Theories of the mechanical, vibrational, and electronic properties of III-V semiconductors have been developed and applied to (i) help determine the feasibility of InN-based visible and ultraviolet lasers and light detectors, (ii) develop a theory of phonons in semiconductor alloys, (iii) elaborate on the physics of photoelasticity, (iv) understand surface reconstruction of semiconductors, and (v) predict the effects of atomic correlations on the light-scattering (Raman) properties of semiconductor alloys.
ANNUAL TECHNICAL REPORT
DATE: 29 September 1987
FOR THE PERIOD: 1 September 1986 to 31 August 1987
AFOSR Contract No: AFSR-85-0331
TITLE: Vibrational, mechanical, and thermal properties of III-V semiconductors
PRINCIPAL INVESTIGATOR: John D. Dow

1. SUMMARY

Theories of the mechanical, vibrational, and electronic properties of III-V semiconductors have been developed and applied to (i) help determine the feasibility of InN-based visible and ultraviolet lasers and light detectors, (ii) develop a theory of phonons in semiconductive alloys, (iii) elaborate on the physics of photoelasticity, (iv) understand surface reconstruction of semiconductors, and (v) predict the effects of atomic correlations on the light-scattering (Raman) properties of semiconductive alloys.

2. OBJECTIVES

Our goal is to develop theories of the mechanical, vibrational, and thermal properties of III-V semiconductor alloys that will lead to a better understanding of the physics of these materials.

3. STATUS OF RESEARCH

We have made progress on the following problems:

1. **Electronic structure of InN and InN-based alloys, including defect levels.** A paper will be published shortly on the materials problems that must be overcome in order to fabricate visible lasers from these materials.

2. **Phonons in Hg$_{1-x}$Cd$_x$Te.** We have identified the "clustering modes" with regions consisting of Te atoms bonded to one Cd atom and three Hg atoms; and we have elucidated the physics of phonons in these alloys.

3. **Photoelastic constants.** We are developing a theory of photoelastic constants in bulk and superlattice semiconductors.

4. **Role of ionicity in zincblende surface relaxation.** We have shown that, contrary to popular opinion, zincblende (110) surfaces relax through an angle that depends significantly on ionicity, as a result of competition between covalent forces seeking 90° bond-angles and ionic forces that resist reconstruction.

5. **Surface geometry of wurtzite (1010) surfaces.** We are calculating the equilibrium positions of atoms on (1010) surfaces of AIN and ZnS.

6. **Effects of correlations on the Raman spectra of alloys.** We have developed a theory which combines Monte Carlo and Recursion techniques to predict the spectra of correlated alloys.
4. RECENT PAPERS


6. D. W. Jenkins and J. D. Dow. Electronic structures and doping of InN, In$_{1-x}$Ga$_x$N, and In$_{1-x}$Al$_x$N. Ph.D. thesis chapter completed; manuscript in preparation.

7. M.-H. Tsai, R. V. Kasowski, and J. D. Dow. Relaxation of zincblende (110) surfaces. manuscript in preparation.

8. Z.-W. Fu and J. D. Dow. Phonons in Hg$_{1-x}$Cd$_x$Te. manuscript in preparation.

5. PROFESSIONAL PERSONNEL

J. Dow, principal investigator
S. Ren, visiting professor
W. Hu, visiting associate professor
M. Tsai, assistant faculty fellow
D. Jenkins, graduate student
R. Hong, graduate student
J. Shen, graduate student
Z. Fu, graduate student

6. INTERACTIONS

The principal investigator has functioned as an advisor to the National Academy of Science Committee on Basic Research on a wide range of topics in materials science, electronics, and solid state physics, and to the Air Force (Capt. K. Malloy) on matters related to semiconductor alloys.

PATENTS

None.
Dependence on ionicity of the (110) surface relaxation of zincblende semiconductors

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Abstract

It is argued that the surface relaxation angle \( \omega \) of zincblende (110) surfaces should depend on ionicity or on longitudinal effective charge \( Z \), approximately as \( \omega = \omega_0 - \omega_1 Z^2 e^2 / \varepsilon a_L \), with \( \omega_1 = 60 \text{eV} \).
It is widely believed that the reconstructions of the (110) surfaces of zincblende semiconductors are determined virtually exclusively by covalent forces, and that the surface anions rotate more-or-less rigidly out of the surface through an angle $\omega = 29^\circ$ for all zincblende (110) surfaces [1][2]. (See Fig. 1.) This relaxation angle $\omega$ minimizes the energy of the covalent bonds. Indeed the (110) zincblende relaxations are thought to be the best understood of the semiconductor surface reconstructions, with analyses of numerous low-energy electron-diffraction data [1][3][4][5][6][7] and medium-energy ion-blocking experiments [8][9][10] lending support both to the rigid-rotation reconstruction model and to the notion that $\omega$ is constant ($\approx 29^\circ$) for all zincblende (110) surfaces.

However, the widely accepted viewpoint that $\omega$ is constant for all zincblendes cannot possibly be correct, and must be strictly valid only in the limit of low ionicity. For the more ionic zincblende semiconductors, the attractive Coulomb forces between the relaxed, negatively charged surface anions and the positively charged cations in and below the surface tend to pull the anions back toward the surface and reduce the relaxation caused by the covalent forces. (See Fig. 1.) This Coulombic effect should reduce the relaxation angle $\omega$ by an amount proportional to $Z^2$, where $Z$ is the (longitudinal) effective charge [11], and the effect should become significant when $Z^2e^2/\epsilon a_L$ is of order 0.5 eV, a typical covalent energy gained by each relaxing surface anion [12]. Here $e$ is the electron's charge, $\epsilon$ is the dielectric constant, and $a_L$ is the lattice constant. Recall that the ionicity $f_i$ is approximately proportional to $Z$: $Z/Z_c = f_i$, where $Z_c$ is the chemical valency [11].
To demonstrate that the relaxation angle $\omega$ cannot be the same for all zincblende semiconductors, we have executed self-consistent total-energy calculations based on the pseudo-function local-density theory [13]. These calculations employed four-atom-thick slabs of GaAs, InP, ZnTe, and ZnS [14], and allowed their (110) surfaces to relax via rigid rotations through angles $\omega$ until the total energies of the slabs reached minima. The resulting equilibrium relaxation angles $\omega$ are plotted in Fig. 2 as functions of $Z^2e^2/\epsilon a_L$ (See Table I.), and, to a good approximation, form a straight line described by the empirical rule

$$\omega = \omega_0 - \omega_1 Z^2e^2/\epsilon a_L,$$

with $\omega_0 = 20.62^\circ$ and $\omega_1 = 6.08^\circ/eV$. The fact that $\omega_0$ is of the same general magnitude as the observed surface relaxation angles indicates that the rigid rotation model, as used here, contains the essential physics of the surface relaxation. Furthermore, the sign and magnitude of $\omega_1$ are as expected.

The relaxation angles $\omega$ extracted from data analyses are difficult to obtain accurately (See Table I.), and actually agree about equally well with either hypothesis; (1) the widely believed $\omega = \text{constant}$ or (2) $\omega = \omega_0 - \omega_1 Z^2e^2/\epsilon a_L$, with $\omega_1$ of order $6^\circ/eV$. (See Fig. 2.) Therefore we think that the $\omega = \text{constant}$ hypothesis should be reexamined experimentally, possibly by studying the (110) surface of zincblende AgI or some other highly ionic zincblende material.
The ionicity of the zincblende surface not only reduces the equilibrium relaxation angle $\omega$, but it also increases the relaxation energy per surface atom and increases surface phonon frequencies, according to the theory. (See Fig. 3.)

We hope that experiments on the (110) surfaces of different zincblende semiconductors will confirm these theoretical ideas quantitatively, establish the role of effective charge and ionicity in determining equilibrium surface geometry, and lead to an even better understanding of these prototypical surfaces.

Acknowledgments -- We gratefully acknowledge enlightening conversations with Richard Martin about effective charges, and the support of the Air Force Office of Scientific Research (Contract No. AF-ASFOSR-85-0331). We also thank the E. I. du Pont Company for the use of their computational facilities, as well as partial support of M.-H. Tsai.
REFERENCES

[12] See Fig. 3 and, for example, K. C. Pandey, Phys. Rev. Letters 49, 223 (1982).
[14] The calculations for each material require about 150 hours of central processor time on an FPS-164 array processor.
Table I. Effective (longitudinal) charges $Z$, lattice constants $a_L$ (in unit of Bohr radii), dielectric constants $\epsilon$, $Z^2e^2/\epsilon a_L$ (in eV), calculated relaxation angle $\omega_{\text{Theory}}$, predicted change in relaxation angle $\Delta \omega$ (based on the empirical rule), and relaxation angles $\omega$ measured by low energy electron diffraction ($\omega_{\text{LEED}}$) and ion back-scattering ($\omega_{\text{ion}}$), respectively. See Ref. [11].

<table>
<thead>
<tr>
<th>Materials</th>
<th>$a_L (a_0)$</th>
<th>$\epsilon$</th>
<th>$Z^2e^2/\epsilon a_L$</th>
<th>$\omega_{\text{Theory}}$</th>
<th>$\Delta \omega$</th>
<th>$\omega_{\text{LEED}}$</th>
<th>$\omega_{\text{ion}}$</th>
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<tbody>
<tr>
<td>CuCl</td>
<td>1.505</td>
<td>10.215</td>
<td>3.6</td>
<td>1.67</td>
<td>10.15°</td>
<td>10.15°</td>
<td></td>
</tr>
<tr>
<td>CuBr</td>
<td>1.35</td>
<td>10.753</td>
<td>4.4</td>
<td>1.048</td>
<td>6.37°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuI</td>
<td>1.715</td>
<td>11.419</td>
<td>5.2</td>
<td>1.347</td>
<td>8.19°</td>
<td></td>
<td></td>
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<tr>
<td>AgI</td>
<td>1.38</td>
<td>12.232</td>
<td>4.9</td>
<td>0.864</td>
<td>5.25°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnS</td>
<td>1.795</td>
<td>10.222</td>
<td>5.1</td>
<td>1.681</td>
<td>11°</td>
<td>10.22° 26° [3]</td>
<td></td>
</tr>
<tr>
<td>ZnSe</td>
<td>1.625</td>
<td>10.710</td>
<td>5.9</td>
<td>1.137</td>
<td>6.91° 29° [4]</td>
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<tr>
<td>ZnTe</td>
<td>1.66</td>
<td>11.529</td>
<td>7.3</td>
<td>0.891</td>
<td>14°</td>
<td>5.42° 28°±2° [5]</td>
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</tr>
<tr>
<td>CdTe</td>
<td>1.715</td>
<td>12.240</td>
<td>7.3</td>
<td>0.895</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>HgTe</td>
<td>2.025</td>
<td>12.208</td>
<td>14.0</td>
<td>0.653</td>
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<tr>
<td>BN</td>
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<td>6.831</td>
<td>4.5</td>
<td>0.538</td>
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<tr>
<td>AlP</td>
<td>0.93*</td>
<td>10.301</td>
<td>7.6</td>
<td>0.301</td>
<td>1.83° 27.5°±3° [6]</td>
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<tr>
<td>AlAs</td>
<td>0.81*</td>
<td>10.700</td>
<td>9.0</td>
<td>0.185</td>
<td>1.12°</td>
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<td>AlSb</td>
<td>1.045</td>
<td>11.594</td>
<td>10.2</td>
<td>0.251</td>
<td>1.53°</td>
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<td>GaP</td>
<td>1.185</td>
<td>10.300</td>
<td>8.5</td>
<td>0.436</td>
<td>2.65° 27.5° [3]</td>
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<td>GaAs</td>
<td>1.03</td>
<td>10.683</td>
<td>10.9</td>
<td>0.248</td>
<td>20°</td>
<td>1.51° 27°±30° [3]</td>
<td>29°±3° [9]</td>
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<td>0.69</td>
<td>11.519</td>
<td>14.4</td>
<td>0.078</td>
<td></td>
<td>0.47° 30°±2° [5]</td>
<td>28.5°±2.6° [10]</td>
</tr>
<tr>
<td>InP</td>
<td>1.485</td>
<td>11.090</td>
<td>9.6</td>
<td>0.563</td>
<td>17°</td>
<td>3.42° 28.1° [8]</td>
<td></td>
</tr>
<tr>
<td>InAs</td>
<td>1.085</td>
<td>11.449</td>
<td>12.3</td>
<td>0.227</td>
<td></td>
<td>1.38° 31°±3° [7]</td>
<td>30°±2.4° [10]</td>
</tr>
<tr>
<td>InSb</td>
<td>0.72</td>
<td>12.243</td>
<td>15.6</td>
<td>0.074</td>
<td></td>
<td>0.45° 28.8° [8]</td>
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<tr>
<td>SiC</td>
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<td>8.217</td>
<td>6.7</td>
<td>0.297</td>
<td></td>
<td></td>
<td>1.81°</td>
</tr>
</tbody>
</table>

* Estimated from the ionicity $f_1$ by $Z = Z_c f_1$. 
Zincblende (110) surface

side view

\[ \text{Force} = \frac{Z^2 e^2}{er^2} \]

Coulomb force pulls surface anions down

\[ \omega \approx 20^\circ \]
END
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