Phonon Dispersions in $Ga_xAl_{1-x}As$ Alloys

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The vibrational properties of $Ga_xAl_{1-x}As$ alloys have been studied using large supercells to simulate the disorder and *ab initio interatomic* force constants. In agreement with recent experimental evidence, our results indicate that well defined GaAs-like and AlAs-like phonon dispersions exist for any concentration. Besides broadening phonon states with definite wave vector, alloying narrows the optic branches and lowers the longitudinal modes more than the transverse ones, thus reducing the LO-TO splitting. The acoustic bands are instead rather insensitive to the composition.

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Much interest is currently being devoted to the vibrational properties of $Ga_xAl_{1-x}As$ alloys,[1-7] both because this system is paradigmatic of a large class of *two-mode* pseudobinary alloys,[2] and also with the aim of clarifying their relation with the corresponding properties of GaAs/AlAs superlattices (SL's).[7] A long debated problem is whether phonon states in semiconductor alloys can still be described in terms of well defined phonon dispersions, as they can in pure crystals. For $Ga_xAl_{1-x}As$ alloys, no neutron-diffraction data exist which could assess the dispersive character of normal modes. The traditional tools of investigation are Raman and infrared spectroscopy which probe long-wavelength vibrations. The Raman spectrum of $Ga_xAl_{1-x}As$ consists of two distinct peaks corresponding to the vibration of each cationic species separately. As a consequence of disorder, the peaks are shifted and broadened with respect to pure materials, with a rather asymmetric line shape. This asymmetry has been interpreted assuming that Raman-active phonon modes are localized by disorder on a scale $\lesssim 100$ Å.[4] However, recent experimental investigations indicate that "Raman-active LO phonons in... Al_x-$Ga_{1-x}As$ have well defined momenta and are coherent over [distances] greater than 700 Å."[6] This band picture of the phonon modes is confirmed and extended by Raman experiments on GaAlAs/AlAs SL's:[8] Raman peaks corresponding to phonons confined in the GaAlAs region display a well defined dependence upon confinement order, which is direct evidence of the dispersive character of lattice vibrations in the alloy.

All the calculations of the vibrational properties of semiconductor alloys performed so far rely on semiempirical force constants, and on some mean-field approximation to treat the disorder (average T matrix, coherent potential, etc.). Modeling alloys without using any mean-field approximations requires the introduction of large supercells. Recently, a very efficient technique has been introduced to calculate *ab initio* the vibrational properties of complex systems, based on density-functional linear-response theory.[9] Such a technique has been successfully applied to GaAs/AlAs SL's.[10] However, the size of the supercells necessary to simulate the effects of disorder in alloys may be so large ($\gtrsim 100$ atoms) that even the above method fails to provide a direct way to treat them. In this paper we pursue a different approach to the vibrational properties of $Ga_xAl_{1-x}As$ alloys which relies on supercells to treat disorder (thus avoiding any mean-field approximations), and on *ab initio interatomic* force constants to calculate the corresponding dynamical matrices. Taking advantage of the chemical similarities between the two different cationic species, we first calculate the interatomic force constants of a periodic virtual crystal whose cationic pseudopotential is the average between the Ga and Al potentials. We then verify that these force constants provide a very accurate description of the vibrational properties of the two pure materials, GaAs and AlAs, as well as of some selected ordered structures of the alloy at composition $x=\frac{1}{2}$. We finally build the dynamical matrices of large supercells (containing approximately 500 atoms), where the cationic sites are occupied at random by Ga ions with probability x and by Al ions with probability $1-x$. The resulting physical properties are then averaged with respect to a few cationic configurations.

Interatomic force constants are defined as $\Phi^{ss'}_{\alpha\alpha'}(\mathbf{R}) = -\partial F^s_\alpha(\mathbf{R})/\partial u^{s'}_{\alpha'}(0)$, where $F^s_\alpha(\mathbf{R})$ is the αth component of the force acting on the sth atom of the elementary cell located at position $\mathbf{R}$, and $u^s_\alpha(\mathbf{R})$ is the corresponding displacement. A convenient way to calculate Φ is through its Fourier transform $\tilde{\Phi}(\mathbf{q})$, which is essentially the dynamical matrix of the system. The advantage is that—for each given point of the Brillouin zone (BZ) —$\tilde{\Phi}(\mathbf{q})$ can be calculated with a numerical effort comparable to that needed by a self-consistent calculation for the *unperturbed* system[9] (in our case, just containing two atoms per cell). The BZ is sampled on a uniform grid, and the interatomic force constants are finally calculated by Fourier transform. Mathematically, the number of real-space force constants so obtained is equal to the number of reciprocal-space points used to sample the BZ. Physically, the discrete BZ sampling is equivalent to solving the problem in real space with a supercell whose linear dimensions are of the order of $2\pi/q_{\text{min}}$. Our calculation in reciprocal space scales linearly with the number of $\mathbf{q}$ points, i.e., with the volume of the supercell, whereas a direct self-consistent calculation for the supercell would scale as the cube of such volume.

So far, interatomic *ab initio* force constants have been calculated only for silicon, using dielectric matrices and local pseudopotentials.[11] In this paper, the force constants are obtained by the linear-response technique of Ref. 9 which is far more efficient, and also allows one to use accurate norm-conserving pseudopotentials. The electronic ground state of the virtual crystal is calculated in the local-density approximation, using norm-conserving pseudopotentials,[12] plane waves up to a kinetic-energy cutoff of 12 Ry, and a set of ten special points in the irreducible wedge of the BZ. Dynamical matrices are then calculated on a uniform mesh in the BZ which corresponds—in real space—to a face-centered-cubic supercell containing 1024 atoms: This size allows us to calculate force constants up to the 42nd shell of neighbors. Dynamical matrices in polar materials are nonanalytic in the long-wavelength limit, due to long-range (dipolar) force constants which cannot be Fourier analyzed on a finite mesh. However, the nonanalytic part of the dynamical matrix is easily expressed in terms of the ionic effective charges and macroscopic dielectric constant of the crystal,[13] which we calculate independently.[9,14] The nonanalytic part so obtained is subtracted from the dynamical matrices, which are then Fourier analyzed to obtain the short-range part of the force constants. Finally, the long-range contribution is added separately.

The virtual-crystal interatomic force constants are used to build approximate dynamical matrices for real systems such as pure materials, superlattices, or alloys, the difference among them being taken into account only through the different cationic masses (in the following, this approximation will be referred to as the "mass approximation"). For GaAs and AlAs, the mass approximation has been tested against very accurate self-consistent calculations of the phonon dispersions of the two pure materials.[10(b),15] It turns out that acoustic and transverse-optic (TO) phonon modes are rather insensitive to the mass approximation, whereas longitudinal-optic (LO) bands are shifted rigidly (upwards for GaAs and downwards for AlAs) by $\approx$5–6 cm^{-1}. We stress that such an accuracy is achieved without any empirical adjustment of the ionic effective charges. In fact, the shift of the LO bands is almost entirely due to the small difference between the GaAs and AlAs effective charges. Analogous tests made for short-period SL's and for some ordered alloy structures[10(b)] indicate that the mass approximation can describe composite systems at the same level of accuracy as pure materials. We finally decided to simulate $\text{Ga}_x\text{Al}_{1-x}\text{As}$ alloys using simple cubic cells whose linear dimensions are 4 times the lattice parameter of the bulk alloy, thus containing 512 atoms. For any given composition x, cations are assigned the Ga mass with probability x, and the Al mass with probability $1-x$. The resulting dynamical matrix is diagonalized at the center of the supercell BZ, and the calculated physical quantities are mediated over five different cationic configurations. We have verified that both the size of the supercell and the number of random configurations are enough to give a resolution better than ≈ 2 wave numbers in the spectral features we have studied.

The physical properties we have studied are the Raman cross section σ_R and the spectral density of states $n(\mathbf{q},\omega)$. Off resonance, the former is given essentially by the derivative of the macroscopic polarizability of the system with respect to the vibrational normal coordinates:

$$\sigma_R^{IF}(\omega) \propto \sum_\nu \delta(\omega^2-\omega_\nu^2) \left| \hat{\boldsymbol{\epsilon}}_F^* \cdot \frac{\partial \boldsymbol{\chi}}{\partial q_\nu} \cdot \hat{\boldsymbol{\epsilon}}_I \right|^2 ,$$

where $\hat{\boldsymbol{\epsilon}}_{I,F}$ are the polarizations of the incoming and diffused photons, $\boldsymbol{\chi}$ is the polarizability tensor, q_ν is the normal coordinate of the νth mode, and ω_ν is the corresponding frequency. The derivative of the polarizability is given by $\partial\boldsymbol{\chi}/\partial q_\nu = \sum_{s,i,\gamma}(\partial\boldsymbol{\chi}/\partial u_{s,i}^\gamma)(\partial u_{s,i}^\gamma/\partial q_\nu)$, where $u_{s,i}^\gamma$ is the γth component of the displacement of the sth atom in the ith unit cell. The mass approximation together with translational invariance and tetrahedral symmetry yields $\partial\chi_{\alpha\beta}/\partial u_{s,i}^\gamma = P(-)^s|\epsilon_{\alpha\beta\gamma}|$, where P is a constant, and ϵ the Levi-Civita tensor. One finally obtains

$$\sigma_R^{xy}(\omega) \propto \sum_\nu \frac{\delta(\omega-\omega_\nu)}{\omega_\nu} \left| \sum_{i,s} \frac{\partial u_{s,i}^z}{\partial q_\nu} \right|^2 , \qquad (1)$$

where $\partial u/\partial q$ is simply related to the eigenvectors of the dynamical matrix. In practice, the δ function appearing in Eq. (1) as well as in other similar expressions, is approximated by a Gaussian:

$$\delta(\omega) \approx \frac{1}{(2\pi\sigma^2)^{1/2}} \exp\left(-\frac{\omega^2}{2\sigma^2}\right),$$

where we have chosen $\sigma^2 = 2\ \text{cm}^{-2}$.

Spectral densities of states (SDOS) are defined as

$$n_\alpha(\mathbf{q},\omega) = \sum_{\nu,s} \delta(\omega-\omega_\nu)\,|\langle \mathbf{q},\alpha,s\,|\,\xi_\nu\rangle|^2 , \qquad (2)$$

where the ξ's are eigenvectors of the dynamical matrix and $|\mathbf{q},\alpha,s\rangle$ is a normalized vector representing a mode of wave vector $\mathbf{q}$ where the sth atom of the unit cell moves along the α direction. An appropriate choice of the α directions gives the *longitudinal* (∥) and *transverse* (⊥) SDOS. In the absence of disorder, the n's are sums of δ functions centered at the appropriate normal fre-

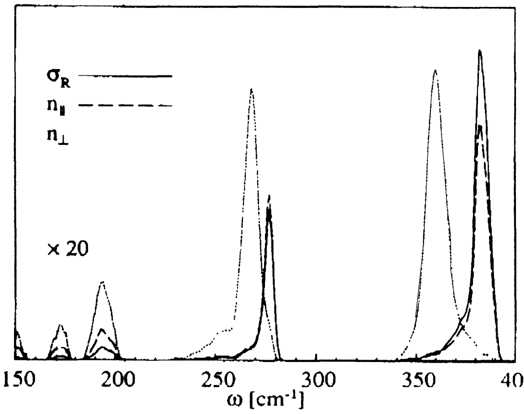

FIG. 1. Raman intensity (solid line), LO_Γ (dashed line), and TO_Γ (dotted line) spectral densities of states of $Ga_{1/2}Al_{1/2}As$. The data below 210 cm^{-1} are magnified by a factor of 20.

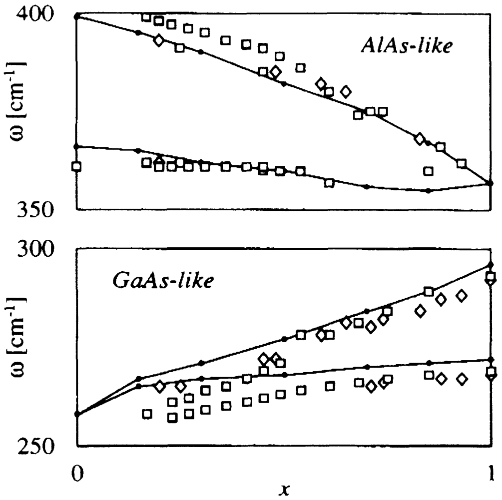

FIG. 2. Dependence of the LO_Γ and TO_Γ peaks of $Ga_xAl_{1-x}As$ upon molar composition x. Experimental data are indicated by squares (from Ref. 1) and diamonds (from Ref. 3).

quencies with definite momentum **q**. When disorder is present, **q** is no longer conserved: In case it is *approximately* so, the δ-like peaks are simply broadened and shifted; otherwise the peak structure is completely lost and normal modes are not characterized by any definite momentum. Because of the finite size of our supercell, Eq. (2) can only be sampled at discrete **q** points. In the ΓX direction, for instance, our geometry is compatible with five uniformly spaced **q** points.

In Fig. 1 we report the Raman cross section and the longitudinal and transverse spectral densities of states at $\mathbf{q}=0$ calculated for $Ga_{1/2}Al_{1/2}As$. As expected, the Raman intensity is very closely approximated by the longitudinal spectral density of states. The asymmetry of the Raman profile experimentally observed is predicted by our calculation. Also notice that some very weak structure is present slightly below 200 cm^{-1}, in the region of disorder-activated longitudinal-acoustic (DALA) modes. The relative intensity is, however, much weaker than observed experimentally, indicating that light scattering by DALA modes is enhanced by electronic processes which are neglected in the present work.

In Fig. 2 we display the position of the TO and LO peaks as functions of the molar composition x. The LO peaks depend more on x than the TO ones, and they both tend to the same value in the extreme diluted limit. The agreement with experiments is good, and of the same order as that between different sets of experimental data. We note that the agreement of our results with experiments could even be improved if they were corrected according to the difference between the pure-material frequencies calculated with and without the mass approximation.^{15}

Figure 3 shows the longitudinal and transverse spectral densities of states for $x=\frac{1}{2}$ along the ΓX direction. The spectral resonances—whose width is of the order of 10 cm^{-1}—move as the wave vector **q** varies in the BZ. The positions of the peaks are indicated by the solid lines in the ω-**q** plane. The main effects of alloying are the broadening and shifting of the peaks, and a modulation of their intensity. In the acoustic region, the dispersive character of the lattice vibrations is quite evident. In the optic region, it is less so due to the narrowness of the

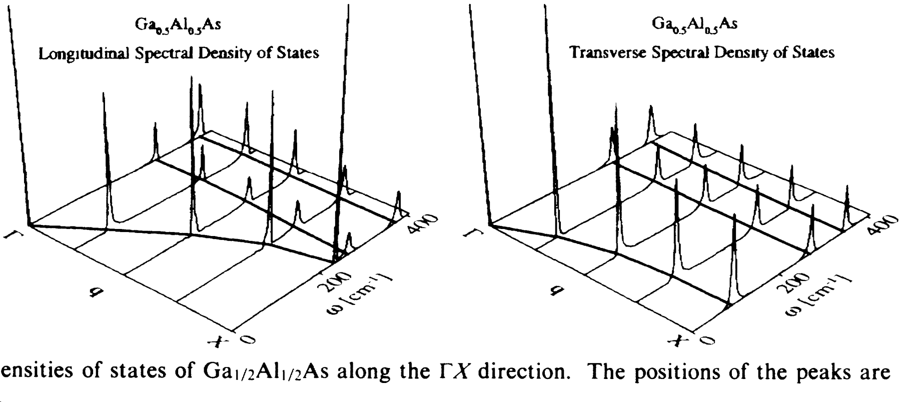

FIG. 3. Spectral densities of states of $Ga_{1/2}Al_{1/2}As$ along the ΓX direction. The positions of the peaks are indicated by the solid lines in the ω-**q** plane.

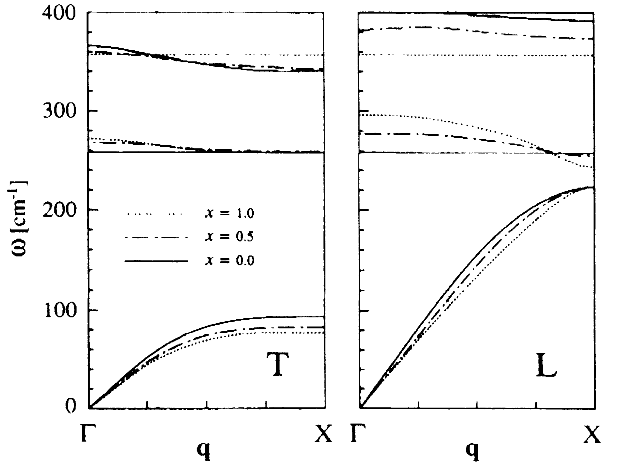

FIG. 4. Phonon dispersions of $Ga_xAl_{1-x}As$ along the ΓX direction for three different molar compositions, x.

phonon branch, whose width may be comparable with that of the resonance. The resonances are, however, sufficiently narrow to allow one to assign a well defined position to the peaks as the wave vector moves in the BZ. The most favorable situation is met for GaAs-like LO modes, in the Ga-rich regime, where one has a large bandwidth (20–50 cm^{-1}) and a small resonance width ($\lesssim 5$ cm^{-1}). As the Ga concentration increases, the bandwidth increases (see below), and the resonance narrows, thus making the dispersive character more evident. This is observed experimentally in Raman spectra of AlAs/GaAlAs SL's.[8]

In Fig. 4 we report the phonon dispersions of $Ga_xAl_{1-x}As$ along the ΓX line, for three different concentrations. Alloying has little effect on the acoustic branches, which are already very close in the GaAs and AlAs pure material. Optic bands are narrowed with respect to the pure-material limit, as a consequence of dilution (in the extremely diluted limit, each band collapses into an isolated-impurity state). Longitudinal bands are lowered and—to a smaller extent—transverse bands raised, resulting in a smaller LO-TO splitting: In the extremely diluted limit, longitudinal and transverse modes are degenerate as a consequence of a vanishing macroscopic polarization.

AlAs-like LO bands—which are very flat already in pure AlAs[10,15]—maintain their flatness upon alloying. This fact is potentially relevant for the purpose of characterizing ultrathin GaAs/AlAs SL's. Recently it has been proposed that the observed dependence of the AlAs-LO_1 Raman-active mode upon the thickness of the AlAs slab should be interpreted as due to cationic intermixing affecting *all* the Al planes.[10] The present observation that the position of the AlAs-LO band depends on Al concentration—whereas its width does not—suggests that the departure of the AlAs-LO_1 frequency in GaAs/AlAs SL's from its bulk value provides a lower bound for Ga concentration in the *purest* Al planes. This confirms the importance of AlAs-like modes for characterizing short-period GaAs/AlAs SL's and indicates that an experimental effort towards a better knowledge of these modes in the pure crystal and in the alloy would provide very useful information.

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