PHYSICAL REVIEW B VOLUME 24, NUMBER 4 15 AUGUST 1981

Density-functional calculation of static and dynamic properties of GaAs

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(Received 30 March 1981; revised manuscript received 10 June 1981)

We present results of "direct" calculations of structure and lattice dynamics of GaAs using local forms of the ionic pseudopotentials and the density functional. The predicted lattice constant, bulk modulus, phonon frequencies, effective charges, and Grüneisen parameters agree well with experiment. Eigenvectors at the X point are determined and used to test phenomenological models. We examine anharmonic energies and suggest a possible transition under pressure to an orthorhombic phase, related to the soft TA(X) phonon.

All structural and lattice-dynamical properties of solids ultimately may be described in terms of the total energy of the electron-ion system as a function of the position of the ions. Direct *ab initio* calculations of the electronic ground-state energies have now become feasible[1,2] using the density-functional method for electron exchange and correlation,[3] and it was shown in Ref. 1 that small differences in the total energy ($\lesssim 0.01\%$) can be calculated to sufficient accuracy to determine the equilibrium structure, elastic constants, phonon frequencies, and anharmonic coefficients. Recently calculations applying this method to Si using *ab initio* nonlocal pseudopotentials[2] have reproduced the energies of all principal phonons to within less than 3%, and have calculated the phase diagram.

In this paper we describe self-consistent density-functional calculations of the structural and lattice-dynamical properties of GaAs, using *local* pseudopotentials for Ga and As,[4] and a local form $(0.8)\frac{3}{2}[3n(\vec{r})/\pi]^{1/3}$ of the exchange-correlation operator, with the result that the structural properties can be obtained with errors not exceeding, in most cases, a few percent. Compared to the work on Si,[1,2] the new elements which are introduced in GaAs are ionicity and the lowered symmetry: Ionicity implies the appearance of long-range forces and requires us to find a method to calculate the effective charges.[5] The lowered symmetry leads to eigenvectors which are not completely determined by symmetry. In particular, the eigenvectors at the X point are not known from experiment, and the present *ab initio* predictions can be used to test phenomenological models of lattice dynamics.[6-8] Finally, in this particular compound, anharmonicity is found to be non-negligible and to have interesting consequences.

We have tested the behavior of the ionic potentials[4] by self-consistent calculations on the (pseudo-)atoms Ga and As which show that the energies and wave functions outside the core are accurately reproduced. The total energy of GaAs in the zinc-blende structure was then evaluated using ≈ 570 waves in the plane-wave expansions and two to four special $\vec{k}$ points, with self-consistency of all components of the potential attained to 0.05 mRy. The calculated total energy as a function of the lattice constant has its minimum at $a = 5.71$ Å, 1.1% above the experimental value 5.65 Å. The second derivative of $E^{\text{tot}}(a)$ at its minimum determines the bulk modulus B, and the calculated value is $B = 0.81 \times 10^{12}$ dyn/cm^2 which is 8.7% above experiment.

The TO and LO phonons at the zone center Γ have a displacement pattern determined by symmetry. They are identical except that the macroscopic electric field present in the LO mode has to be treated separately as is discussed below. The crystal with the atoms displaced in a TO(Γ) mode (with no macroscopic field) can be treated directly as a trigonal crystal structure (point group: C_{3v}). Performing several calculations with different values of displacement u, one obtains the expansion of $E^{\text{tot}}(u)$ whose harmonic part determines the phonon frequency within the adiabatic approximation. We obtained TO(Γ) = 8.19 THz (with estimated uncertainty of 1%), which is 0.04% above the experimental value (see Table I). The crystal with the zone-boundary modes LO(X) or LA(X) can be viewed as a tetragonal structure with four atoms per unit cell. Evaluating total energies, we obtained frequencies given in Table I. We have found that the mode with As displacements is the acoustic one, while the Ga displacements imply the optic mode.

Similar reasonings apply to the TO(X) and TA(X) phonons as well (structure: orthorhombic; point group: C_{2v}); it is to be noted, however, that in GaAs the displacement pattern for these modes is not completely determined by symmetry: The fully symmetric S_1 and fully antisymmetric S_2 patterns [which would be the TO(X) and TA(X) modes in diamond structure] are coupled, and we have to determine not only the eigenfrequencies but also the degree of coupling, which can be expressed as the ra-

TABLE I. Calculated phonon frequencies and the mode Grüneisen parameters $\gamma \equiv -(d\omega/\omega)/(dV/V)$ compared to experiment [at 4 K for TO(Γ), at 95 K for LA(X), TA(X), and at room temperature for LO(X), TO(X)]. All eigenfrequencies correspond to only the *harmonic* part of the expansions of $E^{\text{tot}}(u)$, i.e., to the vibrations with $u \to 0$. All frequencies in THz.

	TO(Γ)	LO(X)	LA(X)	TO(X)	TA(X)
ν(calc)	8.19	7.55	7.20	7.94	1.87
ν(expt)[a]	8.187[b]	7.22	6.89	7.56	2.41
% diff.	0.0%	+4.6%	+4.5%	+5.0%	−22%
γ(calc)	1.42	0.91	1.11	1.56	−3.48
γ(expt)[c]	1.39	?	?	1.73	−1.62

[a]Reference 6. [b]Reference 13. [c]Reference 14.

tio of amplitudes $u(\text{Ga})/u(\text{As})$. Fortunately, our approach is not limited to eigenmodes, and we can determine the increase of E^{tot} due to an *arbitrary* displacement pattern. We proceed by calculating E^{tot} for the patterns S_1, S_2, S_1+S_2, and S_1-S_2 (of several magnitudes each), extracting the harmonic coefficients for the two coupled degrees of freedom S_1, S_2, and solving the 2×2 matrix problem to obtain the eigenfrequencies given in Table I and the ratio of the amplitudes $u(\text{Ga})/u(\text{As})$ given in Table II. The *absolute* errors in both TA(X) and TO(X) frequencies are very similar; however, cancellation of electronic and ion-ion terms results in the low frequency of the TA(X) modes and larger relative error.

TABLE II. Comparison of our predicted values for $u(\text{Ga})/u(\text{As})$ in zone-boundary transverse modes with the results obtained in terms of six phenomenological models, all of which provide excellent fits of eigenfrequencies. For the transverse modes the values $u(\text{Ga})/u(\text{As}) = 1$ would correspond to the pure S_1 and S_2 modes—i.e., to TO(X), TA(X) of diamond structure. Our calculation shows that the LA(X) mode has only As displacements and LO(X) only Ga; in the final column the + or − indicate whether or not the model prediction agrees with our assignment. RIM11 denotes rigid-ion model with 11 parameters, DDM15 denotes deformation-dipole model with 15 parameters, SM14 denotes shell model with 14 parameters, and OVSM10 denotes overlap valence shell model with 10 parameters.

$u(\text{Ga})/u(\text{As})$:	TO(X)	TA(X)	LO, LA(X)
Present calculation	0.902	1.193	+
RIM11[a]	6.030	0.178	−
DDM15[a]	3.283	0.328	+
SM14[b] B(i)	0.832	1.293	−
B(ii)	1.381	0.779	+
C(i)	0.956	1.126	+
C(ii)	1.130	0.952	−
OVSM10[c]	0.574	1.875	+

[a]Reference 8. [b]Reference 6. [c]Reference 7.

No direct experimental measurements of the eigenvectors are available, and very different answers are obtained from the standard phenomenological models.[6–8] The results for seven models are summarized in Table II, and we see that the C(i) variant of the shell model of Dolling and Waugh[6] gives the best agreement with our results for the X point. Indeed, knowledge of eigenvectors is indispensable because, as pointed out by Leigh, Szigeti, and Tewary,[9] a unique phenomenological model cannot be established solely from the eigenfrequencies.

The LO(Γ) phonon cannot be calculated in this direct manner because it has contributions from the macroscopic electric field. At the Γ point ($\vec{k} \equiv 0$), the potential of this field is a monotonic function of a position rather than a periodic function. The contribution of the macroscopic field, however, can be obtained rigorously[10] by an independent calculation of the dynamical effective charge. It is possible to show[5] that the longitudinal effective charge can be calculated from the change in electrostatic potentials due to displacement of a plane of atoms, either Ga or As. The actual calculations were performed in a periodic cell geometry as shown in Fig. 1 for displacement along [100]. Outside the narrow regions $|\Delta x| \lesssim a/4$ around every shifted atomic plane, we have found that both the self-consistent charge density and potential $\bar{V}(x)$ {which is $V(\vec{r})$ averaged over a plane perpendicular to [100]} are nearly identical with $\bar{V}_0(x)$ of undisplaced crystal—except that $\bar{V}$ is shifted by $\pm 1/2\,\delta\bar{V}$. In our calculations we take $\delta\bar{V} = \bar{V}(x=A) - \bar{V}(x=B)$, where A, B are the planes furthest from the displaced atoms, as indicated in Fig. 1. From elementary electrostatics one finds $\delta V = 4\pi\sigma u$ for the shift due to the displacement u of a charged plane: In terms of *effective* charges $\sigma = e_L^*/A$ where A is the area per atom. Our computations yielded $e_L^*(\text{Ga}) = -e_L^*(\text{As}) = +0.16|e|$, compared to the experimental value of $\pm 0.197|e|$, where

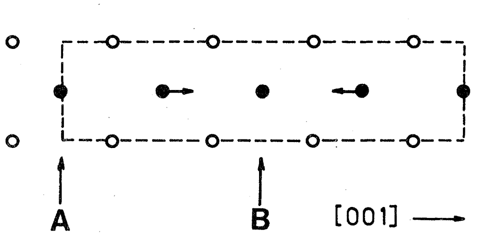

FIG. 1. Supercell for calculation of the longitudinal effective charges e_L^* from the self-consistent potential evaluated at planes A and B. The charge is calculated independently for Ga and As, by displacing the respective atoms.

the sign is not determined experimentally. The corresponding transverse charge is $e_T^*(\mathrm{Ga}) = +0.16\epsilon_0 = +1.7|e|$, compared to $e_T^* = \pm 2.16|e|$ from experiment. As discussed in Ref. 5 the calculated charges may have small errors because of the limited size of the cell used, but the calculations show all essential features of how the effective charges arise from the electronic screening.

Repeating the above calculations with slightly modified lattice parameter a one obtains the phonon frequencies in a crystal under hydrostatic pressure and thus the mode Grüneisen parameter $\gamma i = -(d\omega/\omega)/(dV/V)$. The calculated γ's are given in Table I and show excellent agreement with experiment except for the very sensitive TA(X) mode. Even in that case the *trends* are correct: It is the only mode with a negative γ.

The above procedures are not limited to small displacements u. We have found in GaAs that anharmonicity of all modes is considerable already at very small displacements and, at $\vec{k} = X$, harmonic plus quartic (negative) plus u^6 (positive) terms are required in order to account for variation of E^{tot} up to $u \approx 0.02a$. The most strongly anharmonic among all the $\vec{k} = X$ modes is the TA(X). Its harmonic frequency is reduced by cancellations[1,2]; however, the anharmonic terms are not reduced by nearly so large a factor. This is especially important as the TA(X) mode decreases under hydrostatic pressure—and by inference should be important in other zinc-blende materials such as CuI, which has a particularly low TA(X) frequency—and in which anharmonicity is known to be very important.[11]

The strong anharmonicity and pressure dependence of the TA(X) mode has a very interesting consequence for the stability of zinc-blende-type lattice. We have shown in Fig. 2 the variation of total energy with displacement for an antisymmetric S_2 pattern, which is quite close to the TA(X) mode of GaAs (see Table I). The curve $E^{\mathrm{tot}}(u) - E_0 = Au^2 + Bu^4 + Cu^6$ corresponding to $p = 0$ is monotonically increasing. A similar behavior is found when the crystal is compressed by $\Delta a = -0.1$ Å, which corresponds to hydrostatic pressure of about 40 kbar; however, the relative role of anharmonicity (B, C compared to A) becomes about 1.8 times stronger now. Extrapolating this trend further, we find that at $\Delta a = -0.144$ Å the $E^{\mathrm{tot}}(u)$ curve should exhibit a second minimum (in the range of $u \approx 0.02a$) where the total energy will be the same as at $u = 0$. This suggests a possibility of a first-order phase transition to an orthorhombic structure—one which is close to zinc blende with a TA(X) displacement—*before* the (known) transition to the high-pressure rocksalt phase occurs—although the errors in our determination of frequency of the TA(X) mode (see Table I) suggest that the calculated transition pressure is rather uncertain. We note that there are reports[12] indicating a transition to orthorhombic structure at $p \approx 170$ kbar, i.e., at $\Delta a = -0.28$ Å. Further effort, both computational and experimental, is needed which would also include other zinc-blende-structure compounds in which similar effects should occur.

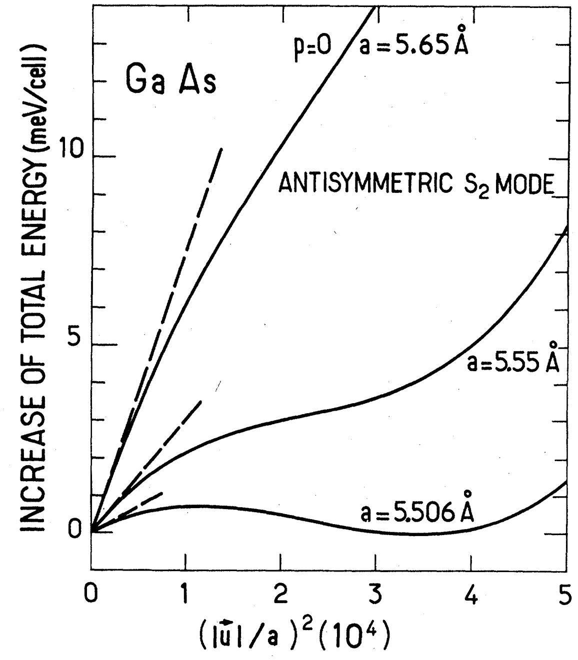

FIG. 2. Variation of total energy with atomic displacement at various pressures; broken lines represent the harmonic approximation, and their slopes determine the phonon frequency. At high pressures the harmonic term decreases more rapidly than the anharmonic ones, and the curve shows a second minimum corresponding to a finite displacement and inducing a first-order phase transition to an orthorhombic structure. The antisymmetric S_2 mode, defined as the TA(X) displacement pattern of a diamond structure, is very close to the TA(X) mode of GaAs (see Table I).

K.K. acknowledges support from the National Science Foundation. This work was partially supported by NATO.

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