Stress treated by quantum mechanics

by Ole H. Nielsen and Richard M. Martin
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These are old handwritten transparency slides for talks by Ole Holm Nielsen, as presented at seminars at Bell Labs and Brookhaven National Lab in June 1983,

The topic of the talk is the novel quantum mechanical theorem of the stress tensor (the *Stress theorem*), which was originally published as:
First-Principles Calculation of Stress by O. H. Nielsen and Richard M. Martin, Physical Review Letters **50**, 697 (1983).

STRESS TREATED BY QUANTUM MECHANICS

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JUNE 6, 1983 $1.75

TIME

More Turmoil Over Central America

STRESS!

Seeking Cures for Modern Anxieties

HELNWEIN

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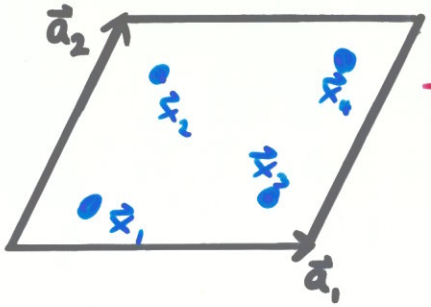
THE STRUCTURE OF SOLIDS:

WHAT DESCRIBES A PERIODIC SOLID (NO SURFACE)?



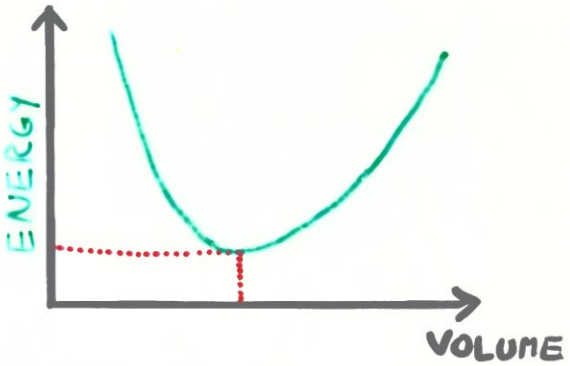
UNIT CELL
+ PERIODIC REPETITIONS
SHAPE & SIZE
ATOMIC ARRANGEMENT

PHYSICAL PROPERTIES:

TOTAL ENERGY = E(SHAPE & SIZE; ATOMIC ARRANGEMENT; T)

LET $T = 0$.

APPLICATION: EQUILIBRIUM STRUCTURE
$\Leftrightarrow$ E = MINIMUM.



WHAT ARE THE CONJUGATE "FORCES" OF THE STRUCTURAL PARAMETERS?

ATOMIC ARRANGEMENT: $\vec{F} = \partial E_{TOTAL} / \partial \vec{x}_{ATOM}$ "HELLMANN-FEYNMAN" FORCES

SHAPE & SIZE: $\sigma_{\alpha\beta} = \partial E_{TOTAL} / \partial \varepsilon_{\alpha\beta}$ MACROSCOPIC STRESS

($\varepsilon_{\alpha\beta}$ = STRAIN: $\vec{x} \rightarrow \vec{x} + \bar{\bar{\varepsilon}}\vec{x}$)

COMPLETE PICTURE REQUIRES: E_{TOTAL}, FORCE, STRESS

WHAT CAN WE LEARN?

CRYSTAL STRUCTURE:

- CRYSTAL SYMMETRY: $E_{CUBIC} < E_{HEXAGONAL}$, ETC. ?
- LATTICE CONSTANTS: E = MINIMUM OR PRESSURE = 0.
- ATOMIC ARRANGEMENTS: FORCE $\vec{F} = \vec{0}$ CONDITION.
- PHASE TRANSFORMATIONS: COMPARE ENTHALPIES H_1, H_2

$$H = E_{TOTAL} + \Sigma_{\alpha\beta} \sigma_{\alpha\beta} \cdot \varepsilon_{\alpha\beta} \quad (\sim E + P \cdot V)$$

VIBRATIONAL PROPERTIES:

WITHIN THE ADIABATIC APPROXIMATION.

- PHONON FREQUENCIES: $\vec{F} = \Phi \cdot \vec{u}$; $\omega^2 = \Phi / M$
- EIGENVECTORS; EFFECTIVE CHARGES.
- ANHARMONIC PHONONS.

ELASTIC PROPERTIES:

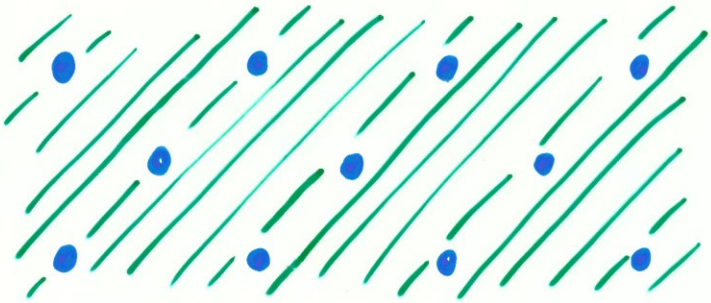
- ELASTIC CONSTANTS: STRESS/STRAIN
- ANHARMONIC ELASTICITY.

THEORETICAL LIMITATIONS: (AT PRESENT)

DUE TO THE LOCAL-DENSITY APPROXIMATION.

- GROUND-STATE ONLY (NO OPTICAL PROPERTIES).
- ZERO TEMPERATURE ONLY.

TOTAL ENERGY



A SOLID:

NUCLEI +

ELECTRONS

$$\text{TOTAL ENERGY} = \sum_i \frac{\vec{P}_i^2}{2m} + V_{e\text{-}e} + V_{e\text{-}N} + V_{N\text{-}N}$$

DENSITY-FUNCTIONAL THEORY

FOR THE <u>GROUND</u> STATE:

$$V_{e\text{-}e} = V_{\text{HARTREE}} + V_{\text{EXCHANGE+CORRELATION}}$$

$$(e^2/r_{ij})$$

HOHENBERG-KOHN-SHAM:

$V_{x\text{-}c}$ IS A <u>UNIQUE</u> FUNCTIONAL OF CHARGE DENSITY.

LOCAL APPROXIMATION:

HOMOGENEOUS ELECTRON GAS: $V_{x\text{-}c}^{HOM} = V_{x\text{-}c}^{HOM}(\rho)$

ASSUME: $V_{x\text{-}c} = \int d^3\vec{r}\; V_{x\text{-}c}^{HOM}(\rho(\vec{r}))\cdot\rho(\vec{r})$

CALCULATIONS:

SOLVE SCHRÖDINGER EQUATION ITERATIVELY

TO SELFCONSISTENCY.

FORCE THEOREM

CONSIDER NUCLEUS (OR A RIGID ION CORE) AT POSITION $\vec{R}$. GIVEN GROUND-STATE WAVEFUNCTION:

$$\text{FORCE} = -\partial E_{\text{TOTAL}}/\partial \vec{R} = -\langle \partial V_{\text{POTENTIAL}}/\partial \vec{R} \rangle_{\text{GROUND-STATE}}$$

HISTORICAL NOTE:

- EHRENFEST (1927) — FIRST DERIVATION
- PAULI (1933)
- HELLMANN (1937)
- FEYNMAN (1939)

> FORCES IN MOLECULES

"HELLMAN-FEYNMAN THEOREM"

Zeitschrift für Physik 45 455 (1927)

455

"COMMENT ON THE APPROXIMATE VALIDITY OF CLASSICAL MECHANICS WITHIN QUANTUM MECHANICS"

Bemerkung über die angenäherte Gültigkeit der klassischen Mechanik innerhalb der Quantenmechanik.

Von P. Ehrenfest in Leiden, Holland.

(Eingegangen am 5. September 1927.)

EXACT RESULT:

$$m\frac{d^2\langle x\rangle}{dt^2} = -\left\langle \frac{\partial V}{\partial x} \right\rangle$$

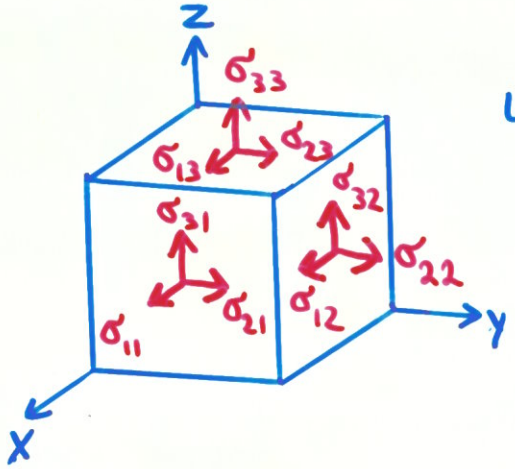
Aus der Schrödingerschen Gleichung läßt sich durch eine kurze elementare Rechnung ohne Vernachlässigung die Beziehung

$$m\frac{d^2}{dt^2}\iiint d\tau \cdot \psi\psi^* \cdot x = \iiint d\tau \cdot \psi\psi^* \left(-\frac{\partial V}{\partial x}\right)$$

ableiten, die für ein kleines und klein bleibendes Wellenpaket (m von der Ordnung 1 g) besagt, daß die Beschleunigung seiner Lagekoordinaten im Sinne der Newtonschen Bewegungsgleichungen zur örtlichen Kraft $-\frac{\partial V}{\partial x}$ paßt.

Es ist wünschenswert, die folgende Frage möglichst elementar beantworten zu können: Welcher Rückblick ergibt sich vom Standpunkt der Quantenmechanik auf die Newtonschen Grundgleichungen der klassischen Mechanik? Durch eine ganze Reihe

STRESS:



UNIT CUBE

$\sigma_{\alpha\beta}$ = FORCE$_{\alpha\text{-COMPONENT}}$ / UNIT AREA (NORMAL = β)

PRESENT WORK:

A <u>NOVEL</u> WAY OF DETERMINING STRESS FROM THE GROUND-STATE WAVEFUNCTION.

AB-INITIO CALCULATIONS ON SOLIDS.

RELATED TO:

- TOTAL-ENERGY CALCULATIONS
- FORCES ("HELLMANN-FEYNMAN THEOREM")

STRESS THEOREM

OR "GENERALIZED VIRIAL THEOREM"

CONSIDER A UNIFORM SCALING OF THE WAVEFUNCTION

$\vec{R}_\alpha \rightarrow \vec{R}_\alpha + \sum_\beta \varepsilon_{\alpha\beta} \vec{R}_\beta$ $\quad \varepsilon_{\alpha\beta}$ = STRAIN TENSOR

STRESS: $\sigma_{\alpha\beta} = \partial E_{TOTAL} / \partial \varepsilon_{\alpha\beta}$

A GENERAL MANY-BODY HAMILTONIAN:

$H = \sum_i \vec{p}_i^{\,2}/2m_i + V_{INTERNAL} + V_{EXTERNAL}$ ← SURFACE FORCES

FOCK (1930): SCALING OF Ψ GIVES NO 1ST-ORDER CHANGE IN $\langle \Psi | H | \Psi \rangle$ (VARIATIONAL PRINCIPLE). THUS

INTERNAL STRESS $\sigma_{\alpha\beta} = \partial \langle H_{INTERNAL} \rangle / \partial \varepsilon_{\alpha\beta} =$

$$-\sum_i \left\langle \vec{p}_{i\alpha} \vec{p}_{i\beta}/m_i - \vec{F}_{i\beta} \, \partial V_{INTERNAL} / \partial \vec{r}_{i\alpha} \right\rangle$$

(NIELSEN, MARTIN, PHYS. REV. LETT. 50 697, 1983)

VIRIAL THEOREM: $3PV = 2E_{KIN} + E_{POT}$ $\quad$ ($1/r$ POTENTIAL)

- BORN, HEISENBERG, JORDAN (1926)
- FINKELSTEIN (1928)
- HYLLERAAS (1929) HE-ATOM
- FOCK (1930) MANY-BODY FORM
- PAULI (1933)
- SLATER (1933) MOLECULES AND SOLIDS

⋮

HOW ABOUT SPATIAL VARIATIONS, I.E. STRESS FIELDS?

- SCHRÖDINGER (1927) — RELATIVISTIC STRESS TENSORS
- PAULI (1933) — KINETIC STRESS
- FEYNMAN (1939) — KINETIC + MAXWELL STRESS
- MARTIN, SCHWINGER (1959) — APPROXIMATE MANY-BODY FORM
- KUGLER (1967) — EXACT MANY-BODY FORM

OUTLINE:

MOMENTUM DENSITY $\vec{P}(\vec{r}) = \frac{1}{2}\sum_i [\vec{p}_i, \delta(\vec{r}-\vec{r}_i)]_+$ $\quad [A,B]_+ = AB+BA$

FORCE DENSITY $\partial\vec{P}(\vec{r})/\partial t = \frac{1}{i\hbar}[\vec{P}(\vec{r}), H] = \cdots$ ($\int d\vec{r}$ GIVES FORCES)

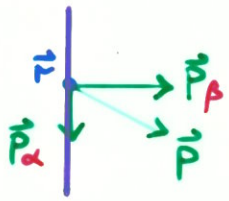
DEFINE STRESS FIELD $\sigma_{\alpha\beta}(\vec{r})$: $\nabla\cdot\sigma_{\alpha\beta}(\vec{r}) = \partial\vec{P}(\vec{r})/\partial t$

A SOLUTION: INTERNAL STRESS IS:

$$\sigma_{\alpha\beta}(\vec{r}) = -\sum_i \left\langle [\vec{p}_{i\alpha}, [\vec{p}_{i\beta}, \delta(\vec{r}-\vec{r}_i)]_+]_+ \right\rangle / 4m_i + \\ + \frac{1}{4\pi}\sum_i \left\langle \frac{\partial V_{\text{INTERNAL}}}{\partial \vec{r}_{i\alpha}} \cdot \frac{(\vec{r}-\vec{r}_i)_\beta}{|\vec{r}-\vec{r}_i|^3} \right\rangle$$

INTERPRETATION:

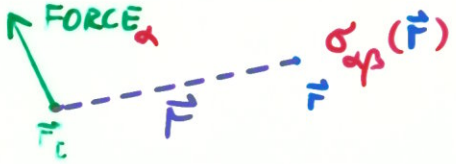
- KINETIC STRESS:



FLUX $\vec{p}_\beta/m$

  - RESEMBLES KINETIC GAS THEORY.

- POTENTIAL STRESS: $\sim(\vec{\nabla}V)_\alpha \cdot \frac{\vec{r}_\beta}{r^3}$



  - RESEMBLES ELECTROSTATICS.

MACROSCOPIC STRESS:

INTEGRATE OVER INFINITE PLANE: $\int \sigma_{\alpha\beta}(\vec{r})\cdot d\vec{S}$

INTEGRATE OVER ALL PARALLEL PLANES: Q.E.D.

PRACTICAL CALCULATIONS

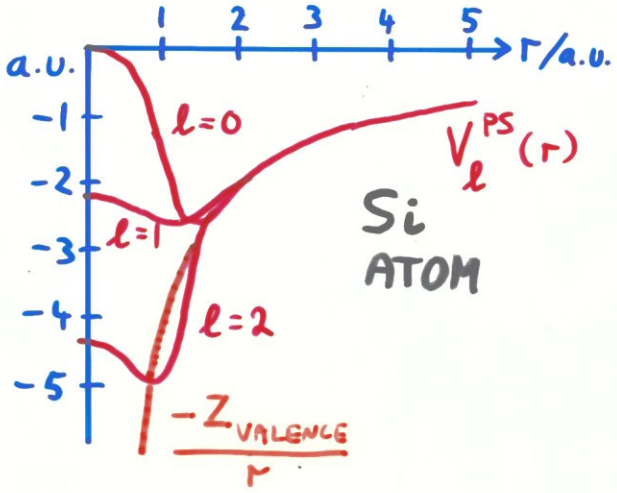
LOCAL-DENSITY-FUNCTIONAL APPROXIMATION FOR ELECTRON EXCHANGE AND CORRELATION.

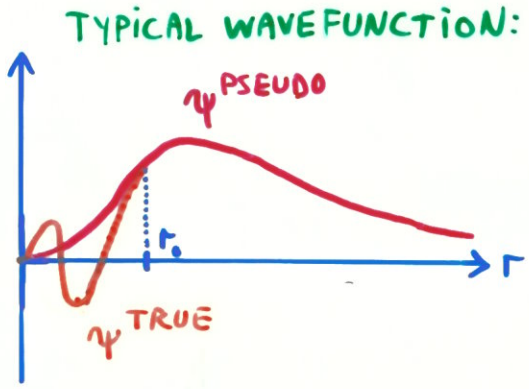
PSEUDO POTENTIAL APPROXIMATION:

EFFECTIVE POTENTIAL FOR VALENCE ELECTRONS, ONLY.

CAN BE DERIVED <u>AB INITIO</u> (INPUT: ATOMIC NUMBER Z):

HAMANN, SCHLÜTER, CHIANG (1979) + KERKER (1979).





FEATURES:

- ψ^{PSEUDO} SLOWLY VARYING, NODELESS.
- $\psi^{PSEUDO} \equiv \psi^{TRUE}$ OUTSIDE SOME r_0.
- EIGENVALUES $E_\psi = E_{\psi_0}$.
- $V_\ell^{PS}(r)$ TRANSFERABLE BETWEEN SIMILAR SYSTEMS.
- FROZEN CORE APPROXIMATION

AB-INITIO PSEUDOPOTENTIALS

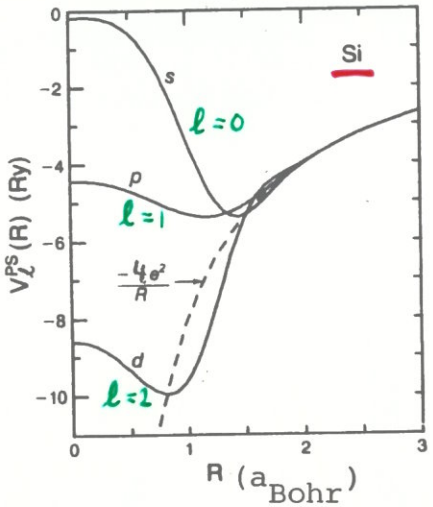
HAMANN, SCHLÜTER, CHIANG (1979); KERKER (1980)

EXAMPLE:

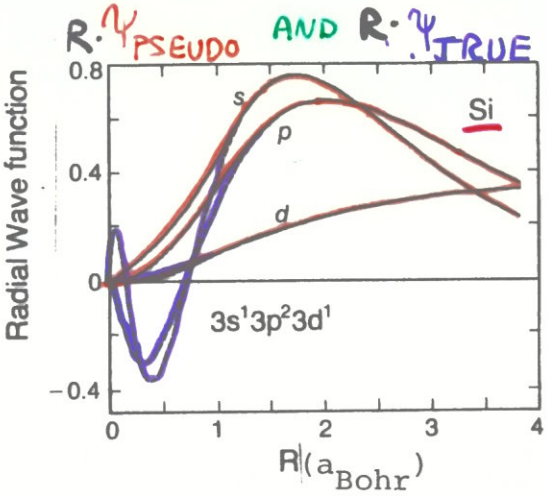
(YIN, COHEN (1982))

SILICON (Z = 14)

Ab initio core pseudopotential



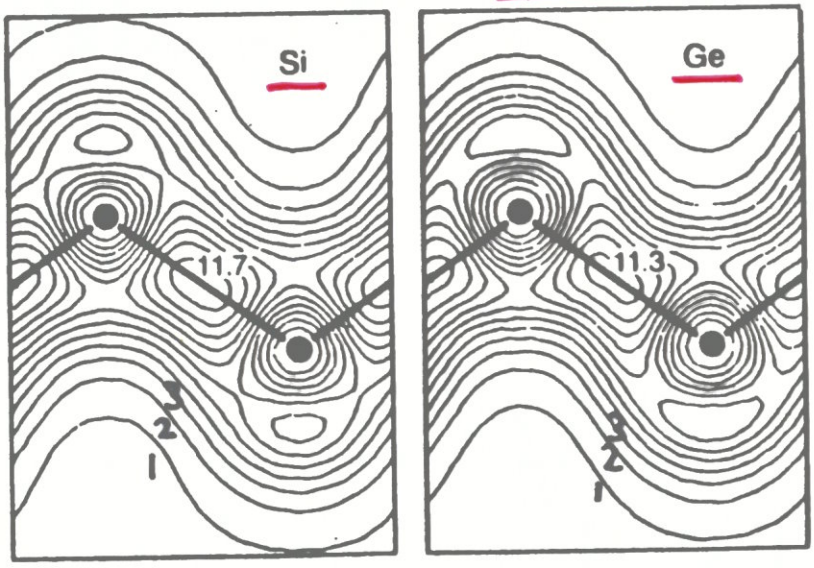
$R \cdot \psi_{PSEUDO}$ AND $R \cdot \psi_{TRUE}$



Comparison between the pseudo (solid lines) and the corresponding all-electron (dashed lines) radial wave functions for the configuration $3s^1 3p^2 3d^1$ of Si.

BULK Si, GE: SELFCONSISTENT CALCULATION

Valence charge density (110 plane)



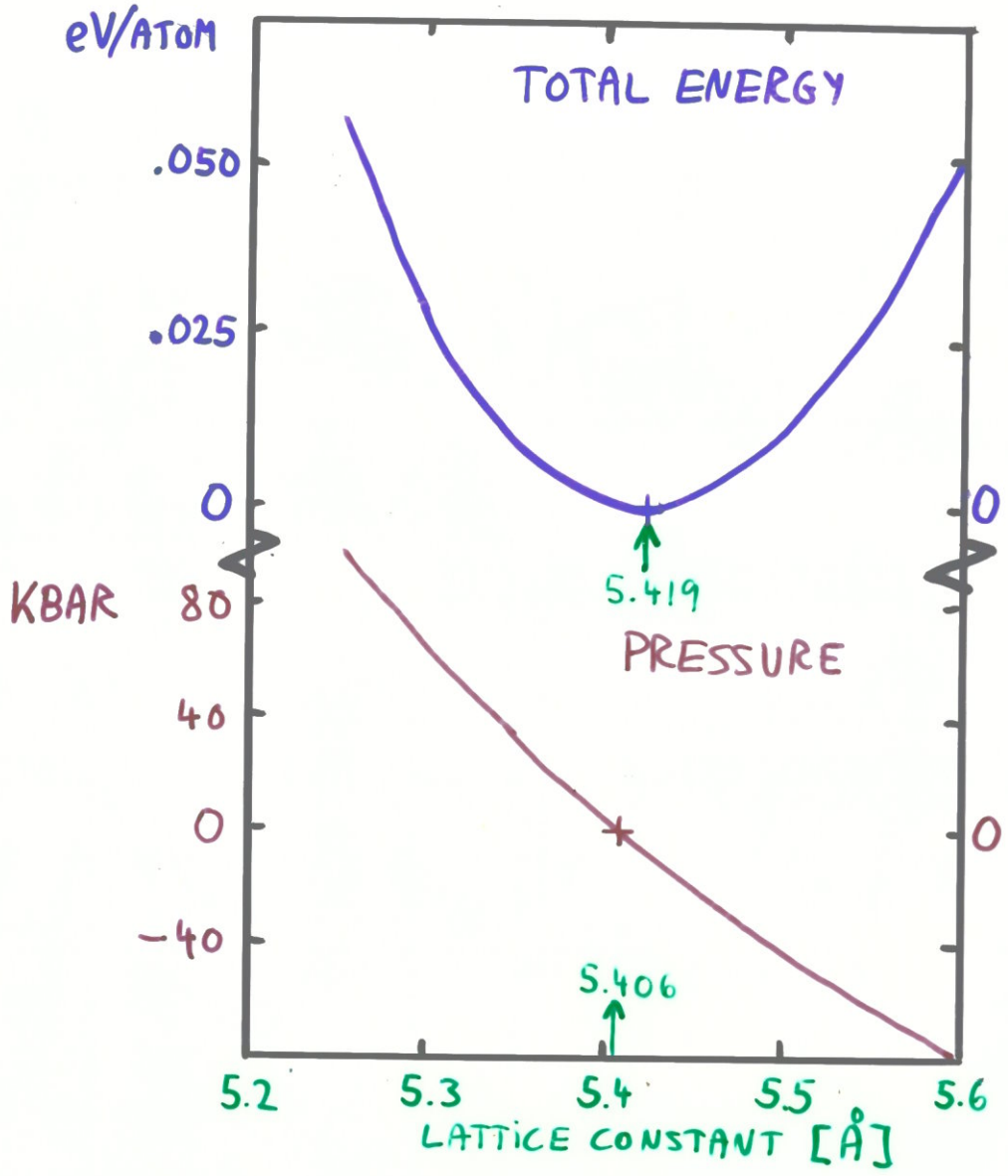
Contour plots of the valence charge density in the (110) plane of the cubic diamond phase of Si and Ge at Ω_{expt}. Charge density is in units of electrons per atomic volume with a contour step of 1. The black dots denote the atomic positions and straight lines denote the atomic chains.

APPLICATIONS OF STRESS:

I. LATTICE CONSTANT AND BULK MODULUS

SILICON: AB-INITIO PSEUDOPOTENTIAL CALCULATIONS.

- COMPARISON WITH ACCURATE PREVIOUS CALCULATIONS
- A VARIETY OF ACCURATE EXPERIMENTAL DATA



PLANE WAVES OF $\vec{K}^2 \leq 24$ RYDBERG

2 SPECIAL $\vec{k}$-POINTS

BEST CALCULATION (10 SPEC. PTS.): $a = 5.400$ Å $B = 0.93$ MBAR $\partial B/\partial P = 4.2$

EXPERIMENT: $a = 5.431$ Å $B = 0.992$ MBAR $\partial B/\partial P = 4.15$

$B = -V \cdot \partial P/\partial V$

TEST CALCULATIONS:

SILICON, $5.25\,\text{Å} \le a \le 5.60\,\text{Å}$, 2 SPECIAL $\vec{k}$-POINTS.

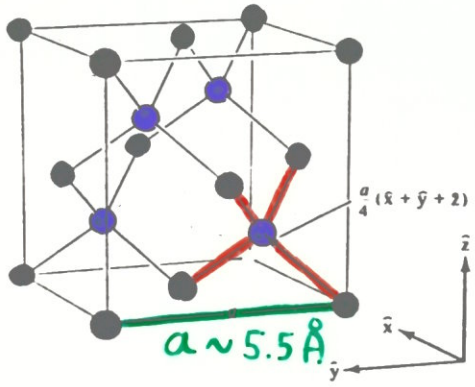
PLANE WAVE CUTOFF:	BY:	a_0 [Å]	$B = V\cdot\frac{\partial P}{\partial V}$ [Mbar]
$\lvert\vec{k}+\vec{G}\rvert^2 \le 12$ Ryd.	E:	5.45 (5.45)	~0.67 (0.98)
		YIN, COHEN (1980, 82).	
	P:	5.364	1.02
CONSTANT NUMBER OF WAVES, ~12Ryd.	E:	5.3697	1.11
	P:	5.3695	1.10
$\lvert\vec{k}+\vec{G}\rvert^2 \le 24$ Ryd.	E:	5.419	0.94
	P:	5.406	0.95
24 Ryd., 10 SPECIAL PTS.	P:	5.400	0.93
EXPERIMENT:		5.431	0.992

CONCLUSION:

- SIMULTANEOUS EVALUATION OF ENERGY AND PRESSURE TESTS CONVERGENCE OF BASIS SET.
- VERY MANY PLANE WAVES ARE NEEDED TO OBTAIN ACCURATELY BULK MODULUS, AND ELASTIC CONSTANTS.
- QUESTION: WHAT IS THE MOST EFFICIENT WAY TO CUT OFF THE BASIS SET ?

RESULTS: USING: { LOCAL-DENSITY APPROXIMATION. AB-INITIO PSEUDOPOTENTIALS. (BACHELET ET AL.)

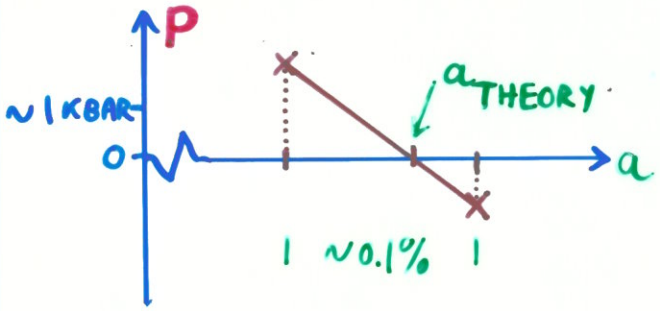
THE SEMICONDUCTORS Si, GE, GAAS.



Conventional cubic cell of the diamond lattice. For clarity, sites corresponding to one of the two interpenetrating face-centered cubic lattices are unshaded. (In the zincblende structure the shaded sites are occupied by one kind of ion, and the unshaded by another.) Nearest-neighbor bonds have been drawn in. The four nearest neighbors of each point form the vertices of a regular tetrahedron.

LATTICE CONSTANT AND BULK MODULUS:

CALCULATE PRESSURE $P = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$ AT 2 LATTICE CONSTANTS:

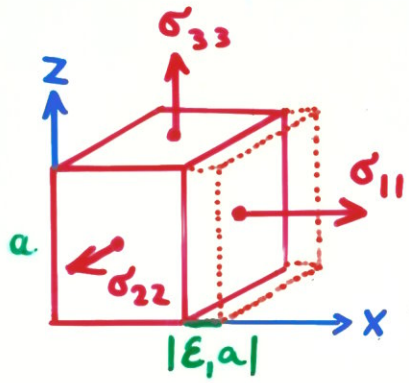


BULK MODULUS $B = -\frac{a}{3}\frac{\Delta P}{\Delta a}$

	Si	GE	GAAS	
a, CALC.	5.400 (-0.6%)	5.59 (-1.1%)	5.55 (-1.6%)	Å
a, EXP.	5.431	5.65	5.642	Å
B, CALC.	0.93 (-6%)	0.72 (-6%)	0.73 (-7%)	MBAR
B, EXP.	0.992	0.768	0.784	MBAR

II. ELASTIC CONSTANTS C_{11} AND C_{12}:

UNIAXIAL COMPRESSION ALONG x-DIRECTION (ϵ_1 - STRAIN)

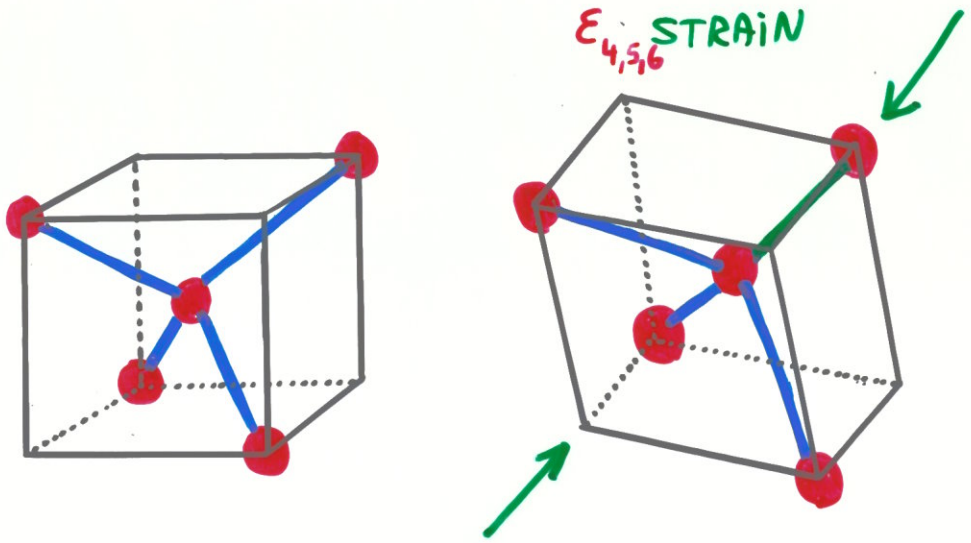


$$c_{11} = \sigma_{11} / \epsilon_1$$

$$c_{12} = \sigma_{22} / \epsilon_1$$

	Si	GE	GAAS	
c_{11}, CALC.	1.59 (-5%)	1.30 (-1%)	1.23 (-1%)	MBAR
c_{11}, EXP.	1.675	1.315	1.223	-"-
c_{12}, CALC.	0.61 (-6%)	0.45 (-9%)	0.53 (-7%)	-"-
c_{12}, EXP.	0.650	0.494	0.571	-"-

III. UNIAXIAL COMPRESSION ALONG (111) DIRECTION.



R_0

$R_0 \cdot (1 - \zeta \cdot \varepsilon_4)$

$R_0 \cdot (1 - \zeta \cdot \varepsilon_4 / 3)$

ζ : INTERNAL STRAIN PARAMETER

LOSS OF SYMMETRY GIVES INTERNAL DISPLACEMENT.

ASSUME HOOKE'S LAW FOR STRAIN ε_4 AND DISPLACEMENT u.

$$\text{FORCE} = \phi \cdot \left(\frac{a}{4} \zeta \varepsilon_4 - u \right) \qquad \phi = \frac{1}{2} M_{Si} \omega_{TO(\Gamma)}^2$$

$$\text{STRESS} = c_{44}^{(0)} \cdot \varepsilon_4 - \frac{1}{\text{VOL.}} \phi \frac{a}{4} \zeta u$$

$\omega_{TO(\Gamma)}$: PHONON FREQUENCY

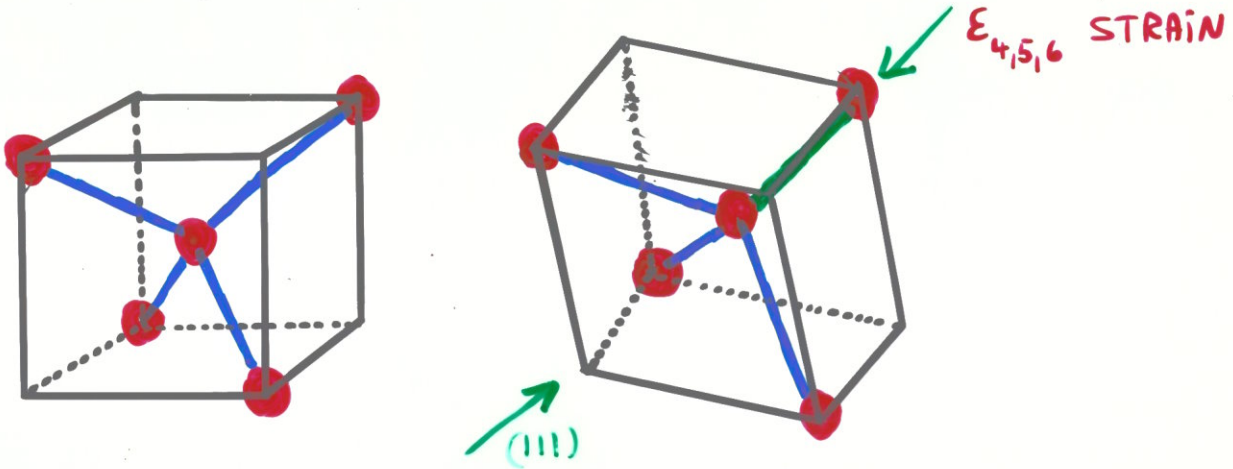
ACTUAL COMPRESSION: FORCE = 0 $\Rightarrow$ SOLVE LINEAR EQS.

FROM SIMULTANEOUS CALCULATION OF FORCE AND STRESS:

	CALC.	EXPT.	
$\omega_{TO(\Gamma)}$	15.64	15.68 THz	
c_{44}	0.85	0.801 Mbar	
ζ	0.53	0.73	← ? X-RAY DIFFRACTION.

III. UNIAXIAL COMPRESSION ALONG (111)-DIRECTION:

COUPLED EQUATIONS FOR ELASTIC CONSTANT C_{44}, TO(Γ) PHONON FREQUENCY AND INTERNAL STRAIN.



BOND LENGTHS: R_0

— $R_0(1+\varepsilon_4) - R_0\varepsilon_4\zeta$

— $R_0(1+\varepsilon_4) - R_0\varepsilon_4\zeta/3$

	Si	GE	GAAS	
C_{44}, CALC.	0.85 (+6%)	0.63 (-8%)	0.62 (+3%)	MBAR
C_{44}, EXP.	0.801	0.684	0.600	-"-
$\omega_{TO(\Gamma)}$, CALC.	15.64	9.05	8.09	10^{12} Hz
$\omega_{TO(\Gamma)}$, EXP.	15.68	9.11	8.187	-"-
ζ, CALC.	0.53 (-27%)	0.44 (-39%)	0.48 (-37%)	
ζ, EXP.	0.73	0.72	0.76	

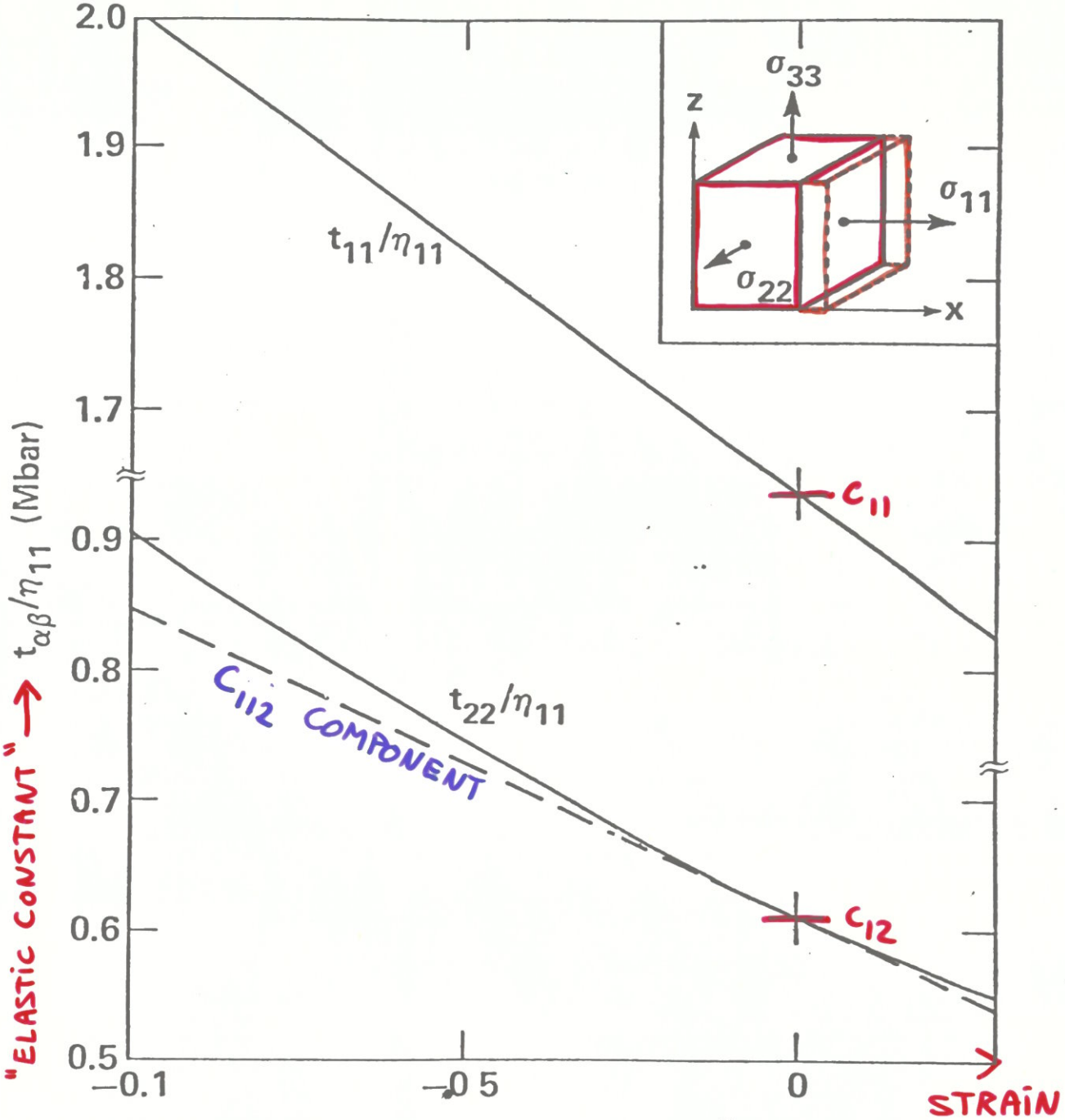
MEASUREMENT OF ζ: X-RAY DIFFRACTION, FORBIDDEN (006)-REFLECTION UNDER COMPRESSION. DIFFICULT!

UNRESOLVED QUESTION: WHO HAS THE CORRECT ζ ?

IV. ANHARMONIC ELASTIC CONSTANTS: SILICON

LAGRANGIAN STRESS AND STRAIN:

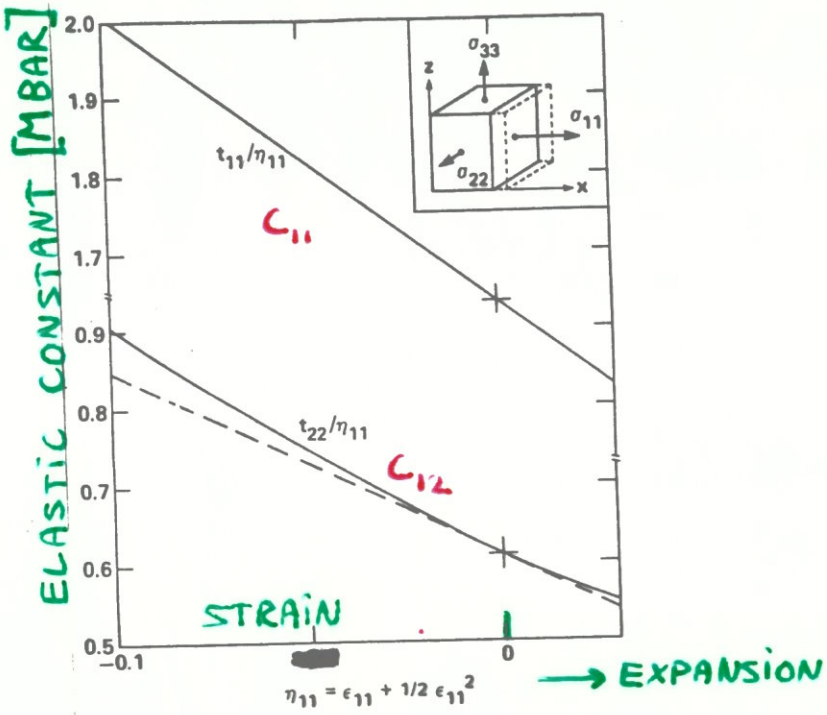
$$t_{11}/\eta_{11} = c_{11} + \tfrac{1}{2} c_{111} \cdot \eta_{11} + \tfrac{1}{6} c_{1111} \cdot \eta_{11}^2 + \cdots$$



	CALC.	EXPT.		CALC.	EXPT.	
c_{11} =	1.59	1.675	c_{12} =	0.61	0.650	MBAR
c_{111} =	−7.5	−8.3	c_{112} =	−4.8	−4.5	−11−
c_{1111} =	≈0	—	c_{1112} =	32	—	−11−

ANHARMONIC ELASTIC CONSTANTS: SILICON.

LARGE UNIAXIAL STRAINS: UP TO 10%



POWER SERIES:

$$\Delta E = \sum_{\mu\nu} c_{\mu\nu}\eta_\mu\eta_\nu + \sum_{\mu\nu\lambda} c_{\mu\nu\lambda}\eta_\mu\eta_\nu\eta_\lambda + \cdots$$

LAGRANGE STRAIN $\bar{\bar{\eta}} = \bar{\bar{\epsilon}} + \frac{1}{2}\bar{\bar{\epsilon}}^2$

	CALCULATION	EXPERIMENT	
c_{111}	−7.5 (−9%)	−8.25(10)	MBAR
c_{112}	−4.8 (+6%)	−4.51(5)	MBAR
c_{123}	≈0	−0.64(10)	MBAR
$c_{144}+2c_{166}$	−5.8 (−5%)	−6.08(45)	MBAR
c_{456}	−0.8	−0.64(20)	MBAR
$\partial B/\partial P$	4.0 (−4%)	4.15	
$\partial\zeta/\partial\epsilon_4$	−2.5	?	
c_{1111}	≈0	?	MBAR
c_{1112}	32	?	MBAR

CONCLUSIONS

- FOR THE FIRST TIME: A COMPLETE DESCRIPTION OF PERIODIC SOLIDS BY ENERGY, STRESS AND FORCES.
- STRESS THEOREM FOR ARBITRARY SYSTEMS.
  - CLOSE RELATION TO FORCE AND VIRIAL THEOREMS.
- DENSITY-FUNCTIONAL CALCULATIONS ARE FEASIBLE USING THE AB-INITIO PSEUDOPOTENTIAL METHOD.
- STRESS PERMITS LARGE COMPUTATIONAL SAVINGS.
- ACCURATE RESULTS: SI, GE, GAAS

  $a, B, \partial B/\partial P, c_{11}, c_{12}, c_{44}, c_{ijk}, \omega_{TO(\Gamma)}, \ldots$
- FUTURE:
  - STRESS FIELDS – NEW WAY TO CALCULATE FORCES.
  - PHASE TRANSFORMATIONS (HYDROSTATIC & UNIAXIAL).
  - SURFACE TENSION.
  - ??