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Absolute deformation potentials of Al, Si, and NaCl

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We present an approach to the calculation of *absolute* deformation potentials (ADP's) based on *ab initio* all-electron methods. The ADP of a given single-particle state is obtained from the variation of its energy between a compressed and an expanded region of the same material. Core levels are used to calculate the band offset at the compressed-expanded homojunction. We present results for a simple metal (Al), a semiconductor (Si), and an insulator (NaCl) under uniaxial strain. We find that (i) the ADP of the valence-band maximum is positive in Si, as predicted by a simple tight-binding model, but it is negative in NaCl, in conflict with tight binding; (ii) while most conduction-band states have negative ADP's, in agreement with the tight-binding picture, some conduction states have positive ADP's; (iii) core levels have nonvanishing ADP's, so they cannot be used as "absolute" reference energies in the presence of strain.

I. INTRODUCTION

The concept of deformation potential was introduced in 1950 by Bardeen and Shockley¹ to describe the interaction between electrons and acoustic phonons. They assumed that the matrix elements of the electron-phonon interaction are related to the derivatives of the electronic energy levels with respect to macroscopic strain (deformation potentials). This conjecture, known as deformation potential theorem, has been recently proved by Resta² in the framework of density-functional theory.

While the *relative* deformation potential between two energy levels of the same system (i.e., the derivative with respect to strain of the energy *difference* between the two levels) is a well-defined quantity that can be measured and calculated in a straightforward manner,^{3,4} the concept of *absolute* deformation potential (ADP) is much more subtle. Due to the long-range nature of Coulomb interactions, in fact, the absolute position of an energy level in an infinite solid is ill-defined, and only energy differences are accessible to either calculations or experiments. Thus, the deformation potentials of an infinite solid are defined only within an additive constant that represents the derivative of the reference energy with respect to strain. While it has often been assumed that a given reference energy is strain independent, this assumption is arbitrary and cannot be rigorously proved. In fact, if one defines "absolute" to imply "without reference," then it is impossible to define an "absolute" deformation potential in an infinite solid. As Van de Walle and Martin⁵ have recently pointed out, however, the de-

formation potentials which are relevant for the electron-phonon problem can be expressed in terms of the *lineup* of the energy levels between two regions of the same system subject to different strain conditions. Since these quantities can be calculated without any assumption about the existence of a strain-independent reference energy, they can be properly referred to as *absolute* deformation potentials. Resta, Colombo, and Baroni⁶ have shown that for nonpolar materials and uniaxial strains these ADP's are well-defined bulk properties. We will use here the concept of "absolute deformation potential" within this definition.

Most of the experimental results in this area have been obtained indirectly by fitting the deformation potentials to mobility or absorption data. This procedure is rather uncertain, due to the difficulty of modeling the many, complex scattering mechanisms involved. Consequently, the results are spread over a wide range of values. For example, values ranging between -21 and -3.4 eV (Ref. 7) have been reported for the deformation potential of the conduction-band minimum (CBM) of InP. Recently, a direct approach was suggested by Nolte, Walukiewicz, and Haller.⁸ Assuming strain independence of the energy levels associated with transition-metal impurities across a strained-unstrained homojunction, and measuring conduction-band to impurity-level transition energies on both sides of the homojunction, these authors derive the conduction-band deformation potentials of several materials. A different approach has been proposed by Cargill, Angilello, and Cavanagh.⁹ The strain induced in Si by As doping is related to the CBM deformation poten-

tial;¹⁰ by singling out the effect of atomic size differences, these authors obtain the deformation potential of the CBM of Si for (001) strain.

A number of theoretical approaches have been applied to the deformation potential problem. The simple tight-binding model of Harrison,¹¹ assuming arbitrarily that the diagonal matrix elements of the Hamiltonian (atomic-orbital energies) are volume independent, would predict *positive* deformation potentials for bonding states and *negative* deformation potentials for antibonding states. On the other hand, the free-electron model (in which energies scale as $\Omega^{-2/3}$, where Ω is the unit-cell volume) would predict negative deformation potentials for every state. Most of the previously published calculations^{4,5,12-15} are based on the assumption that a given reference energy can be considered as “absolute,” i.e., strain independent. This is the case, for example, of the pseudopotential calculations of Blacha, Presting, and Cardona,⁴ of the self-consistent tight-binding method of Priester and co-workers,¹³ of the linear muffin-tin orbital calculations of Verges *et al.*¹⁴ and Cardona and Christensen,¹⁵ and of the “model-solid theory” of Van de Walle and Martin.⁵ Not surprisingly, these calculations have led to rather diverging conclusions. For example, for the deformation potential of the valence-band maximum (VBM) of Si, Blacha, Presting, and Cardona⁴ obtain -10.2 , Verges *et al.*¹⁴ obtain -7.9 , Cardona and Christensen¹⁵ obtain -1.6 (screened deformation potential), and Van de Walle and Martin⁵ obtain $+2.5$ eV. The reason for this uncertainty can be traced back to the difficulty of defining a reference energy which does not depend on macroscopic strain. Recently, promising *ab initio* calculations based on the pseudopotential method have been proposed^{5,6} which do not rely on the existence of any strain-independent reference energy.

In this work we present an approach to the calculation of ADP's based on *ab initio* all-electron methods. No assumption is made about the existence of a strain-independent reference energy. The ADP of a given state is obtained from the band offset at the interface between a compressed and an expanded region of the same material; the core levels are used to calculate the band offset of the compressed-expanded homojunction, but not as “absolute” reference levels. We present results for the ADP's of a simple metal (Al), a semiconductor (Si), and an insulator (NaCl) under uniaxial strain. We find that (i) the ADP of the valence-band maximum is positive in Si, as predicted by the simple tight-binding model, but it is negative in NaCl, in conflict with tight binding; (ii) most conduction-band states have negative ADP's, in agreement with the tight-binding picture, but some states have positive ADP's; (iii) the ADP's of core levels are small but not negligible, so that core levels cannot be used as “absolute” energy levels in the presence of strain.

II. METHOD

The ADP of the band n at wave vector \mathbf{k} of a periodic solid is defined as

$$D_{n,\mathbf{k}}^{\alpha,\beta} = \frac{\partial E_{n,\mathbf{k}}}{\partial \varepsilon_{\alpha,\beta}}, \quad (1)$$

where $E_{n,\mathbf{k}}$ is the energy of the (n, \mathbf{k}) single-particle state and $\varepsilon_{\alpha,\beta}$ is the (α, β) component of the strain tensor ε . We will assume that the \mathbf{k} points in the Brillouin zone move with strain according to the formula $\mathbf{k} \rightarrow (1 + \varepsilon)^{-1} \mathbf{k}$. In this way, high-symmetry \mathbf{k} points on the surface of the Brillouin zone remain on the Brillouin-zone edge when strain is applied. In the following, we will restrict ourselves to uniaxial strain: for a given normalized direction $\hat{\mathbf{n}}$, the strain tensor ε will then depend on a single parameter ε , i.e., $\varepsilon_{\alpha,\beta} = \varepsilon \hat{n}_\alpha \hat{n}_\beta$. Note that uniaxial strain is accompanied by a volume change $\Delta\Omega$ such that $\Delta\Omega/\Omega = \text{Tr} \varepsilon = \varepsilon$. The ADP of the state (n, \mathbf{k}) can be expressed^{5,6} in terms of the band offset $\Delta E_{n,\mathbf{k}}^{(+/-)}$ at the interface between two regions of the same material, subject to different strain conditions: one with compressive ($\varepsilon < 0$) uniaxial strain and the other with tensile ($\varepsilon > 0$) uniaxial strain. For a sufficiently small strain difference $\Delta\varepsilon$ we have

$$D_{n,\mathbf{k}} \simeq \frac{\Delta E_{n,\mathbf{k}}^{(+/-)}}{\Delta\varepsilon}. \quad (2)$$

If the value of $|\varepsilon|$ is the same on both sides of the interface, Eq. (2) is correct to second order in $\Delta\varepsilon$. The homojunction band offset $\Delta E_{n,\mathbf{k}}^{(+/-)}$ can be calculated in a way which parallels the calculation of the band offset at heterojunction interfaces.¹⁶ Our basic assumption is that the energy difference $E_{n,\mathbf{k}} - E_c$ between the state (n, \mathbf{k}) and the core level c is the same in the compressed pure material *and* in the compressed region of the homojunction (see Fig. 1). A similar relation is assumed for the expanded material. Denoting by E_c^- (E_c^+) the energy of the core level c in the compressed (expanded) material, we can write (see Fig. 1)

$$\Delta E_{n,\mathbf{k}}^{(+/-)} = (E_{n,\mathbf{k}}^+ - E_c^+) - (E_{n,\mathbf{k}}^- - E_c^-) + \Delta E_c^{(+/-)}. \quad (3)$$

The first two terms in parentheses in Eq. (3) give the energy difference $E_{n,\mathbf{k}} - E_c$ in the expanded and compressed material, respectively. They are calculated here self-

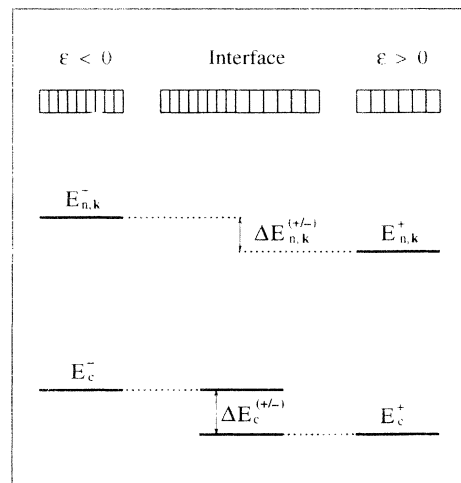


FIG. 1. A schematic diagram of the energy levels involved in the calculation of absolute deformation potentials (see text for the explanation of symbols).

TABLE I. Absolute deformation potential of the valence-band maximum of Si for (001), (110), and (111) uniaxial strain. The VBM of Si consists of three degenerate states, which are split by uniaxial strain; the values reported in the table refer to the averages of the deformation potentials of these three states. All values are in eV.

	(001)	(110)	(111)
Present work	1.5	1.7	2.7
Resta, Colombo, and Baroni ^a	1.5	2.6	3.0
Van de Walle and Martin ^b	1.3	0.4	3.1
Experiment ^c	1.8±0.7		

^aReference 6.

^bReference 5.

^cReference 9.

consistently using the linearized augmented plane wave (LAPW) method¹⁷ in the local-density approximation.¹⁸ The core states are calculated fully relativistically, while the valence states are treated semirelativistically. The last term in Eq. (3) accounts for the lineup of the core levels at the interface between the compressed and the expanded material. This quantity is obtained from a self-consistent LAPW calculation for a compressed-expanded superlattice. We have checked the dependence of the ADP's obtained from Eqs. (2) and (3) on (i) the choice of the core level c , (ii) the strain difference $\Delta\epsilon$, and (iii) the

superlattice period n . We have found that (i) for deep core levels (i.e., $1s$, $2s$, and $2p$) the calculated ADP is independent of the choice of the core level c in Eq. (3) to within 0.05 eV; (ii) the ADP is independent of the choice of ϵ up to at least $\Delta\epsilon=0.02$; this implies that in this strain interval the dependence of $\Delta E_{n,k}^{(+/-)}$ is at most quadratic in $\Delta\epsilon$; (iii) for the (001) direction the ADP's of Si change by less than 0.1 eV in going from $n=8$ to $n=12$ ML's; for the (110) direction, however, the convergence with the number of monolayers is expected to be slower.¹⁹ While *relative* deformation potentials are independent of the strain direction (within our numerical accuracy), *absolute* deformation potentials depend, through the third term in Eq. (3), on the strain direction \hat{n} . This is due to the nonanalyticity of the long-wavelength expansion of the electrostatic potential induced by an atomic displacement.^{6,20}

III. RESULTS AND DISCUSSION

To demonstrate our method, we have calculated the ADP of the VBM of Si for different directions of uniaxial strain. We have used the calculated minimum-energy structure of Si (diamond lattice with lattice parameter $a_{eq}=5.41$ Å) as the zero-strain configuration. When strain is applied, the cell-internal atomic positions are determined by the internal-strain parameter ζ ; we have

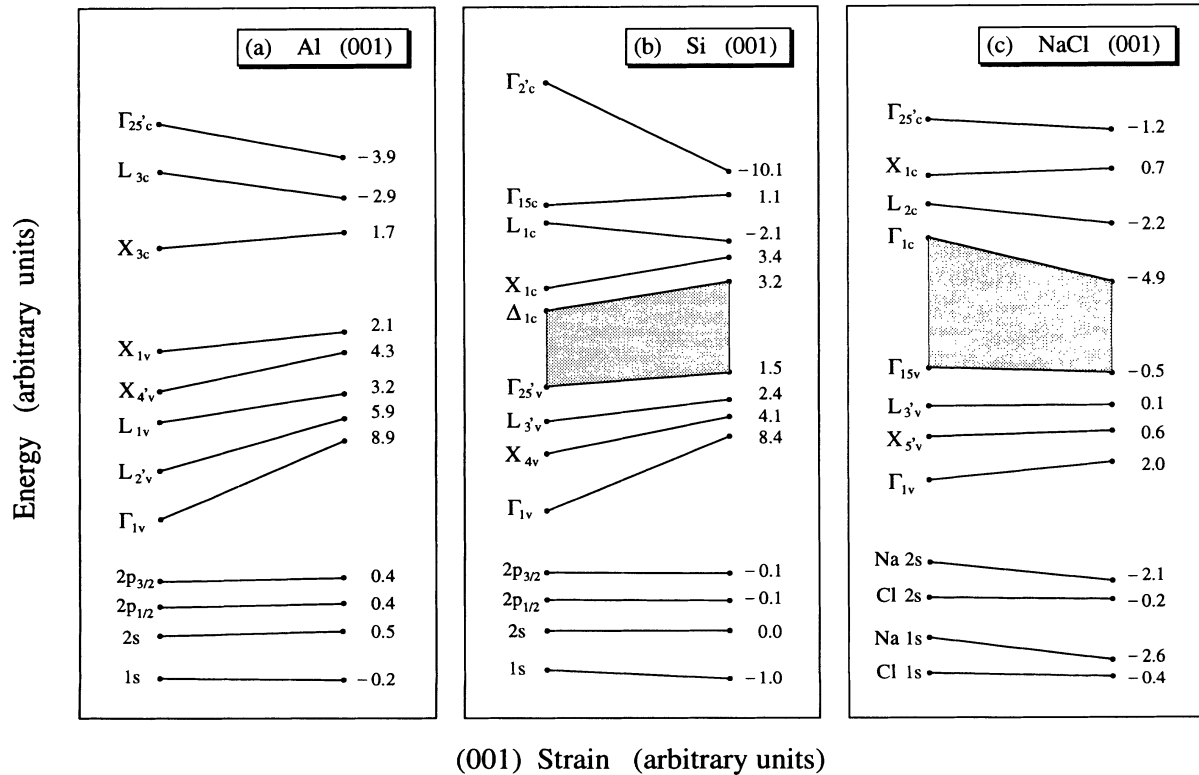


FIG. 2. Absolute deformation potentials of a few states of (a) Al, (b) Si, and (c) NaCl for (001) uniaxial strain. The labeling of the states (on the left) corresponds to the unstrained crystals; the corresponding absolute deformation potentials (on the right) are given in eV. For degenerate states, the crystal-field average of the ADP's is shown. The shaded areas separate valence from conduction states.

used the value $\zeta=0.53$ obtained by Nielsen and Martin.²¹ The crystal-field averaged ADP of the valence-band maximum (sometimes denoted by a_v) is compared in Table I with the previous *ab initio* calculations of Van de Walle and Martin⁵ and of Resta, Colombo and Baroni,⁶ and with the experimental results of Cargill, Angilello, and Kavanagh.⁹ As we can see, the agreement is quite good for the (001) and (111) directions. In the case of the (110) direction, our result is probably affected by the slow convergence of the ADP with respect to the dimension of the supercell.¹⁹

The ADP's of a simple metal (Al), a semiconductor (Si), and an insulator (NaCl) are shown in Fig. 2 for (001) uniaxial strain. Note that the (001) interface of the compressed-expanded homojunction of NaCl is nonpolar; therefore, the displacement of the interfacial atomic planes in the direction of the strain does not change the ADP.⁶ Although the energy gaps shown in Fig. 2 are not to scale, the slopes of the lines (absolute deformation potentials) are plotted to scale, so that the ADP's of different states and different materials can be directly compared. The following conclusions can be drawn from Fig. 2.

(i) The ADP's of core levels are small, but not negligible. Therefore, core levels cannot be considered as "absolute" reference energies when strain is present. However, core levels can be used as *approximate* reference energies when the magnitude of the strain is sufficiently small, so that the core-level deformation effect is negligible.¹⁶ The latter approach has been used, for example, by Shih and Spicer²² to study the valence-band offset of HgTe-CdTe alloys.

(ii) Different core levels have different ADP's. This implies that the *relative* deformation potentials between core levels do not vanish. For example, the relative deformation potential between Si 1s and Si 2s is ~ 1 eV. This seems to be in contrast with the measurements of Grant *et al.*,²³ who find that the core-level energy difference between Ge 3s and Ge 3d in pure Ge and between As 3d and Ga 3d in GaAs is independent of strain. We note, however, that core levels having the same principal quantum number in the same atom [e.g., Al 2s, Al 2p_{1/2}, and Al 2p_{3/2} in Fig. 2(a), Si 2s, Si 2p_{1/2}, and Si 2p_{3/2} in Fig. 2(b)] have similar ADP's, so their relative deformation potentials almost vanish. This could explain the results of Grant *et al.* for intra-atomic core-level deformation potentials.

(iii) While the ADP of the valence-band minimum (Γ_{1v}) is large and positive, the ADP of higher valence-band states is smaller, and can even become negative. For example, the ADP of the VBM of Si ($\Gamma_{25'v}$) is slightly *positive*, but the ADP of the VBM of NaCl (Γ_{15v}) is *negative*. This different behavior can be explained qualitatively in terms of the interplay between the *bonding-energy* contribution and the *bandwidth* contribution to the ADP (see Fig. 3). The bonding energy (i.e., the energy of the bonding state between two atoms, corresponding roughly to the center of the occupied bands) becomes less negative when the volume increases, because the bonding-antibonding splitting decreases when the atoms move apart. Thus, the bonding-energy contribution to

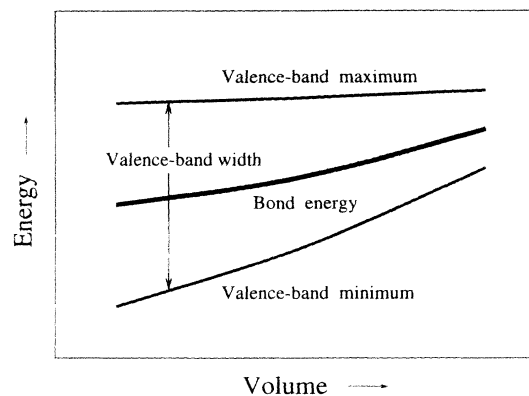


FIG. 3. Behavior of the valence-band edges as a function of volume. Note that while the valence-band width decreases with volume, the bond energy increases with volume. As a result, the valence-band maximum has a smaller ADP than the valence-band minimum.

the ADP of the valence-band states has a positive sign. On the other hand, the valence-band width always decreases with volume, because the overlap between atomic orbitals, and therefore the band dispersion around the bonding energy, are reduced when the atoms move apart. In the case of the valence-band minimum, these two effects add up to produce a large, positive ADP. In the case of higher valence-band states (e.g., the valence-band maximum), the two contributions have opposite sign and lead to a partial cancellation. While in covalent systems (e.g., Si) the bonding contribution is predominant and the ADP of the VBM is positive, in ionic compounds (e.g., NaCl) the bonding effect is smaller, and the ADP of the VBM becomes negative.

(iv) Most conduction-band states have negative ADP's, in agreement with a simple tight-binding model. However, some conduction states, such as X_{3c} in Al, Δ_{1c} , X_{1c} , and Γ_{15c} in Si, and X_{1c} in NaCl, have positive ADP's. This implies that the (indirect) band gap of Si increases when volume increases while the (direct) band gap of NaCl *decreases* when volume increases.

In conclusion, we have presented a method for calculating *absolute* deformation potentials using *ab initio* all-electron methods. The results for Si compare well with previous calculations and experimental measurements. We have discussed some results for the ADP's of Al, Si, and NaCl under uniaxial strain. We have shown that (i) the ADP of the VBM is positive in covalent materials but can become negative in ionic materials, in conflict with the simple tight-binding model; (ii) while most conduction states have negative ADP, in agreement with the tight-binding picture, some have positive ADP; (iii) the ADP of core levels is small but not negligible.

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- ¹J. Bardeen and W. Shockley, *Phys. Rev.* **80**, 72 (1950).
- ²R. Resta, *Phys. Rev. B* **44**, 11 035 (1991).
- ³G. Martinez, in *Handbook of Semiconductors*, edited by M. Balkanski (North-Holland, Amsterdam, 1980), p. 181.
- ⁴A. Blacha, H. Presting, and M. Cardona, *Phys. Status Solidi B* **126**, 11 (1984).
- ⁵C. G. Van de Walle and R. M. Martin, *Phys. Rev. Lett.* **62**, 2028 (1989).
- ⁶R. Resta, L. Colombo, and S. Baroni, *Phys. Rev. B* **41**, 12 358 (1990).
- ⁷S. Adachi, *Physical Properties of III-V Semiconductor Compounds* (Wiley, New York, 1992), p. 127.
- ⁸D. D. Nolte, W. Walukiewicz, and E. E. Haller, *Phys. Rev. Lett.* **59**, 501 (1987); *Phys. Rev. B* **36**, 9392 (1987).
- ⁹G. S. Cargill, J. Angilello, and K. L. Kavanagh, *Phys. Rev. Lett.* **61**, 1748 (1988).
- ¹⁰I. Yokota, *J. Phys. Soc. Jpn.* **19**, 1487 (1964).
- ¹¹W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).
- ¹²P. Pfeffer, I. Gorczyca, and W. Zawadzki, *Solid State Commun.* **51**, 179 (1984); I. Gorczyca, *Phys. Status Solidi B* **108**, 205 (1981).
- ¹³C. Priester, G. Allan, and M. Lannoo, *Phys. Rev. B* **38**, 13 451 (1988); D. Bertho, D. Boiron, A. Simon, C. Jouanin, and C. Priester, *ibid.* **44**, 6118 (1991).
- ¹⁴J.A. Verges, D. Glötzel, M. Cardona, and O. K. Andersen, *Phys. Status Solidi B* **113**, 519 (1982).
- ¹⁵M. Cardona and N. E. Christensen, *Phys. Rev. B* **35**, 6182 (1987).
- ¹⁶S.-H. Wei and A. Zunger, *Phys. Rev. Lett.* **59**, 144 (1987).
- ¹⁷S.-H. Wei and H. Krakauer, *Phys. Rev. Lett.* **55**, 1200 (1985), and references therein.
- ¹⁸D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980); J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ¹⁹N. E. Christensen, S.-H. Wei, and A. Zunger, *Phys. Rev. B* **40**, 1642 (1989).
- ²⁰P. Lawaetz, *Phys. Rev.* **183**, 730 (1969).
- ²¹O. H. Nielsen and R. M. Martin, *Phys. Rev. B* **32**, 3792 (1985).
- ²²C. K. Shih and W. E. Spicer, *Phys. Rev. Lett.* **58**, 2594 (1987).
- ²³R. W. Grant, J. R. Waldrop, E. A. Kraut, and W. A. Harrison, *J. Vac. Sci. Technol. B* **8**, 736 (1990).

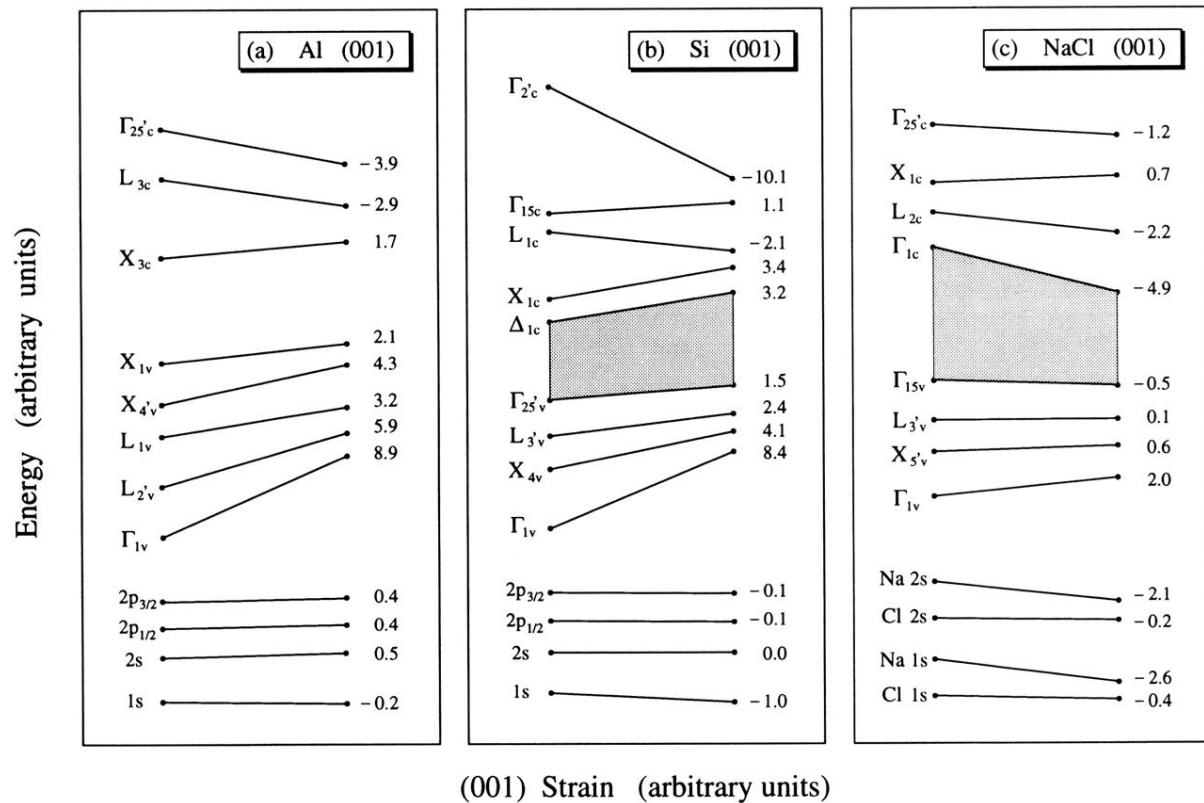


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