

Let us use a Born Hamiltonian, with interatomic central-force constants $\alpha=3.83\times10^4$ dyn/cm, for GaAs, and $\alpha'=4.00\times10^4$ dyn/cm, for AlAs. The corresponding noncentral-force constants are $\beta=2.39\times10^4$ dyn/cm and $\beta'=2.66\times10^4$ dyn/cm. These values were extracted from a model[12] that fits the acoustic part of the density of states (DOS) reasonably well. In the particular stacking of the experiment,[6] $N=30$, $M=12$, $N'=14$, and the total number of A-B blocks is 377, which corresponds to a generation number of 13 in the Fibonacci series.

Figure 2(a) shows the vibrational DOS at $k=0$ for the interface planes, obtained with

$$\rho(\omega)=-(2M\omega/\pi)\,\mathrm{Im\,Tr}\sum_i\mathbf{G}_{k=0}(i,i).$$

It should be noticed that the acoustic band ($0\le\omega\le165$ cm^{-1}) is quite different from the GaAs optical bands ($165\le\omega\le235$ cm^{-1}) and from the AlAs optical modes ($280\le\omega\le330$ cm^{-1}). These latter modes should be around 400 cm^{-1}. However, they cannot be adjusted simultaneously with the lower part of the spectrum without consideration of second-neighbor interactions and dynamical charge transfer.[13] Neither were long-range Coulomb forces, responsible for LO-TO splittings, considered. However, since the experiment only shows the acoustic region, it is proper to use the Born

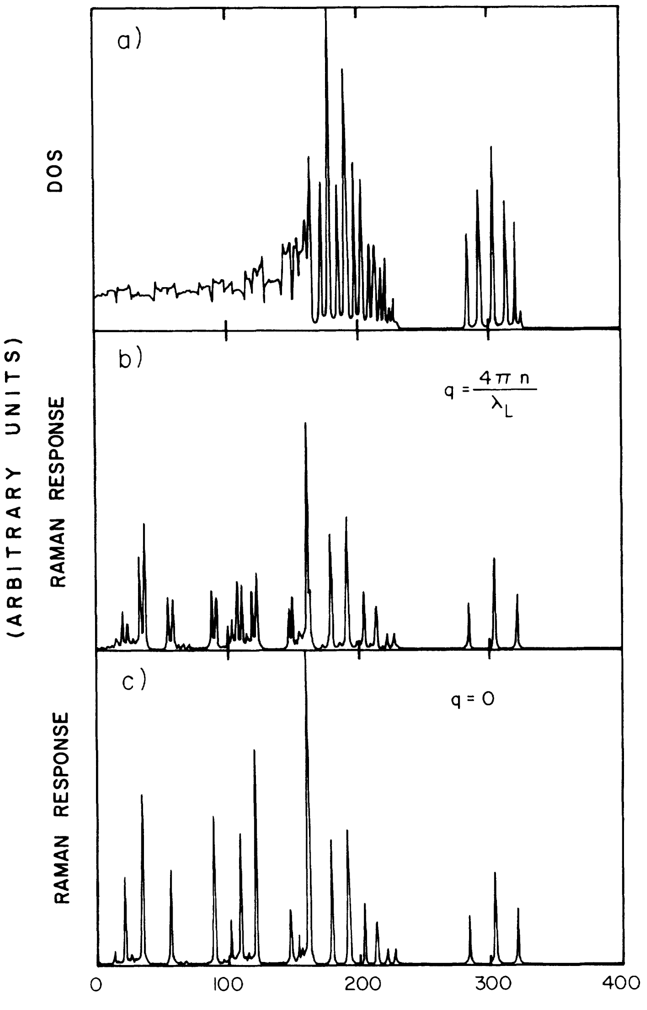

FIG. 2. (a) Vibrational density of states of all interface sites at $k=0$. Polarized Raman spectra calculated from the present theory for (b) back scattering and (c) $q=0$.

Hamiltonian. The self-similarity properties of this spectrum will be thoroughly discussed elsewhere.[11]

In Fig. 2(b) the result from (2) is plotted for $q=4\pi n/\lambda_L$, proper for backscattering, where the refractive index $n=4.5$ was taken from Colvard *et al.*[14] and the wavelength of light, $\lambda_L=5145$ Å, was taken from the experiment.[6] It is to be noted that the RS does not contain all the modes, but resembles the incommensurate "Brillouin zone" folding picture, as though there were selection rules. Furthermore, the splitting of the acoustic modes into doublets is remarkable, resembling the splitting found in true superlattices,[14] where the dispersion relation should be $\omega \sim k$.

In order to see the exact frequencies of the Raman-active modes, the RS was calculated at $q=0$, and is shown in Fig. 2(c). It should be noticed that the intense peaks in the acoustic region at frequencies $\omega_1=13.4$, $\omega_2=21.7$, $\omega_3=35.0$, and $\omega_4=56.7$ cm^{-1} follow the "golden section" ratio, that is $\omega_1/\omega_2=\omega_2/\omega_3=\omega_3/\omega_4=\sigma\equiv(\sqrt{5}-1)/2$. We observe a deviation of this behavior in ω_4/ω_5, where there is a slightly softer mode at $\omega_5=88.8$ cm^{-1}, which agrees much better with the experiment.[6] Notice also that the splitting is not exactly symmetric around each frequency, contrary to the expected zone-folding effect, and that the behavior of the optical modes is quite different from that of the acoustic ones, which resembles the results from theories that make use of the photoelastic continuum approach,[14] as expected in the limit of long-wavelength excitations.

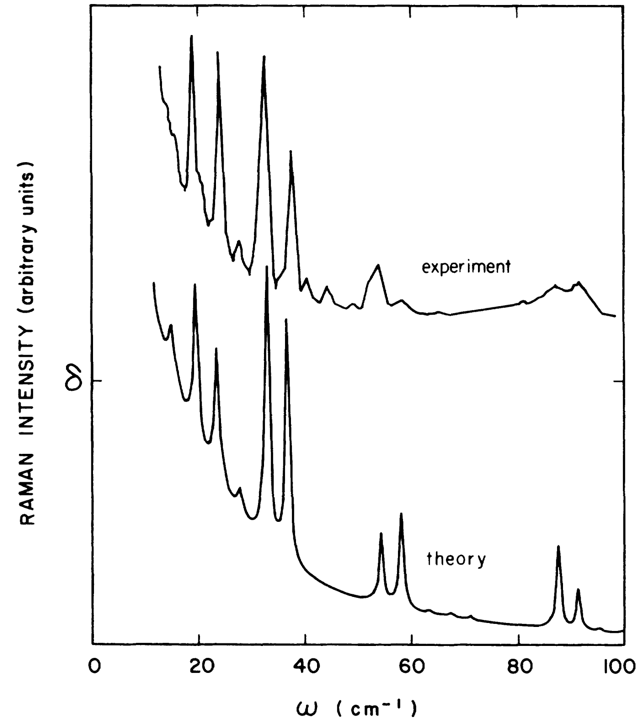

FIG. 3. Comparison between the theoretical and experimental results. The vertical scale for the experimental data (from Ref. 6) has been shifted by δ.

A close comparison with experimental data is shown in Fig. 3. The theoretical data are the same as in Fig. 2(b), except that the thermal factor $n+1$ for the population of phonons at room temperature has been included. A Lorentzian of half-width of 15 cm^{-1}, centered at zero, has been added to the RS. A small imaginary part of (0.5 cm^{-1}) has been added to the frequency. All this processing is only needed in order to simulate artificially the experimental conditions. The only parameters of the theory are the force constants and the refractive index of the medium, which have been extracted from other sources, not adjusted to the RS.

In spite of the remarkable agreement between theory and experiment, there are a few slight differences between the two spectra. The relative intensities of the peaks are not so well reproduced because of effects on the polarizability tensor not included in the theory, as discussed above. In the experiment one notices some Raman-active modes at about 40 cm^{-1}, which are not predicted by the theory. This can be explained by the fact that the reported experimental RS is not the polarized part,[7] only the (x,x) configuration,[6] and therefore some of the transverse modes should be present in the experimental data.[14] It should be noticed also that the spacing between the doublets is not large enough in the theoretical RS. This is because the value for n was taken when $\lambda_L = 4579$ Å,[14] smaller than the one used in this experiment. Thus, one should not be surprised if a bigger value for n (~ 5.5) fits better.

In conclusion, a simple theory has been presented and applied to real Fibonacci heterostructures. This theory has the virtue, besides its simplicity, of providing a direct relationship between the microscopic properties of vibrations, at all frequencies, and the coherence effects measured in the macroscopic sample. Because of the efficiency of the calculation, this theory is perfectly suitable for application to other finite systems, such as real periodic superlattices. The model can be easily extended, if needed, to more realistic Hamiltonians, which could describe the phonons more accurately in all of reciprocal space and in all frequency ranges. Electrons and other excitations can also be modeled by the present theory.

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