$-\langle\Delta y\rangle]^2\rangle \propto \langle\Delta y\rangle$, as can be seen from Figs. 2 and 3.

The rather explosive growth of the departure from the Millikan behavior in going from the slip-dominated regime (large-particle limit) to the new physics regime (small-particle limit) suggests a certain nonlinear coupling between the slowly decaying flow field and the fluctuating force. The strength of the coupling increases with increasing Brownian diffusion velocity and the Basset contribution, i.e., the persistence of the flow field, indeed grows as $\sqrt{p}$. No exact theory is available at present.

We benefitted from numerous discussions with colleagues in formulating many questions which influenced the course of the experiment. In particular we acknowledge the help of Professor R. J. Emrich and Professor J. A. McLennan. This work has been supported in part by Grant No. PHY-79-9267 from the National Science Foundation. One of us (P.D.F.) receives additional support as a Byllesby graduate fellow.

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Ab Initio Force Constants of GaAs: A New Approach to Calculation of Phonons and Dielectric Properties

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It is shown that self-consistent calculations of the electronic charge density in large periodic cells containing a single displaced atom provide all the information needed for *ab initio* determination of force constants, phonon dispersion curves, effective charges, and the static dielectric constant. Results are presented for GaAs.

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Two methods have been developed to calculate structural energies from the electron-ion Hamiltonian, (1) perturbation expansions[1] for phonons considered as small perturbations upon the crystal structure and (2) direct calculations[2-7] of the total energy of a crystal with "frozen phonon" displacements of arbitrary magnitude, treated on an equal basis with the energy of the undistorted lattice. The simplicity of the direct method has made it possible to carry out accurate calculations[2-7] with no essential approximations other than the local density form for exchange and correlation.[8] Remarkable successes have been found for Si, Ge, and GaAs including prediction of stable crystal structures,[3] displacive phase transitions,[4] elastic constants,[2,6] and frequencies,[2-6] pressure dependences,[2-6] and anharmonic terms[2,4,6] for phonons at $k=0$ and at several high-symmetry points on the boundary of the Brillouin zone. The drawback of the method used to date is that application to other k points is very difficult because calculations of much larger size would be required. This is a serious limitation; for example, it is not possible to treat directly LO phonons for $k \to 0$ in ionic crystals because of the nonanalytic k dependence of the macroscopic electric fields.[1,4] The perturbation method can deal with Coulomb interactions and with phonons at any k (Refs. 1, 9); however, it is restricted to small displacements and its use has been limited because it requires a large computation of the dielectric matrix[9]—a formidable amount of information of which only a small part is needed for determination of phonon properties.

In this Letter we present a new method in which *ab initio* force constants between planes of atoms in real space are calculated directly. The harmonic force constants determine entire phonon dispersion curves $\omega(k)$, in addition to which can be calculated anharmonic terms to any order. Our approach is based upon self-consistent calculations of the electronic charge density in a crystal with a single plane of atoms displaced. With use of the Hellman-Feynman theorem,[10] forces on a displaced atom K and all other atoms K' can be found, thus determining from a single calculation many independent force constants $\Phi(K, K')$. We show that periodic supercells of manageable size are sufficient to determine all forces including long-range Coulomb terms[11] and that it is possible to calculate directly macroscopic effective charges ($e_L{}^*$ and $e_T{}^*$) and the static dielectric constant ϵ.

We apply the method to GaAs determining interplanar force constants, phonon dispersion, and eigenvectors for all branches in the [100] direction. This case is chosen because we have previously[4] calculated the equilibrium lattice constant (5.71 Å, 1% above experiment) and phonon energies at Γ and X, which provide an independent check on the results of the present method. For any $\vec{k} = (k, 0, 0)$ the (100) atomic planes vibrate as rigid units so that the problem is exactly equivalent to a diatomic linear chain with alternating Ga and As atoms. The solution[12] is completely determined by the Ga and As masses and the set of interplanar force constants, defined as the force on a given atom per unit displacement of an entire plane.

Consider first the transverse (T) vibrations. Figure 1 defines a periodic cell consisting of twelve atoms with one Ga atom per cell displaced by $u = 0.01a$ in the [011] direction. We find the self-consistent solutions for the charge density $n(r)$ by proceeding in exactly the same way as in other "supercell" calculations described in detail in Ref. 13. From this charge density the forces on all the atoms in the cell can be calculated rigorously, as follows from the Hellman-

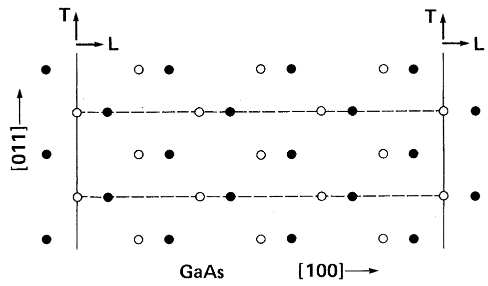

FIG. 1. Periodic supercells defined by displacement of (100) planes. Description of phonons propagating in the [100] direction requires four self-consistent calculations with one Ga (As) plane per cell displaced in the [011] transverse (T) or [100] longitudinal (L) direction. The longitudinal case also contains information which determines the effective charges ($e_L{}^*$ and $e_T{}^*$) and dielectric constant ϵ.

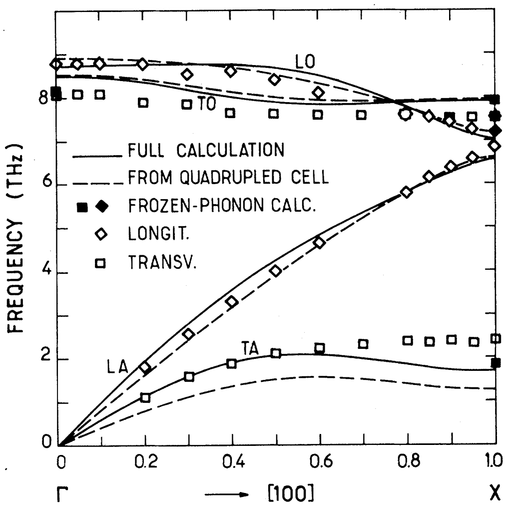

FIG. 2. Phonon dispersion along the [100] direction predicted from force constants calculated by use of periodic supercells containing twelve atoms (solid lines) and eight atoms (broken lines). We consider as most accurate solid lines for transverse and broken lines for longitudinal branches (see text). Open symbols denote experimental points (Ref. 14), and solid symbols, previous "frozen-phonon" calculations (Ref. 4) at Γ and X using the same Hamiltonian.

Feynman theorem.[10] In this way, from one self-consistent calculation we find forces on each atom in the unit cell, i.e., twelve independent interplanar force constants $\Phi(K,K')$ (if one assumes that they extend only up to the sixth neighboring plane). This procedure is then repeated with As displaced. From the set of force constants we obtain the TA and TO phonon branches shown in Fig. 2. The results show that all features of the experimental dispersion curves[14] are well reproduced. Note, for example, the shape and position of the TO branch, the agreement in the elastic region, and the characteristic flattening of the TA branch which is determined by shear forces and is very sensitive to the longest-range forces. Our calculations show that the longest-range forces are not Coulombic and that shear forces at the fifth neighboring plane are ≈9% of the shear first neighbor force (≈0.8% of the strongest first neighbor force). We have also performed calculations on smaller (quadrupled) unit cells, which provide force constants up to fourth neighbors (which, however, are affected by the nonvanishing fifth neighbor interactions). The resulting dispersion curves are shown by broken lines. As expected, the agreement of TA branch is worsened while the change in the TO is indiscrenible.

The solid points in Fig. 2 show the results at Γ and X obtained previously[4] by the frozen-phonon method with use of exactly the same Hamiltonian; the mismatch of order 5%–6% indicates the accuracy of the present calculations and sets a limit upon the influence of forces beyond the sixth neighboring plane. The internal consistency of the calculations can be judged from the fact that the first-neighbor interplanar constants determined by two independent calculations (with Ga and As displaced, respectively) agree, i.e., $\Phi(K,K') = \Phi(K',K)$, to within 4%, and that the translation invariance condition[1,15] $\Phi(K,K) = -\sum'_{K'}\Phi(K,K')$ is obeyed to within 1%.

The displacement pattern for obtaining longitudinal forces is shown by the arrows labeled L in Fig. 1. The calculation proceeds exactly as in the transverse case to provide the perturbed electronic charge density and forces on the atoms. From this point it would be straightforward to determine longitudinal force constants if the crystal were nonpolar. [We describe elsewhere[16,17] results for $\omega(k)$ in Ge, where independent calculations give the LO and TO at $k=0$ degenerate to <1.1%.] In a polar crystal such as GaAs, however, the LO modes generate macroscopic electric fields which give the LO-TO splitting and require special attention. The longitudinal displacement of charged planes gives rise to local fields restricted to the neighborhood of each displaced plane plus a macroscopic field whose magnitude depends upon the boundary conditions.[18] In the large periodic cells the boundary conditions require the average field to vanish, which is equivalent to adding a depolarizing field E_d, constant over the crystal. This can be seen in Fig. 3 where we show the self-consistent potential $V(x)$ including E_d, which is the average slope of $V(x)$ in the central part of the cell (dashed line). The field E_d gives rise to forces $f_d(K)$ of equal magnitude on each atom in the cell and opposite sign for Ga and As. If we subtract the forces $f_d(K)$ then the remaining forces contain all effects of the local and macroscopic fields accompanying an L mode for any $k \neq 0$. Our results show that the forces on the three central atoms in Fig. 1 are due only to E_d because they have the proper relation for Ga and As [and they are very small in Ge (Ref. 16)]. Thus $f_d(K)$ can be evaluated and subtracted leaving the desired longitudinal forces which extend only to the fourth neighboring plane. The resulting dispersion curves are shown in Fig. 2 as solid lines, which agree well with the experimental points and with our previous frozen-phonon results[4] at X. We also have determined the longitudinal force constants using a smaller eight-atom unit cell where the convergence is easier to achieve. The results are shown in Fig. 2 by broken lines. Since we have demonstrated that the fifth- and sixth-neighbor forces are

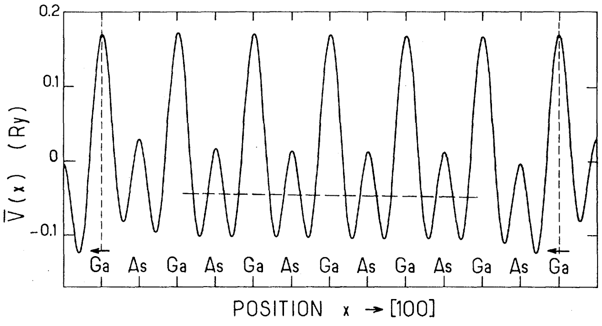

FIG. 3. Self-consistent potential averaged over (100) planes for longitudinal Ga displacements indicated by arrows here and in Fig. 1 (L). The slope of the "average" potential in the central part of the cell (broken lines) is the depolarizing field E_d, from which can be calculated the effective charges and dielectric constant as discussed in the text.

small for L modes, the forces and $\omega(k)$ resulting from the smaller computations are to be considered as more reliable.

The self-consistent charge density and potential found for the longitudinal case contains in addition much more information which can now be utilized. The depolarizing field is $E_d = 4\pi P$ where P is the polarization density resulting from the displacement of a single atom per cell. As we have shown previously,[18] this polarization is determined by the longitudinal effective charge e_L^* of an atom in the displaced plane, so that $E_d = +4\pi e_L^* u/V_{\text{cell}}$. For E_d calculated as in Fig. 3 we find $e_L^*(\text{Ga}) = +0.162|e|$ and $e_L^*(\text{As}) = -0.165|e|$ (i.e., $|e_L^*/e| = 0.163 \pm 0.002$) which compare very well with the value $|e_L^*/e| = 0.158 \pm 0.005$ which we found previously[4,18] using a different displacement pattern that avoids the depolarizing field. Moreover, in the present method we can calculate independently the "transverse" effective charge e_T^*, defined[1,15] as the force on an atom K per unit internal field (such as E_d), $e_T^*(K) = f_d(K)/E_d$. We use the force on the central atom (to eliminate extraneous short-range forces as discussed above) in the two independent cases and we find $e_T^*(\text{Ga}) = +2.005|e|$ and $e_T^*(\text{As}) = -1.725|e|$ (i.e., $|e_T^*/e| = 1.87 \pm 0.14$)—compared to the experimental value ±2.16. Furthermore, using the relation $e_T^* = e_L^* \epsilon$, where ϵ is the static electronic dielectric constant including all local-field effects,[1] we find $\epsilon = 11.4 \pm 1.6$, compared to the experimental value 10.9. Finally, there is another fundamental relation,[15]

$$\omega_{\text{LO}}^2(\Gamma) - \omega_{\text{TO}}^2(\Gamma) = (4\pi/mV)(e_T^*)^2/\epsilon = (4\pi/mV)e_L^* e_T^*. \tag{1}$$

The small difference on the left-hand side has a large relative uncertainty; nevertheless our most reliable results (broken lines in Fig. 2) obey (1) to within 19%.

In conclusion we have demonstrated the power of direct calculations of the self-consistent charge density for crystals with planes displaced in patterns like those shown in Fig. 1. From the density can be extracted forces on many inequivalent atoms (using the Hellman-Feynman theorem[10]) and thus force constants, phonon dispersion, eigenvectors, and even macroscopic electrical properties, such as effective charges and dielectric constants. Other information, such as the internal strain parameter, anharmonicity nonlinearity of the effective charges, and dielectric constant also can be calculated by this method and will be presented elsewhere.[16]

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