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Materials & Molecular Research Division

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Ab initio CALCULATIONS OF MATERIALS PROPERTIES

S. G. Louie

September 1984

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LBL Report No. 19362

AB INITIO CALCULATIONS OF MATERIALS PROPERTIES

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To appear in the proceedings of DOE workshop on "Theory and Modeling for Materials Design," September 16-19, 1984, Texas A&M University, College Station, Texas.

As Dr. Phillips mentioned this morning, it has become possible to do calculations on real materials with quite good accuracy in the last few years from first principles. In this talk, I would like to illustrate this by giving several examples, mostly from some recent work that we have done at Berkeley. Before I proceed, I would like to acknowledge my collaborators--Che-ting Chan, James R. Chelikowsky (at Exxon), Marvin L. Cohen, Mark Hybertsen, and David Vanderbilt.

Let me begin by defining the term "ab initio electronic structure calculations." By this, I mean calculations that do not require empirical input; that is, the only input are the atomic numbers and masses of the constituent elements. From these calculations, one would then obtain quantities such as equilibrium crystal structures and lattice constants, bulk moduli, shear moduli, cohesive energies, vibrational properties, and even phonon-phonon and electron-phonon interaction parameters. This development has given rise to many exciting possibilites.[1] For example, it is now possible to predict new materials and their properties and to study the electronic and atomic structures of surfaces, interfaces, and defects. One can also investigate the phase stability of systems under extreme conditions of pressures and temperatures.

There are several important factors that contributed to making these kinds of calculations possible. They include better approximations to the density functional formalism; better band structure and total energy calculational techniques including the invention of ab initio pseudopotentials; and, of course, the availability of large and fast computers. The remainder of the talk is organized as follows: a brief discussion of the theoretical methods is given and then the rest of the time will be spent on applications.[2] In discussing applications, the bulk

properties, which include the structural properties, solid-solid phase transformations, and vibrational properties, will be presented first. Next, we describe calculations of microscopic interaction parameters between elementary excitations in the solid state. Phonon-phonon and electron-phonon interactions are used as examples. Then, we turn to surface structural determination and discuss the case of the 2x1 reconstruction on the diamond (111) surface. Finally, a discussion on the possibility of calculating excited-state properties from first principles is presented.

The basic quantity upon which we shall first focus is the total energy of the system as a function of the coordinates of the nuclei. This energy contains several terms--the core-core interaction energy, the electron-core interaction energy, the kinetic energy of the electrons, the classical electron-electron static interaction term, and a remaining term involving the many-body interaction among the electrons.

$$E_{tot} = E_{c-c} + E_{e-c} + E_e^{kin} + E_{e-c}^{Coul} + E_{xc} \qquad (1)$$

Within the density functional formalism,[3] the total electronic energy is a functional of the charge density. Thus, in principle, the only input to a total energy calculation is the atomic numbers. For example, in a study of crystal phase stability under pressure, calculations are carried out for a number of assumed crystal structures to determine the lowest energy at a given volume. For vibrational properties, the additional input of the atomic masses is needed.

There are two major approximations in the calculations described below: (1) the use of the local density approximation for the electron-electron interactions and (2) the use of ab initio pseudopotentials for the electron-ion interaction. The major advantage of using pseudopotentials is

to eliminate the core electrons from the problem which is equivalent to a frozen-core approximation but has the added feature of much smoother valence wavefunctions. The ab initio pseudopotentials are generated from atomic calculations with no empirical input.[4] Professor Kleinman will discuss more on pseudopotentials in a later talk.

The calculations employ two important statements in the density functional formalism. The first one, as already mentioned, is that the ground-state total energy of an electronic system in an external potential can be expressed as a functional of the charge density. That is, it may be determined without a knowledge of the full many-body wavefunction. The total energy is usually partitioned into an interaction term with the external potential, a classical electrostatic term for the electron distribution, and a term which is a universal density functional that contains the kinetic energy and the exchange-correlation energy. The second important statement (derived from a variational principle of E_{tot} with respect to the density) is that the correct charge density may be obtained from solving a set of self-consistent single-particle Schrodinger equations

$$\left\{-\frac{1}{2}\nabla^2 + V_{ext}(\underset{\sim}{r}) + V_H(\underset{\sim}{r}) + \mu_{xc}(n,\underset{\sim}{r})\right\}\psi_i(\underset{\sim}{r}) = \varepsilon_i\psi_i(\underset{\sim}{r}) \qquad (2)$$

where μ_{xc} is the functional derivative of the exchange-correlation energy E_{xc} with respect to the electron density, n. This formalism, thus, reduces a complicated many-body problem to a tractable single-particle problem.

One remaining difficulty is the evaluation of the unknown exchange-correlation functional, E_{xc}. The approximation usually made is the local density approximation[3] in which the exchange-correlation potential at a given position in space is replaced by that of the homogeneous electron gas of the same density. Thus, the steps in a calculation are: (1) determine

the external potential, that is, the position of the atoms; (2) determine the charge density from a self-consistent field calculation; and (3) evaluate the total energy from the charge density.

As examples for bulk structural properties calculations, we present here results for several insulators and metals. Figure 1 shows the calculated total energy of carbon in the diamond structure as a function of volume.[5] In the calculation, a linear combination of gaussian orbitals basis set is used to expand the electron wavefunctions. The minimum of the curve gives the lattice constant; the curvature gives the bulk modulus; and by comparing the minimal energy to the pseudoatom energy, the cohesive energy is determined. Table I presents a comparison of the calculated results with the experimental values for diamond and silicon. This kind of calculation has been done for many other types of materials,[2] including simple metals, compound semiconductors, transition metals, and insulators. Typically, the lattice constants are in excellent agreement with experiment to within a fraction of a percent. Cohesive energies and bulk moduli give agreement at a few percent level. Table II provides some results for the transition metal tungsten.[6]

Another major objective is to use these theoretical techniques for calculating quantities which cannot be easily measured experimentally. Some examples of these include the prediction of new crystals and the study of solid-solid structural transformations under pressures or at high temperatures. Figure 2 shows one such study for silicon by Yin and Cohen.[7] Here the calculated total energy per atom is presented for silicon in seven different crystal structures. The lowest energy curve (corresponding to the diamond structure) is predicted to be the preferred structure at zero pressure. This is consistent with experiment, and the theoretical equilibrium volume is at virtually the experimental value. At smaller

volumes, the diamond structure curve is above in energy than some of the other curves. This means that if pressure is applied to silicon, it will eventually transform from the diamond structure into other crystal structures. The first transition is to the β-tin structure occurring along the indicated Gibbs line (dashed line in Fig. 2). The negative of the slope of the Gibbs line is the transition pressure. Also indicated in Fig. 2 are the initial and final volumes of the crystal at the transition pressure. Table III provides a comparison between theory and experiment illustrating that the local-density pseudopotential method does give very good results for this kind of study.

The advent of total energy calculations also makes possible an ab initio determination of vibrational properties such as phonon frequencies and eigenfunctions using a frozen-phonon calculation of the type shown in Fig. 3. Here the potential energy vs. displacement for a zone-center optical phonon in diamond polarized in the (111) direction is presented.[5] Each theoretical point represents a calcualtion for one structure, namely, a crystal with the phonon of amplitude u frozen in. Making use of the standard Born-Oppenheimer assumption, the second derivative of the curve at the minimum gives the harmonic elastic constant and, hence, the phonon frequency. Specifically, if the distortion energy is expanded in a Taylor series

$$\Delta E = \frac{1}{2!} K_2 u^3 + \frac{1}{3!} K_3 u^3 + \frac{1}{4!} K_4 u^3 \ldots \tag{3}$$

then the phonon frequencies are given by

$$K_2 = \begin{cases} M\omega^2(\underset{\sim}{k}) & \text{for } \underset{\sim}{k} = 0 \text{ or at zone edge} \\ \frac{1}{2} M\omega^2(\underset{\sim}{k}) & \text{otherwise} \end{cases} \tag{4}$$

Table IV presents the calculated results for the diamond phonon frequencies at the various points in the Brillouin zone.[8] The agreement with experiment is excellent. More importantly, since these numbers are from total energy differences, microscopic information on various contributions that give rise to the restoring forces may be obtained. By analyzing the distortion energy, it is possible to isolate the core-core, electron kinetic energy, electron-core, and electron-electron contributions separately. This kind of information is extremely valuable in analyzing and understanding phonon anomalies in various semiconductors and transition metals.

In addition to obtaining the individual phonon frequencies and eigenfunctions, it is possible to evaluate a whole dispersion curve along a particular direction. There are two equivalent approaches. One way is to move one plane of atoms and calculate the Hellmann-Feynman forces on all the other planes using a supercell technique. From the force constants, the dynamical matrix for wave propagation in the direction perpendicular to the planes may be constructed, and, hence, the dispersion curve may be calculated. Another way is to calculate the phonon frequencies using the frozen-phonon technique for a particular branch at several $\underline{k}$-points. From the frozen-phonon results, the dynamical matrices evaluated at these $\underline{k}$-points may be inverted for the interplanar force constants. Again, the dispersion curve can then be calculated from the force constants. Results calculated using the latter approach for the longitudinal modes of diamond[8] are presented in Fig. 4. The solid curve is obtained using interplanar force constants up to those of the sixth nearest-neighbor planes.

We have, moreover, extended the frozen-phonon method to obtain, for the first time, a first-principles determination of higher order anharmonic elastic coupling constants.[9] In Fig. 3, the third and fourth derivatives

give us the third and fourth order anharmonic coupling constants for this polarization. By looking at several polarizations with greater accuracy and at more values of u, we are able to completely characterize the zone-center optical coupling constants through fourth order. That is, the amplitudes for the three- and fourth-phonon interaction processes (Fig. 5) for $\underset{\sim}{k}$ near zero have been calculated from first principles. By making use of straightforward perturbation theory, we can even then calculate the renormalized four-phonon vertex in which exchange of an optical phonon is allowed. Similar calculation for $\underset{\sim}{k}$-vectors away from zone center have also been carried out using a supercell technique.

A surprising result emerged from the diamond phonon-phonon calculation. It had been assumed that the fourth-order coupling was positive; in fact, it had been proposed as long ago as 1969 by Cohen and Ruvalds[10] that a strong enough positive coupling could give rise to a two-phonon bound state that might explain an anomalous peak in the two-phonon Raman spectrum of diamond. Unfortunately, no reliable experimental or theoretical information has been available on the underlying coupling constants during the last 15 years, and the two-phonon bound-state model has remained controversial. Our calculation shows the renormalized coupling to be <u>negative</u> in which case no bound state could form. Therefore, an alternative explanation for the Raman anomaly is probably the correct one.

The same theoretical methods can be applied to calculate the electron-phonon interaction parameters in a solid. The standard expression for the matrix element of scattering an electron from state $\underset{\sim}{k}$ to state $\underset{\sim}{k}'$ with an emission or absorption of an phonon is given by

$$g(\underset{\sim}{k}',\underset{\sim}{k};\lambda) = \left(\frac{\hbar}{2M\omega_{q\lambda}}\right)^{1/2} \langle \psi_{\underset{\sim}{k}'} | \varepsilon_{\underset{\sim}{k}-\underset{\sim}{k}'} \cdot \underset{\sim}{\nabla} V | \psi_{\underset{\sim}{k}} \rangle \qquad (5a)$$

where

$$\hat{\varepsilon}^{\lambda}_{\underset{\sim}{q}} \cdot \underset{\sim}{\nabla} V = \frac{H_{\underset{\sim}{q}\lambda} - H^{0}}{u_{\underset{\sim}{q}\lambda}} \quad . \tag{5b}$$

All the ingredients needed for evaluating Eq. 5 can be obtained from the theory--the phonon frequency from a frozen-phonon calculation, the electronic wavefunctions from the band structure calculation, and Eq. 5(b) from the difference between the self-consistent Hamiltonians for cases with and without the frozen-phonon distortion. This approach has been applied with success to Al[11] in calculating the electron-phonon parameter, λ, which determines the superconducting transition temperature.

Another important area of application for total energy calculations is surface structure determination, a major problem in surface science. We discuss here one such calculation on the 2x1 (111) surface of diamond.[12] The goal is to find the correct structure by minimizing the total energy with respect to the atomic positions of the first several layers from the surface. In addition to information on surface atomic rearrangements, many other physical and chemical properties may be obtained. Among these are surface electron wavefunctions and energies, work functions, surface energies, chemisorption geometries, bonding energies and charge distributions, and vibrational properties of the surface.

There has been a number of models proposed in the literature for the 2x1 reconstructed diamond (111) surface. This surface is of interest as the insulating limit for the group IV (111) surfaces which show a variety of surface reconstructions.[13] In our study, energy minimization was carried out for all the topologically distinct models in the literature using slab geometries of at least 10 atomic layers. These include the ideal relaxed

model, the Haneman buckling model,[13] the Pandey π-bonded chain model,[14] the Chadi molecule model,[15] and the Seiwatz single chain model.[16] Of these, only the Pandey π-bonded chain model (which has chains of dangling bonds on the surface) has a lower energy than that of the relaxed 1x1 surface (see Table V). A minimum-energy structure is determined for this model after extensive consideration of atomic position relaxations for all atoms in the slab. The other models are found to be implausible on the basis of their total energies and surface state disperisons as compared to photoemission results. Also, contrary to previous suggestion, no dimerization of the surface chain is found to be favorable. Thus, we conclude that the fully relaxed undimerized π-bonded chain structure is a likely candidate for this surface in terms of energetic considerations and is consistent with experiments reported to date. The detailed structure of the surface is illustrated in Fig. 6. The driving force for this reconstruction is a mechanism that allows the highly unfavorable dangling bonds to move to near-neighbor positions so that they can participate in π bonding.

Thus far, the discussion has been focused on total energies and ground-state properties. The local density approximation (LDA), unfortunately, does not work as well when applied to the excited-state properties of insulators and semiconductors. The energy band gap for these materials calculated in the LDA is typically 30-50% off in comparison with experimental values. There is, however, no formal justification for interpreting the LDA eigenvalues as quasiparticle energies since the density functional formalism is a ground-state theory.[3] To obtain the band gaps, one should calculate the energy of the quasiparticles by solving[17]

$$\left(-\frac{1}{2}\nabla^2 + V_{ext} + V_H\right)\psi(\underset{\sim}{r}) + \int d^3r' \sum (\underset{\sim}{r},\underset{\sim}{r}',E)\psi(\underset{\sim}{r}') = E\psi(\underset{\sim}{r}) \qquad (6)$$

where Σ is the Dyson mass operator which, unlike the exchange-correlation potential in LDA, is nonlocal and energy dependent. There are several approaches in attempting to calculate Σ. The particular approach that we used is Hedin's screened-exchange Coulomb hole approximation[18]

$$\Sigma = iGW \tag{7}$$

where G is the addressed Green's function and W is the screened Coulomb interaction. The calculation thus requires the full dielectric matrix and the crystalline single-particle Green's function. We evaluate both G and W using the LDA results since they are found to be not far from the correct values. A number of previous attempts have been made along this line. However, the off-diagonal elements of the dielectric matrix (that is, local-field effects) were neglected in the past work. We find that local-field effects are extremely important in obtaining good quantitative results. Some preliminary results for the calculated quasiparticle energies for Si using the static dielectric matrix are presented in Table VI.[19] The many-body results are generally in better agreement with experiment than the LDA eigenvalues. In particular, there are substantial improvements in the values of the direct optical transitions.

In summary, this talk has given a brief discussion of several selected calculations of materials properties using a method combining ab initio pseudopotentials and the local density functional approximation. It is evident from these results and from results of a number of other workers[1] that the LDA gives excellent ground-state properties for a wide variety of materials systems. However, for ab initio calculations of excited-state properties, it appears that one has to go beyond the density functional

theory and consider the many-body problem more carefully.

ACKNOWLEDGMENTS

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QUESTIONS AND ANSWERS

QUESTION: (Bill Goddard) Those are extremely impressive results. A question has to do with how you describe bond breaking processes. Surfaces often have broken bonds. Have you considered taking a case like diamond and breaking it apart into atoms and actually doing the calculation all the way out? This is relevant to looking at chemical processes, and it's also relevant for looking at surface states.

LOUIE: We have not done precisely that calculation. However, calculations on cohesive energies and surface energies indicate that one gets accuracy of the order of few tenths of an electron volt.

QUESTION: Can information on energy barriers for surface reconstructions be obtained from the calculations?

LOUIE: Yes, we can (and have) carried out calculations by transforming, say, the ideal (1x1) surface into a Pandey chain model and following the total energy curve continuously.

QUESTION: Does the theory work for magnetic surfaces?

LOUIE: I have not done calculations for magnetic surfaces. Art Freeman's group has done some spin polarized calculations for 3d transition metal surfaces, and their calculated magnetization seems to agree with experiment.

QUESTION: Band gaps in a semiconductor can be formulated in terms of differences in ground-state energies. One should, therefore, be able to get them out from density functional calculations.

LOUIE: Yes, formally, that is possible, but how does one go about calculating them? Excited states in the solid state are much more complex than excited states for localized systems such as atoms. The discrepancies between LDA results and experimental values are most severe for the insulators. However, even for metals, there are problems. For example, the

calculated relative position of the d-bands of the transition and noble metals to the Fermi level does not correspond exactly to that from photoemission measurements. This is because one should really calculate the quasiparticle energies since a photoemission experiment measures excited-state properties.

QUESTION: Among the ground-state quantities, the cohesive energies appear to be more difficult to obtain accurately.

LOUIE: I agree. The cohesive energy, the binding energy, is the trickiest quantity to get out because it involves the energy difference between atoms in the isolated and solid state. The local density approximation is not expected to have exactly the same degree of validity in both cases. Also, the answer changes slightly depending on the form of the local density exchange-correlation potential used. Presently, there is a number of LDA exchange-correlation potentials in the market. In the past few years, we have been using the potential derived from the electron gas data calculated by Ceperley and Alder. We believe the Ceperley-Alder results are probably the best electron gas data to date.

QUESTION: I did not see any transverse modes in your diamond phonon results. Have you calculated them and their dispersion curves? Also, can you include temperature effects in the structural transition studies?

LOUIE: We have done calculations for the transverse modes. There are both TO and TA mode results in Table IV. We, however, have not carried out calculations for their dispersion curves. This simply requires calculation of phonon frequencies for a few more $\underline{k}$-points and then inversion of the dynamical matrices for the interplanar force constants. One can, indeed, include temperature in structural phase transition studies. In fact, the temperature-induced phase transition for the case of beryllium has been

studied. The free energy which includes a phonon entropy term now determines the structural transformation. I have a figure here on the beryllium calculation that I could show you if you're interested.

QUESTION: What do you believe is the accuracy of these calculations? Can they be applied to more complicated systems?

LOUIE: My belief is that one can get accuracy within a few percent of experiment for ground-state properties using the local density approximation. At this moment, we are limited by computer capabilities (both speed and memory space), so we are not able to look at more complicated systems such as metal-semiconductor interfaces. For excited-state properties, such as optical spectra, it is still not clear at this moment what kind of effort is needed to obtain accurate first-principles results.

QUESTION: (Peter Feibelman) In the calculation of the diamond surface, how big are your matrices? And how do you solve the Poisson equation?

LOUIE: In that particular calculation of the 2x1 reconstructed surface, we have 12 localized orbitals per atom, and there were 20 atoms per surface unit cell in the slab. Thus, the matrix size that we are dealing with is 240x240. As for the solution of the Poisson equation, we do not put the 20 atoms in a supercell and perform fast fourier transforms because that would be too costly. Instead, we divide the slab into layers (in the order of few hundred layers for a 10 atom thick slab) and perform two-dimensional fast Fourier transforms for the charge on each of the layers. This way one can solve the Poisson equation very accurately and very fast.

Table I. Ground-state properties of diamond and Si.

	Lattice Constant (Å)	Cohesive Energy (eV/atom)	Bulk Modulus (Mbar)
Diamond			
Theory	3.56	7.84	4.37
Experiment	3.57	7.37	4.42
Silicon			
Theory	5.41	4.76	0.93
Experiment	5.43	4.63	0.99

Table II. Ground-state properties of tungsten.

	Expt.	Theory	Error
Cohesive energy (eV)	8.9	8.46	-5%
Lattice constant (Å)	3.16	3.13	-1%
Bulk modulus (Mbar)	3.23	3.34	3%

Table III. Diamond to β-tin transitions for Si and Ge (after Ref. 7)

	V_t^d	V_t^β	V_t^β/V_t^d	P_t(kbar)
Si				
Theory	0.928	0.718	0.774	99
Expt.	0.918	0.710	0.773	125
Δ	1.1%	1.1%	0.1%	-20%
Ge				
Theory	0.895	0.728	0.813	96
Expt.	0.875	0.694	0.793	100
Δ	2.3%	4.9%	2.5%	-4%

Table IV. Diamond phonon frequencies.

Mode	$\omega_{theory}(cm^{-1})$	$\omega_{expt}(cm^{-1})$	$\Delta\omega$
LTO(Γ)	1347	1332	15
LO($\vec{k}$=1/3X)	1353	—	
LO($\vec{k}$=2/3X)	1328	—	
LOA(X)	1219	1185	34
TO(X)	1173	1069	104
TA(X)	772	807	-35

Table V. Calculated total energies of diamond (111) 1x1 and 2x1 surface reconstruction models.

Surface Model	Energy (eV/surface-atom)
Ideal 1x1	0.00
Buckled ($\Delta z = \pm 0.26$ Å)	0.35
Chadi π-bonded molecule	0.28
Seiwatz single chain	1.30
Ideal Pandey π-bonded chain	-0.05
Relaxed 1x1	-0.37
Relaxed Pandey π-bonded chain	-0.68
ΔE_{tot}, ±2% dimerization	+0.01
ΔE_{tot}, ±4% dimerization	+0.04
ΔE_{tot}, ± 6% dimerization	+0.09

Table VI. Quasiparticle energies in silicon.

	LDA	Present Work	Expt.
Γ_{1v}	-11.93	-12.72	-12.5
Γ_{15c}	2.57	3.59	3.4
$\Gamma_{2'c}$	3.29	4.20	4.2
X_{4v}	-2.87	-2.91	-2.9
X_{1c}	0.68	1.76	1.3
$L_{3'v} \rightarrow L_{1c}$	2.73	3.65	3.45
$L_{3'v} \rightarrow L_{3c}$	4.58	5.73	5.50

FIGURE CAPTIONS

Fig. 1 Total energy vs. volume for carbon in the diamond structure. The continuous curve is the Murnaghan equation of state fit to the calculated points.

Fig. 2 Total energy curves for various assumed crystal structures of Si as a function of volume normalized to the observed volume. The dashed line is the common tangent between the diamond and white tin phases (from Ref. 7).

Fig. 3 Frozen-phonon energy vs. bond displacement.

Fig. 4 Calculation of phonon dispersions for diamond in the [100] direction by extracting force constants from frozen-phonon results. Only the longitudinal modes are plotted. The squares are frozen-phonon results. The triangles and dots represent measured points.

Fig. 5 Three- and four-phonon interaction diagrams.

Fig. 6 Illustration of bond length changes (with respect to bulk) which occur upon relaxation of (a) 1x1 and (b) 2x1 Pandey chain models for the diamond (111) surface.

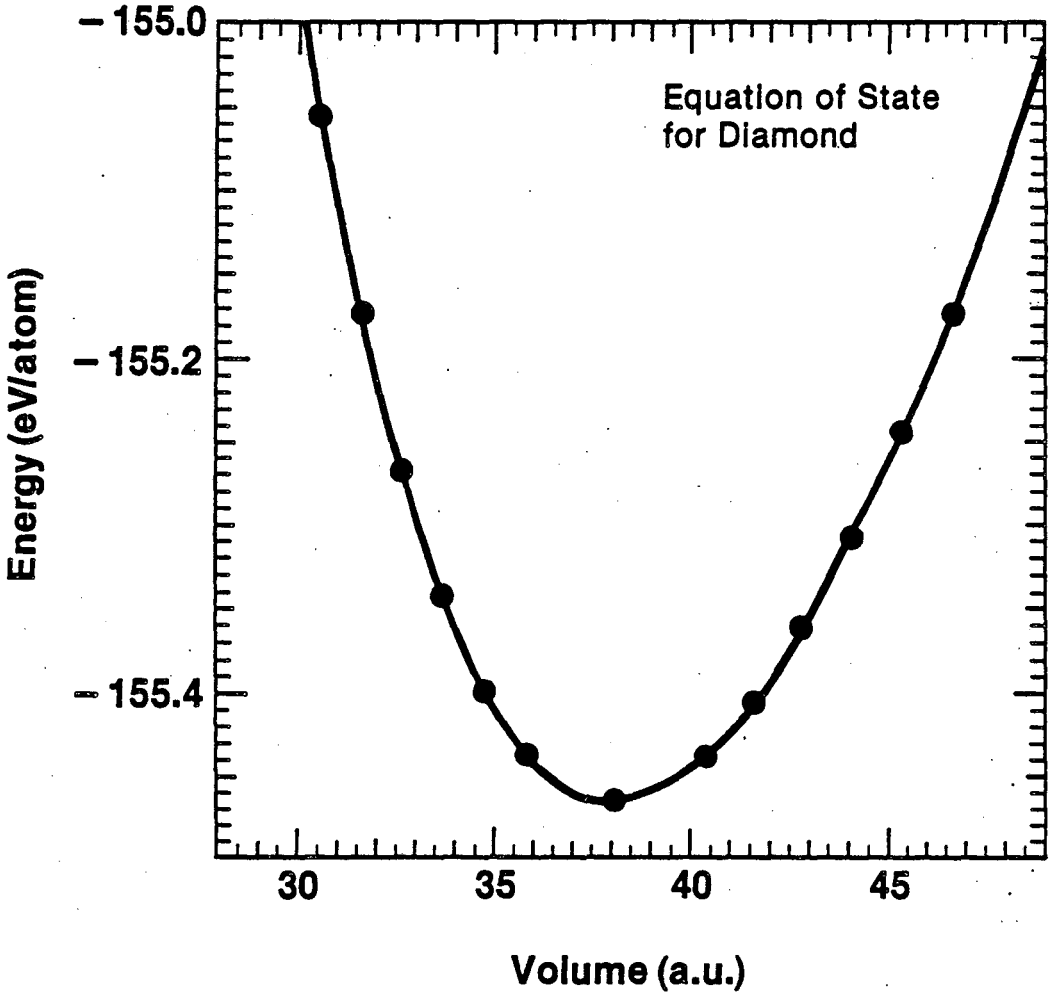

Equation of State
for Diamond
−155.0
−155.2
−155.4
Energy (eV/atom)
30
35
40
45
Volume (a.u.)

Fig. 1

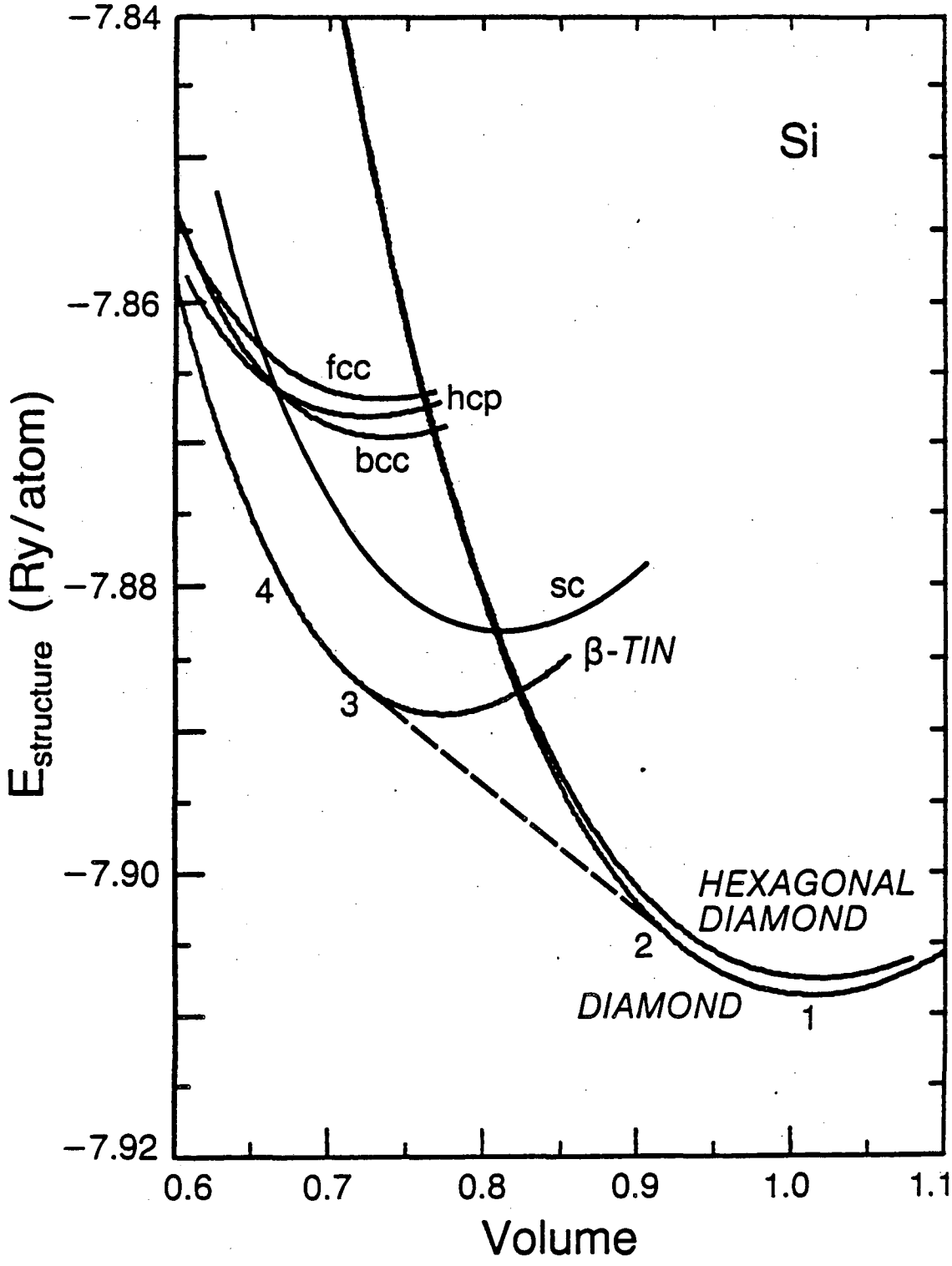

Si
−7.84
−7.86
−7.88
−7.90
−7.92
$E_{structure}$ (Ry/atom)
0.6
0.7
0.8
0.9
1.0
1.1
Volume
fcc
hcp
bcc
sc
β-TIN
4
3
2
1
HEXAGONAL DIAMOND
DIAMOND

Fig. 2

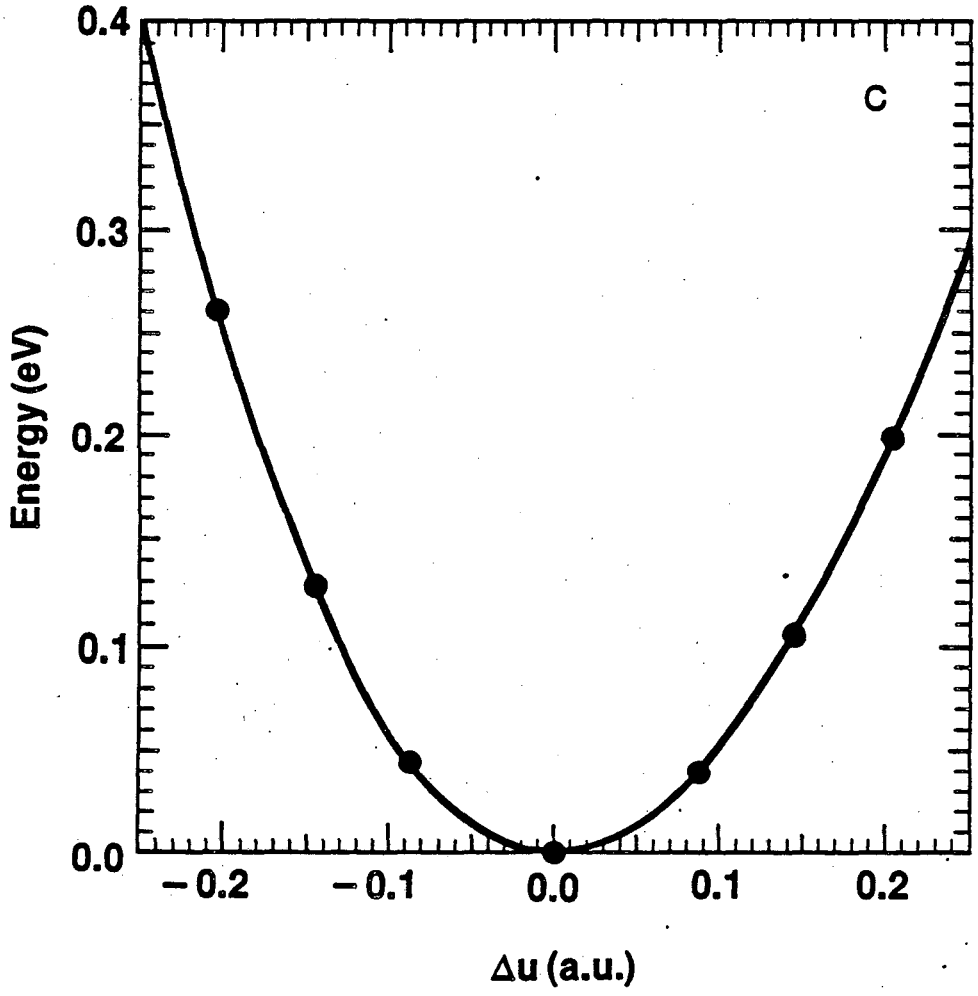


Fig. 3

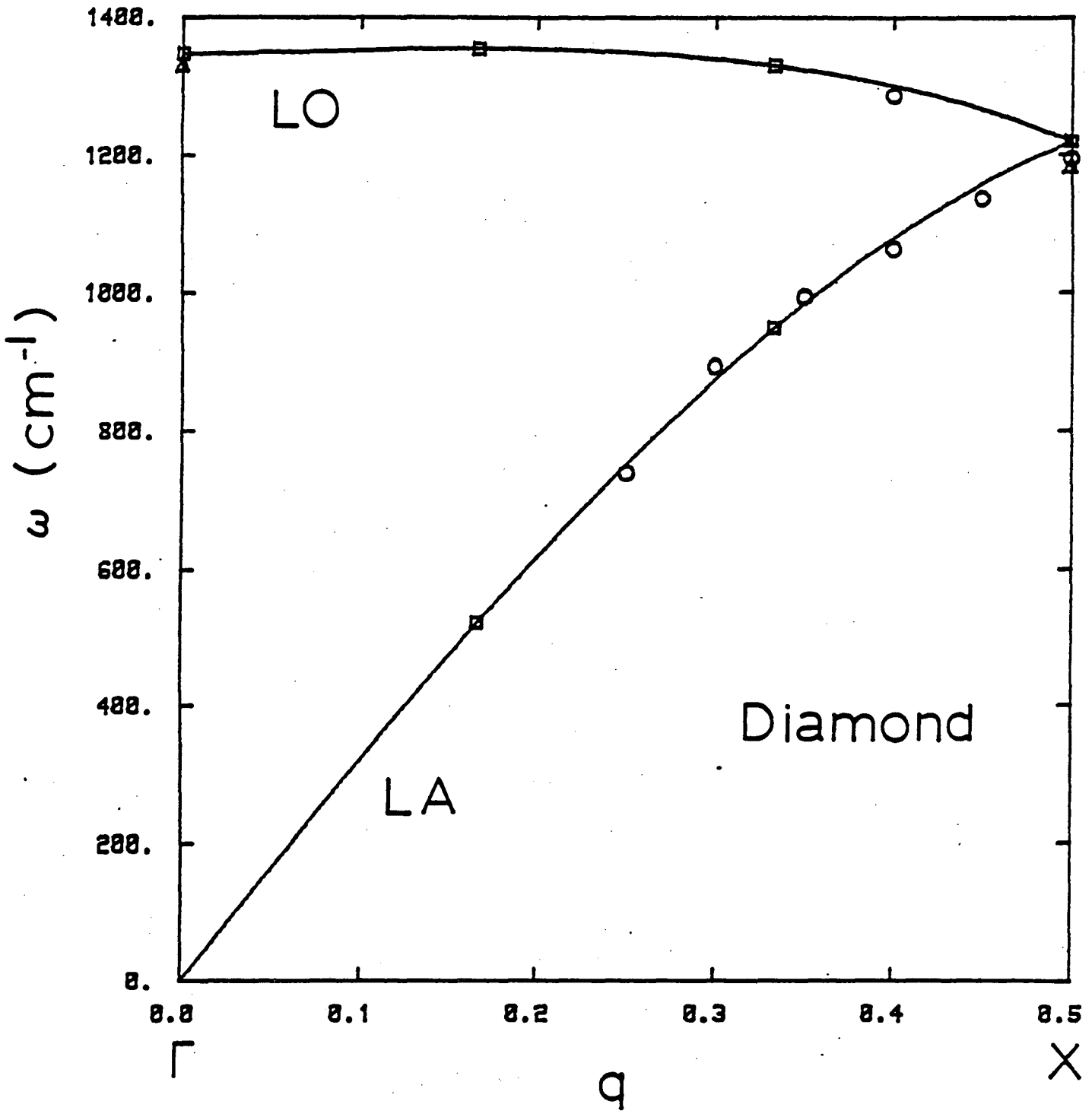

1400.
1200.
1000.
800.
600.
400.
200.
0.
ω (cm⁻¹)
LO
LA
Diamond
0.0
0.1
0.2
0.3
0.4
0.5
Γ
X
q

Fig. 4

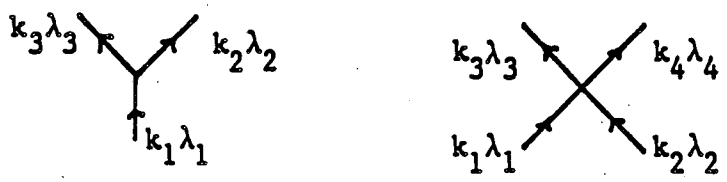
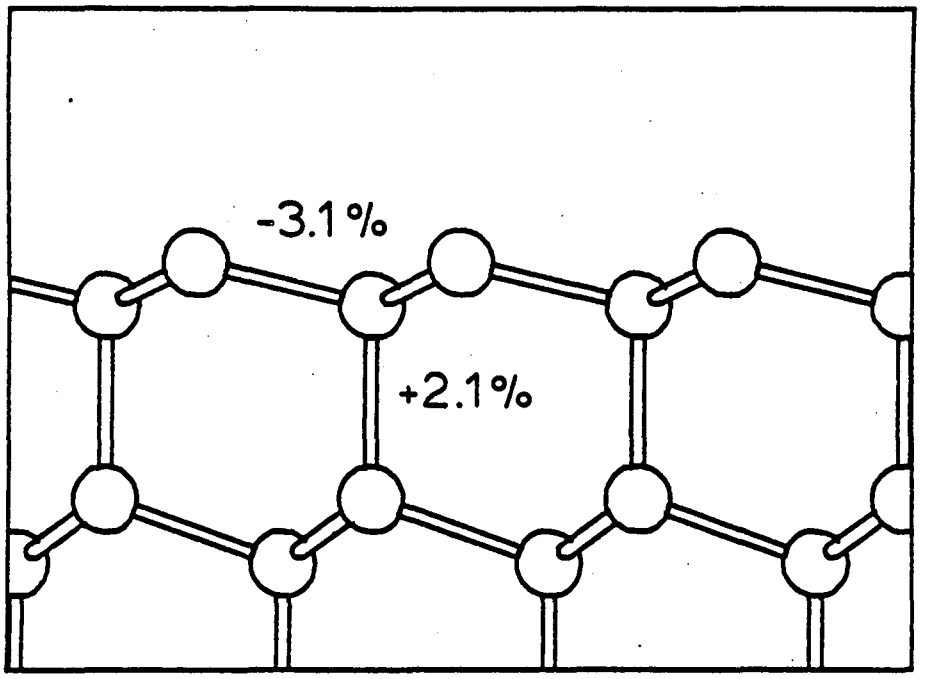

$k_3\lambda_3$
$k_2\lambda_2$
$k_1\lambda_1$
$k_3\lambda_3$
$k_4\lambda_4$
$k_1\lambda_1$
$k_2\lambda_2$

Fig. 5

(a)



(b)

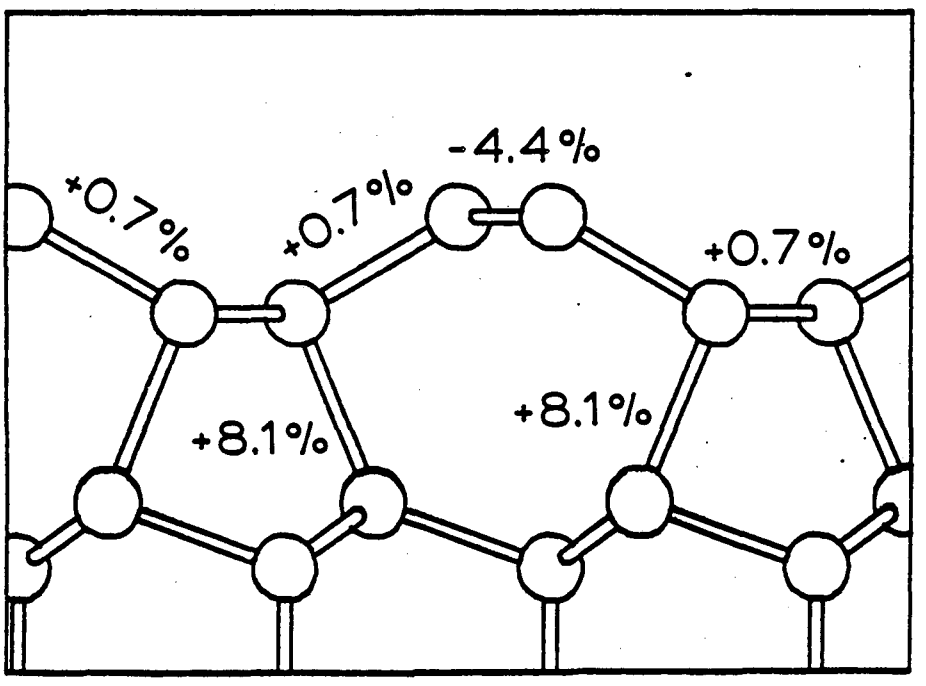


Fig. 6

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