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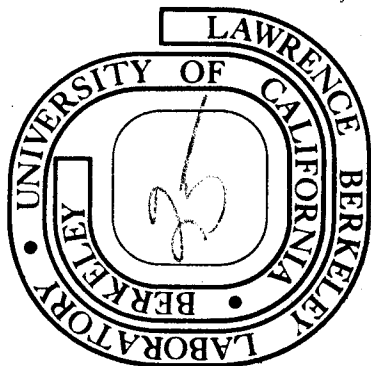
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Electronic Structure of Silicon*

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Abstract

It is shown that a purely local pseudopotential calculation is able to accurately reproduce the major optical gaps and cyclotron masses. However, deviations from the experimental results become manifest in photoemission and x-ray charge density results as we extend our calculations to the lower valence bands. These deviations indicate the necessity of an energy-dependent nonlocal s-well potential, a conclusion which is also supported by an analysis of the Heine-Abarenkov pseudopotential scheme. A detailed comparison is made between experimental results obtained from optical, photoemission, x-ray and cyclotron resonance measurements, and the results of both the local calculation and an energy-dependent nonlocal calculation. Yang and Coppens recent determination of the valence charge density in silicon makes it possible to assess the accuracy of the pseudocharge densities for the first time.

I. Introduction

In spite of the fact that several local empirical pseudopotential calculations exist for silicon,¹⁻⁴ a thorough comparison of the results of such a calculation with the abundant amount of experimental data available for silicon has yet to be performed. Most authors have been primarily concerned with an analysis of the optical spectrum, and have usually not compared their results to the cyclotron mass data available, or to the more recent results of photoemission measurements. This situation is an unfavorable one, for it leaves open the possibility that while the local, empirically fit, pseudopotential may be able to accurately obtain the optical gaps, it may fail to give equally good results when compared to other experimental measurements. The results of recent x-ray and ultraviolet photoemission spectroscopy (XPS and UPS)^{5,6} will serve to illustrate the point. Although optical spectra (in good agreement with experiment) have been calculated for numerous diamond and zincblende semiconductors based upon a local pseudopotential,⁷ when these local calculations are extended to yield the valence band electronic density of states the results are far from satisfactory.^{6,8,9} Therefore, in this paper it will be of primary import to compare the results of our calculations to a wide spectrum of experimental measurements.

In particular, we will be interested in the accuracy of the local pseudopotential compared with a nonlocal pseudopotential calculation, for such nonlocal pseudopotential computations have resulted in spectacularly improved band

structures.¹⁰⁻¹⁴ Recent calculations, for example, on Ge and GaAs have been capable of obtaining the major optical gaps to within ~ 0.08 eV,^{12,13} and have shown that local pseudopotential calculations can result in inaccurate band topologies.¹² Moreover, improved densities of states in the nonlocal calculations were also obtained. In this context energy dependent pseudopotentials have also been used;^{8,9} however, a nonlocal, energy dependent pseudopotential has yet to be examined. Hence, it would be of some value to ascertain the importance of nonlocal and energy dependent corrections in the case of silicon.

Further, silicon which has been the subject of many theoretical calculations^{1-4,15-26} has not been as well understood as some of the other diamond and zincblende semiconductors. Several examples of this situation come to mind. One is the band ordering of the lower conduction bands at Γ . Unlike germanium in which it is well accepted that Γ_2 lies below Γ_{15} , in silicon the placement of Γ_2 has been, until quite recently, a matter of some controversy. In most of the early band structure calculations for silicon the Γ_2 conduction band was found to lie above the Γ_{15} conduction band. However, some later calculations have found the reverse ordering.^{21,24,25} Another transition which has been of some consternation is the determination of the first direct optical transition. Pseudopotential calculations have placed the first direct transition at Γ or L, but experimentally the situation here is unclear in contrast to other semiconductors

(e.g. germanium). Finally with respect to a more general viewpoint, there is a recent calculation on silicon by Kane.²² In Kane's calculation a Heine-Abarenkov type core-valence interaction fitted to spectroscopic data was used. This ion potential was then screened by a parametrization of the valence-valence electron interaction. Kane found that the major optical gaps and the cyclotron masses were incompatible within his empirical fitting scheme. If masses were fit to experiment, then the optical gaps were in error by $\sim 0.5-0.7$ eV. This was attributed to need of a nonlocal exchange potential. Therefore, it would be of some interest to determine whether a purely local pseudopotential would experience the same difficulty.

Finally, we note that several new and important experimental techniques have been developed which have not been incorporated into empirical calculations. Besides the recent photoemission data of XPS and UPS, there is the recent experimental work of Aspnes and Studna involving the use of low field electroreflectance.^{27,28} This is a powerful technique which has been able to resolve the E_0 and $E_0 + \Delta_0$ structure in silicon, and unequivocally determine the correct band ordering of Γ_2' and Γ_{15} .²⁷ (Γ_2' is higher than Γ_{15} .)

In addition there is the recent work of Yang and Coppens²⁹ in which they were able to determine a very accurate valence charge density for silicon through the use of recent precise x-ray experiments.⁷⁰ This calculation is quite significant as there has been much interest using the

pseudocharge density in calculating the Slater exchange term and achieving self-consistency,⁴ particularly for the purpose of doing surface calculations.³⁰

It is for these reasons, then, that we feel a new look at silicon via the empirical pseudopotential method (EPM) should prove both interesting and rewarding.

We intend to examine silicon by the following methods. We shall use a purely local pseudopotential approach and analyze the results of the calculation by means of a comparison with the experimental results of optical and photoemission measurements along with the experimental cyclotron resonance masses and the recent valence charge density determination by Yang and Coppens. To examine the effects of nonlocality we shall then repeat the calculation using a nonlocal pseudopotential based on examination of a Heine-Abarenkov potential for Si.⁺³

The paper is outlined as follows.

In section II we shall discuss the basic pseudopotential scheme. The local (or on the sphere) approximation will be discussed and examined. We shall examine the Heine-Abarenkov potential and its implications for the case of silicon, and we shall discuss a recent self-consistent calculation done on silicon by Appelbaum and Hamann.⁴

In section III the methods used to calculate the theoretically determined band structure, photoemission results, reflectivity, cyclotron masses, and pseudocharge densities will be discussed.

In section IV we will discuss the experimental results and compare them to the theoretical results. In particular, we shall be interested in comparing the local calculation to the nonlocal calculation.

Finally, in section V we shall summarize our conclusions and results.

II. The Potential

The fundamental concept involved in any pseudopotential calculation is that the ion core can be omitted or "pseudized away." Computationally this is crucial for it means that the deep ion potential has been removed and a simple plane wave basis will yield rapid convergence. There are many ways of arriving at this result,⁷ but one of the most straightforward is due to Phillips and Kleinman.³¹

Simply stated, we may rewrite the one-electron hamiltonian as

$$\mathcal{H} = p^2/2m + V_p(\underline{r}) \quad (1)$$

where

$$V_p(\underline{r}) = v(\underline{r}) + \sum_t (E_k - E_t) |b_t\rangle \langle b_t| \quad (2)$$

$V(\underline{r})$ is the true crystal potential and $|b_t\rangle$ is a core state with eigenvalue E_t . This new potential has the same eigenvalues, E_k , but because the real potential has been cancelled in the core region by the second term in (2),³² the resulting eigenfunctions of (1) are smoothly varying in the core region in contrast to the true eigenfunctions. While this permits

the pseudoeigenfunctions to be expressed in terms of plane waves, the pseudopotential in (2) is dependent not only on the energy eigenvalues, E_k , but on the l -angular momentum components present in the core states.

In spite of the fact that [2] is inherently nonlocal and energy dependent much of the optical spectra for semiconductors can be explained by ignoring this fact.⁷ If we assume the pseudopotential is a simple function of position, then we may take,

$$V_p(\underline{r}) = \sum_{\underline{G}} V(\underline{G}) \exp(i\underline{G} \cdot \underline{r}) \quad (3)$$

where

$$V(\underline{G}) = V^a(\underline{G}) \cos(\underline{G} \cdot \underline{\tau}) \quad (4)$$

$$\underline{\tau} = a/8(111)$$

(a being the lattice constant).

The $V^a(\underline{G})$, or atomic form factors can be defined by

$$V^a(\underline{G}) \equiv \frac{2}{\Omega_c} \int V_p^a(\underline{r}) \exp(i\underline{G} \cdot \underline{r}) d^3r \quad (5)$$

where we have taken the crystal potential to be a sum of atomic pseudopotentials, V_p^a . Ω_c is the unit cell volume.

The local empirical pseudopotential method (EPM), in fact, is based upon the above simplification. If we then take the above pseudopotentials to be spherical so that $V_p^a(\underline{r}) = V_p^a(|\underline{r}|)$, this means the form factors depend upon the magnitude of \underline{G} , with a corresponding reduction in the number of required form factors. These form factors are the empirically determined parameters fit to experimental data such as optical gaps.

The validity of this approach rests upon two arguments. They are as follows: 1) $E_k \gg E_t$ so that $(E_k - E_t)$ can be replaced by a mean energy in (2) such as E_F (providing one is interested in only a limited energy range) and 2) the cancellation is equal for all ℓ (or at least the ℓ -components of the valence wavefunctions which are significant). Until recently (e.g. recent comparisons to XPS and UPS data), these assumptions have been found to be satisfactory.

In order to better understand the possible failings of such a local approach we now examine a model pseudopotential devised by Heine and Abarenkov.³³ In this model they assume that the positive ion pseudopotential may be written as

$$v_{\ell}^a(r) = \begin{cases} -A_{\ell}(E) & r \leq R_m \\ -Ze^2/r & r \geq R_m \end{cases} \quad (6)$$

and

$$v_{NL}^a(r) = \sum_{\ell=0}^{\infty} v_{\ell}^a(r) P_{\ell}$$

where P_{ℓ} projects out the ℓ th angular momentum component of the wavefunction. R_m is the model radius, which is taken to be equal for all ℓ . For convenience, it is assumed that $A_{\ell}(\ell \geq 2) = A_2$, this can be done in the Si case as the higher ℓ values are negligible in the region of interest.

To determine $A_{\ell}(E)$, after selecting a value for R_m , the spectroscopic term values are examined for an electron in the atomic ion core potential (e.g. Si^{+3}). The well depths

A_ℓ are then adjusted to reproduce these spectroscopic terms; the behavior for the first three A_ℓ is shown in Fig. 1. One can observe that the $\ell = 0$ and $\ell = 2$ well depths are quite dependent on the energy of the spectroscopic term to which it is fit. This should be of particular importance if one wishes to use the potential over a large energy range. To obtain the values of $A_\ell(E)$ for a particular energy not corresponding to a term value, an extrapolation of the A_ℓ to the desired energy is required. For this purpose, as we have indicated in the figure, a linear interpolation is used, a procedure which has been justified, at least for the $\ell = 0,1$ cases by Shaw.³⁴

In order to reduce this nonlocal potential to a local form, one can evaluate it at an appropriate mean energy such as E_F and use the "on-the-sphere approximation."⁷ This well-known approximation converts the nonlocal potential to a local one by means of the following

$$V^a(q) = \langle k_F | V_{NL}^a(E, r) | k_F + q \rangle$$

where

$$E = E_F, \quad |k_F| = |k_F + q| \quad |q| \leq 2k_F$$

$$q_{\parallel} = -k_F \quad |q| \geq 2k_F$$

We now have a local ionic potential; this potential must now be screened appropriately before it can be used in calculating the electronic properties of a solid such as an optical spectrum.³⁵

An examination of Figure 1 indicates quite clearly where the assumptions of a local potential may fail in silicon. While $A_1 \approx A_2$ at E_F so p-d nonlocality might be ignored, the fact that A_0 is not equal to A_1 and A_2 means that the s-nonlocality probably cannot be ignored. Indeed, if one extrapolates a rydberg away from E_F as might be the case in attempting to fit photoemission data the relative value of A_0 to A_1 (or A_2) increases by a factor of two or more.

From a pseudopotential view point the s-potential is the most "favorable" in that it is cancelled to a greater extent than either the p- or d- potentials. One, therefore, might like to take the approach of using a local potential along with p- and d- corrections, rather than an s-correction as we shall do. The reason for considering only the s-well is basically computational. Since the s-well is so energy dependent relative to both the p- and d-wells we would have to include energy dependence for both, resulting in four additional parameters rather than two, if nonlocality is restricted to the s-well alone.

We may add here that while it is true $A_1(E_F) \approx A_2(E_F)$, the d-well, as the s-well, is quite energy dependent. However, unlike the s-well which affects the bottom valence and lower conduction bands (a span of ~15 eV), the d-well has influence only on the upper conduction bands or a rather

limited energy range (at least for the region of interest in our calculations).

Finally, with respect to Fig. 1, we note that a possible reason for the relatively better cancellation of the s-potential can be understood in terms of the core states.³⁶ From (2) we observe that the true silicon crystal potential is cancelled by the 1s, 2s and 2p core states. Because there are two s-states which serve to cancel the core potential, but only one p-state one might expect a better cancellation for the s-potential which is the case. Similarly, the d-well is uncanceled by any core states, resulting in a more attractive well depth than either the s- or p-wells. The role of d-nonlocality and its role in other semiconductors, e.g. Ge and GaAs, where it has proved to be of significant importance will be discussed in our concluding remarks.

While it would be desirable to use a model potential with no empirical adjustments, such a calculation would be most difficult. For example, there is no reliable determination of E_F , the energy relative to a free ion of an electron at the fermi level, ϵ_F , in a solid where ϵ_F is on an absolute energy scale.³⁵ Estimates of this value can be quite different. Kane, using an adjusted Heine-Abarenkov type calculation¹⁶ used a value of -2.3 Ryd on the scale of Fig. 2 to evaluate the $A_l(E)$, while Animalu and Heine used -2.93 Ryd. Such a difference can result in a very significant change in the resulting band structure as we shall discuss shortly. Another difficulty is in the screening of such a

potential. While the use of a Slater exchange term seems to be a well accepted technique in ab initio calculations, Kane has noted that such an approximation is questionable, and he has suggested the use of a nonlocal screening potential.²⁶ In any event, we have performed a nonlocal type calculation using a Heine-Abarenkov type core potential which we have screened, self consistently, in the manner of Appelbaum and Hamann.⁴ This involved the use of the pseudocharge density to calculate the Hartree potential and Slater exchange terms. We find that a very small change in the core potential can result in a rather large change in the resulting band structure. For example, a 1% change in the core potential can result in a 0.5 eV change in the band structure. This means that some sort of empirical adjustment is almost certainly required.

In any type of empirical calculation the question arises of where adjustments should be made. Kane, as mentioned previously, has parameterized the valence-valence interaction, and recently Appelbaum and Hamman have parameterized the core potential which they then screen in a self-consistent manner. Traditionally, however, the EPM approach has fit the first few fourier coefficients of the total potential. In fact, it has been observed that usually only three form factors per each type of atom are needed for a satisfactory fit.⁷ Such a truncation is made so that the $V(G)$ are equated to zero for $G^2 > (2\pi/a)^2$.

Contrary to Appelbaum and Hamann's comments⁴ that such a truncation appears to have been performed in arbitrary fashion, there are some very good reasons for using the aforementioned cutoff. First, from the practical point of data fitting, Kane has shown that the higher $V(G)$'s become linearly dependent.¹⁶ For the specific case of silicon he found that by increasing the number of nonzero $V(G)$'s an improved fit to the band structure was not obtained. In fact Kane noted that one has, loosely speaking, between two and three truly independent parameters. In addition, Cohen and Heine⁷ have pointed out that the higher coefficients can be "absorbed" into the lower coefficients by a partial diagonalization of selected off diagonal matrix elements. In particular it is possible to transform to zero all $V(G)$ beyond some cutoff q_t ,⁷ so in this sense there is no loss of generality in using a truncated $V(G)$. Finally keeping $V(G)$'s beyond some reasonable cutoff such as $q_t = 3k_F$ (the value suggested by Cohen and Heine) and attaching physical meaning to them goes against the philosophy of the pseudopotential approach. This is a consequence of the fact that the higher coefficients "test out" the core region of the pseudopotential. It is this region, however, which has been pseudized away, and this process we know is an arbitrary one.⁷ In fact, we have performed calculations in which the $V(G)$ were not truncated until $q_t^2 = (2\pi/a)^2 25$, and we find, as one would expect, that nearly identical band structures can be obtained. The only observable difference obtained was that

the pseudocharge density in the core region was slightly altered, but we would not expect the results to be accurate in this region in any event.

Another point to consider is the possibility that such a truncated potential might not be self-consistent with the pseudocharge density. This, however, is not the case, for the pseudocharge density is very smooth with the fourier coefficients of the charge density falling off quite rapidly. And, since the screening potential involves even more smoothly varying functions, e.g. $[\rho(r)]^{1/3}$, this is not a problem.³⁷

We may mention in this sense that the meaning of achieving a self-consistent potential with respect to an adjustable core potential is not clear, as any total potential can be made self-consistent to some type of core potential. Only if the core potential is accurately known, e.g. through a fitting to spectroscopic term values, and not radically altered in an empirical fitting scheme can self-consistency truly have significance. Hence, within this framework most of the present local pseudopotential calculations for silicon involving a truncated fourier expansion of the potential, but whose form factors are close to a model potential such as Heine and Animalu's,³⁵ are probably just as "self-consistent" as the recent Appelbaum and Hamman calculation.⁴

Therefore, we propose to follow the usual local EPM procedure, using three form factors, near the Heine-Animalu screened results, and make empirical refinements. Then, to incorporate what appears to be the most important nonlocal

correction for silicon we will use an energy dependent s-well and, again, make empirical adjustments.

III. Methods of Calculation

The band structure is calculated as in reference 2. The potential is expanded as in (3), with the form factors listed, along with the lattice constant in Table I. These form factors are fairly close to the Heine-Animalu screened potential³⁵ except for $V(\sqrt{3})$; this is not surprising since we would expect a difference to arise from the fact that the Heine-Animalu potential was screened with a free electron dielectric function. Similar conclusions have been reached by other authors.^{38,12} The eigenvalues and eigenvectors are found by solving the secular equation,

$$\det | \mathcal{H}_{\underline{G}, \underline{G}'}(\underline{k}) - E(\underline{k}) \delta_{\underline{G}, \underline{G}'} | = 0 \quad (7)$$

where for $\mathcal{H}_{\underline{G}, \underline{G}'}$, in the local approximation, we use

$$\mathcal{H}_{\underline{G}, \underline{G}'}^L = \frac{\hbar^2}{2m} (\underline{k} + \underline{G})^2 \delta_{\underline{G}, \underline{G}'} + V(|\underline{G} - \underline{G}'|) \cos((\underline{G} - \underline{G}') \cdot \underline{\tau})$$

The matrix site was chosen so that at Γ , 27 plane waves were treated exactly with another 86 treated approximately via Löwdin perturbation theory.¹ Equation (7) was solved over a grid of 308 k-points in the irreducible part of the Brillouin zone.

We then repeat the calculation using a nonlocal potential of the form,

$$V_{NL}^a(|\underline{r}|) = V_L^a(|\underline{r}|) + \mathcal{Q}_0(E) \theta(|\underline{R}_M - \underline{r}|) \mathcal{P}_0 \quad (8)$$

$$\theta(x) = \begin{cases} 1 & x \geq 0 \\ 0 & x < 0 \end{cases}$$

where it is assumed, as discussed before, that the only significant nonlocal correction is from an s-well. A first approximation to the size of $Q_0(E_F)$ can be obtained by an inspection of Fig. 1 under the usual assumption that the screening can be treated by a local potential, and included in the local term of (8). It has been suggested that a proper (i.e. nonlocal) screening procedure might reduce the nonlocality of the ion potential.²² In such a case we might expect our nonlocal correction to be reduced from the value suggested by inspection of the Heine-Abarenkov core potential. We note, as before, that $A_1(E_F) \approx A_2(E_F)$, so that one expects $Q_0(E_F) \approx A_{1,2}(E_F) - A_0(E_F)$. Likewise the value of $\partial Q_0/\partial E$ can also be approximated from Fig. 1 by $\partial A_0/\partial E$. The resulting empirical values for Q_0 , $\partial Q_0/\partial E$ and the local form factors are given in Table I. R_m was taken to be that of Heine and Animalu's result (i.e. $R_m = 1.06 A^0$).

The eigenvalues are still given by (7), but now we have,

$$\mathcal{H}_{\underline{G}, \underline{G}'}(E, \underline{k}) = \mathcal{H}_{\underline{G}', \underline{G}}(\underline{k}) + \frac{8\pi}{\Omega_c} Q_0(E) I(K, K') \quad (9)$$

where $K = |\underline{k} + \underline{G}|$, $K' = |\underline{k} + \underline{G}'|$ and

$$I(K=K') = \frac{1}{2} R_m^3 \{ [j_0(KR_m)]^2 - j_{-1}(KR_m) j_1(KR_m) \}$$

$$I(K \neq K') = \frac{R_m^2}{K^2 - K'^2} [K j_1(KR_m) j_0(KR_m) - K' j_1(K'R_m) j_0(KR_m)] \quad (10)$$

The above derivation is from ref. 7 in which the definition of the usual spherical bessel functions, j_n , are also given.

The inclusion of the required energy dependence of $Q_0(E)$ can be accomplished in a simple, but approximate, manner.

We take, for the matrix element involving K and K' ,

$$a_0(E) \approx a_0(E_F) + \frac{\partial a_0}{\partial E} \{ [E^0(K)E^0(K')]^{1/2} - E^0(K_F) \} \quad (11)$$

where $E^0(K) = \hbar^2 K^2 / 2m$ and $K_F = (6\pi^2 z / \Omega_c)^{1/3}$.

This form has the advantage in that it accurately simulates the true energy dependence,³⁹ and results in a considerable reduction of computing time compared with other techniques.⁸

It is possible also to mimic the energy dependence through the use of an effective mass parameter,^{7,35} a point which will be discussed in more detail in our concluding remarks.

The same grid used in the local calculation was used for the nonlocal calculation. However, in order to insure good convergence, at Γ , 59 plane waves were now treated exactly, and another 87 included by Löwdin perturbation theory.⁴⁰ In both cases, convergence should be good to within ~ 0.05 eV.

Once (7) has been solved throughout the Brillouin zone, one can then proceed to calculate the electronic density of states and optical spectra. The density of states is given by

$$N(E) = \frac{1}{N} \sum_{\tilde{k}} \sum_n \delta(E - E_n(\tilde{k})) \quad (12)$$

where the sum is over wave vector and band index. N is the number of unit cells, so that if $E(k)$ is in eV, then $N(E)$ is in units of (states/eV-atom). The required sum in (12) was evaluated by a technique due to Gilat and Raubenheimer.⁴¹ The energy gradients required in this method were calculated from $\tilde{k} \cdot \tilde{p}$ perturbation theory.

The optical spectrum can be calculated as follows. First the imaginary part of the dielectric function is evaluated using the expression,

$$\epsilon_2(\omega) = \frac{e^2 \hbar^2}{\pi m} \sum_{n_c, n_v} \int \frac{f_{n_v n_c}(\tilde{k}) dS}{E_{n_v n_c}(\tilde{k}) |\nabla_{\tilde{k}} E_{n_v n_c}(\tilde{k})|} \quad (13)$$

where $E_{n_v n_c}(\tilde{k}) = E_{n_c}(\tilde{k}) - E_{n_v}(\tilde{k})$ and

$$f_{n_v n_c}(\tilde{k}) = \frac{2\hbar^2}{2m} |\langle n_c, \tilde{k} | \nabla | n_v, \tilde{k} \rangle|^2 / E_{n_v n_c}(\tilde{k})$$

is the interband oscillator strength. The sum is over the initial valence band index n_v and the final conduction band states, n_c . S is a surface in k -space of constant interband energy. Four valence bands, and six conduction bands were included in the sum. Again the Gilat-Raubheimer scheme was used to evaluate the integral. The expression for $\epsilon_2(\omega)$ is based upon several assumptions such as neglecting excitonic effects, but has been quite satisfactory for the purpose of analyzing reflectivities^{7,42} (particularly in the case of Si where exciton effects should not be large). Once the imaginary part of the dielectric function has been evaluated, the real part may be calculated from a Kramers-Kronig transformation, and a reflectivity calculated.⁷ To compare the theoretical results to the experimental derivative spectra, the logarithmic derivative of the reflectivity is computed by numerical means. Since the calculated reflectivity is susceptible to noise arising from the discrete nature of the grid over which $\epsilon_2(\omega)$ is calculated, some averaging is usually performed.⁴³

We have also calculated the cyclotron resonance masses using the mass parameters of Dresselhaus, et al.⁴⁴ as modified by Kane.²²

$$\begin{aligned}
 F' &\approx \frac{2}{m} \sum_n \frac{|\langle \Gamma_{25'} | P_x | \Gamma_{2'}^n \rangle|^2}{E_{25'} - E_2^n} \\
 G' &\approx \frac{2}{m} \sum_n \frac{|\langle \Gamma_{25'} | P_x | \Gamma_{25}^n \rangle|^2}{E_{25'} - E_{15}^n} \\
 H' &\approx \frac{2}{m} \sum_n \frac{|\langle \Gamma_{25'} | P_x | \Gamma_{12'}^n \rangle|^2}{E_{25'} - E_{12'}^n}
 \end{aligned} \tag{14}$$

where we have neglected an interaction term between Γ_{25}^+ and Γ_{25}^- which should be negligible.¹⁴ Pseudowavefunctions were used to evaluate the required matrix elements. Contrary to comments made by other authors,^{24,45} these matrix elements are quite accurate when compared to OPW calculations.⁴⁶ We have also calculated the conduction band minimum mass by directly calculating the band shape over a fine grid of points in the neighborhood of the minimum.

Finally the pseudocharge density was calculated by using the special point scheme of Chadi and Cohen.⁴⁷ Instead of evaluating the sum,⁴⁸

$$\rho(\tilde{r}) = e \sum_{\tilde{k}} \sum_{n_v} |\psi_{n_v, \tilde{k}}(\tilde{r})|^2 \tag{15}$$

over a fine grid throughout the Brillouin zone as performed by Walter and Cohen,⁴⁹ only a few representative points need be considered. The two point scheme of Chadi and Cohen, with

$\tilde{k}_1 = (2\pi/a)(1/4, 1/4, 1/4)$ and $\tilde{k}_2 = (2\pi/a)(3/4, 1/4, 1/4)$ (and appropriate weighting factors), yields a valence band pseudo-charge density accurate to within 1-2%,⁵⁰ as compared to a sum throughout the zone. Therefore, we have used this two point scheme. Approximately 90 plane waves were used in the calculation of the required pseudowavefunctions.

IV. Results

The eigenvalues for the local and nonlocal calculation at the symmetry points Γ , X and L are listed in Table II. The band structures for both cases are given in Figure 2. The results for the local and nonlocal cases are quite similar, except for the lower valence bands (which have a good deal of s-character), and the band ordering at Γ for the upper conduction bands (i.e. Γ_{12} , and Γ_1).

In Table III we have identified the theoretically determined structure in the reflectivity derivative spectrum, and as usual associate the structure with van Hove singularities (or critical points) in the Brillouin zone. Silicon, as noted by other authors,³ has a large number of critical points, and the identifications in Table III should be considered as representative for the specific energy region under consideration. Saravia and Brust³ have done a very thorough analysis of band topologies of three model potentials for silicon. Our results are quite similar to their "Model II"³ and the interested reader is referred to their extensive contour maps.

A comparison between the experimental results of ref. 15 and our calculated derivative spectra is given in Figure 3. Overall the agreement is quite satisfactory for both the local and nonlocal cases. In particular, the placement of the reflectivity peak positions for both cases is accurate to within ~ 0.15 eV. The nonlocal energy dependent result is superior at the higher energies, with the E_1' structure in slightly better agreement than the local calculation. On the other hand, the local calculation is slightly superior in the E_2 region, at least as far as the placement of the 4.3 eV reflectivity structure is concerned, although both the theoretical curves have a different line shape than the experiment. In the nonlocal curve the reflectivity structure at 4.15 eV is in perhaps the greatest discord with the experimental results. The reason for this can be traced back to the band shape near the X_4-X_1 region. The band gap at X for the nonlocal case is on the order of ~ 0.2 eV smaller than the local case. We also note that the indirect gap is smaller for the nonlocal case. If we were to slightly increase the X_4-X_1 transition by ~ 0.2 eV the resulting reflectivity curve (and indirect gap) should be in better accord with experiment. In the E_1 region we are not able to resolve the find structure present in the experimental results.

The first reflectivity peak at 3.45 eV has been the subject of some controversy. Piezoelectric experiments (both ac⁵¹ and dc⁵²), chemical shifts in Ge-Si alloys,⁵³

electroreflectance⁵⁴ and some wavelength modulation techniques⁵⁵ have suggested that the peak has Δ symmetry. However, more recent work has suggested that the peak has Λ -symmetry^{56,57} and this assignment is also suggested by analogy with other zincblende structures.⁵⁵

In both the local and nonlocal results this reflectivity peak arises from contributions from points near Γ , along Λ and off the Λ -direction. However, the dominant contribution arises from the Λ transition. The complexity of this peak in our theoretical calculations, that is, contributions from several critical points, has also been suggested by several authors, e.g. Λ Welkowsky and Braunstein through an examination of experimental reflectivity data.⁵⁸ In this respect, we note that the $\Gamma_{25'}-\Gamma_{15}$ and $\Lambda_3-\Lambda_3$ critical points must lie very close in energy or more widely spaced reflectivity structures would be present in our calculated reflectivities.

While the topological differences between the local and nonlocal calculations in this region are small, it is interesting, and perhaps significant, that our nonlocal calculation is "flatter" along the Λ -symmetry direction. This trend has been observed previously, in nonlocal calculations involving a d-well.^{11,12,13} We find in the nonlocal calculation that from the L point midway to Γ , the energy difference between bands 4 and 5 is less than 0.01 eV, while over the same range in the local calculation the gap varies by ~ 0.15 eV. This means that the nonlocal band structure has a nearly two dimensional M_0 point at L in agreement with recent

electroreflectance data by Grover and Handler;⁵⁷ however, the transverse mass for this critical point in the nonlocal case is quite similar to the one calculated in the local case, and not in agreement with Grover and Handler's value. We find the transverse mass $\mu_t \sim 0.1m$, whereas the experimental value found by Grover and Handler is closer to $0.02m$.

Another controversial transition has been the previously mentioned $\Gamma_{25}'-\Gamma_2'$. In most diamond and zincblende semiconductors Γ_2' lies below Γ_{15} . Only in silicon have theoretical calculations found the reverse to be true. This ordering, however, has been confirmed by the low field electroreflectance data of Aspnes and Studna.²⁷ They have been able to resolve, for the first time, the E_0 and $E_0+\Delta_0$ transitions, and find the spin-orbit critical points to occur at 4.185 ± 0.010 eV and 4.229 ± 0.010 eV at 4.2°K . This is in good accord with the theoretical value for both the local and nonlocal cases as can be noted in Table II.

We observe that the experimental results of Aspnes and Studna contradicts the assignment of Kunz²¹ which placed Γ_2' below Γ_{15} . This assignment was based upon an analysis of soft X-ray data. However, we feel the assignment of Aspnes and Studna to be more conclusive. Soft X-ray data can be difficult to interpret as the leading edge may exhibit excitonic effects.⁵⁹ In fact, one finds that the agreement between the soft X-ray spectra and the theoretical results with Γ_{15} placed lower than Γ_2' are in satisfactory agreement away from the suspect leading edge.⁶⁰ Furthermore, Ge-Si

alloying experiments tend to confirm the Aspnes-Studna assignment.⁶¹

In Table IV we compare our results for the local and nonlocal cases with the experimental results of photoemission measurements. The agreement is quite good for both cases, but the nonlocal calculation appears to be superior for the L_1 and L_2 levels. Unfortunately the ordering of the Γ_{12} and Γ_1 conduction bands is not made clear by the experimental results, since both theoretical results are in fairly good agreement with the experimentally determined transitions. The nonlocal results, however, are again in slightly better accord. In Figure 4 we compare our calculated electronic density of states to the results of XPS. We have not included the transition matrix elements, hence the theoretical peak heights do not match the experimental ones, but the peak placement for the nonlocal results are in excellent agreement.

In Table IV the experimentally determined cyclotron mass parameters are given along with the theoretically calculated parameters. The position, the magnitude, and transverse and longitudinal masses of the conduction band minimum as determined by experiment are also compared to the theoretical results. It is interesting that a simple three parameter purely local pseudopotential is able to so accurately reproduce and that the nonlocal calculation gives such excellent results the mass results. This should be contrasted with Kane's calculation in which he was unable to fit both the masses and gaps. The difficulty was attributed to the failure of

the local Slater exchange term, but it was observed that changes outside the "linear regime" of his empirical adjustments might remedy the situation.

Finally we compare our local and nonlocal valence pseudocharge densities to the recent calculations of Yang and Coppens.²⁹ Using the results of very accurate X-ray experiments now available,⁶⁶ they were able to obtain an extremely accurate valence charge density for silicon. In Figure 5 we present their valence charge density results which has been prepared by the removal of the core states by the use of Clementi wavefunctions.⁶⁷ They estimate a standard deviation of $0.3 e/\Omega_c$ in the charge density near the bonding region. However, at the nuclear sites the error is larger due to anomalous scattering, but we would not expect the pseudocharge density to be accurate in this region either. In Figure 6 we give the theoretical pseudocharge density results for both the local and nonlocal calculations. The fourier coefficients of the charge density are given in Table VI for both results; these coefficients are similar to the results of an OPW calculation by Brinkman and Goodman.¹⁷

Since our local calculation resembles that of Walter and Cohen's,⁴⁹ Yang and Coppen's observations²⁹ made regarding the Walter-Cohen calculation are valid here. A comparison of the local result to the experimental charge density shows as Yang and Coppens point out, that in both cases the maximum of the valence charge density occurs at the midpoint

of the bond, and that the bond height maxima of $28 e/\Omega_c$ and $26 e/\Omega_c$, for both experiment and theory respectively, are in very good agreement. We find similar results are also true for the nonlocal calculation. This is indeed quite encouraging, especially in view of recent SCOPW calculations.⁶⁸ In these calculations, while the calculated crystalline form factors are found to be an improvement over the free atom form factors, there still existed significant discrepancies.⁶⁸ Unfortunately since difference densities (i.e. $\rho_{\text{val}} = \rho_{\text{total}} - \rho_{\text{core}}$) have not been prepared for the SCOPW case, a direct comparison cannot be made between their results and our calculations.

That the pseudopotential should do so well away from the nuclear region is perhaps not as surprising as it may seem. It is in the bonding region where we would expect our wavefunctions to be most accurate. On the other hand, the fact that the agreement is so good is unexpected, as energies are always more accurate than the corresponding wavefunctions. Calculations for the temperature dependence of the "forbidden" (222) reflection in silicon, involving pseudocharge densities, have also been able to accurately reproduce the experimental results.⁶⁹ However, in the local case we do find some discrepancy with experiment: namely, the orientation of the bond. The local pseudopotential bond axis is aligned perpendicular to the bonding direction, while experiment finds a bond elongated parallel to the bonding direction. This result is outside of the experimental error quoted by Yang and Coppens.²⁹ But in the case of the nonlocal pseudopotential we find a pseudocharge density in which the bond is elongated parallel to the bonding direction.

The rotation of the bond from the local perpendicular orientation to the nonlocal parallel orientation result can be traced directly to the energy dependent nonlocal s-well's effect on the bottom valence band. A band by band comparison of the local and nonlocal pseudocharge densities is given in Figures 7 and 8. The bottom valence bands in the energy-dependent nonlocal case see a much weaker (i.e. less repulsive) s-well than do the upper valence and conduction bands. This permits the s-like bands in the nonlocal case to remain the same for the upper bands, but differ for the lower bands. Hence, in the nonlocal case we have, for the bottom bands, charge "leaking" into the core regions, while in the local case it remains excluded. This accounts for the "bond-like" feature appearing in the local case for the bottom bond, while in the nonlocal case the charge appears uniformly spaced between the atoms. The second valence band also mimics to some extent the changes occurring in the first band. But it is the major change in the first band which causes the change in bond orientation.

V. Conclusions

We find that with the addition of an energy dependent nonlocal s-well correction to the usual local pseudopotential we are able to account quite satisfactorily for the experimentally determined optical gaps, masses, electronic density of states and charge densities in silicon. This should be contrasted with recent nonlocal calculations on Ge,^{10,11}

GaAs,^{12,13} and ZnSe¹⁴ which have indicated the need for a nonlocal d-well. This fact can be accounted for by an examination of the Heine-Abarenkov pseudopotentials.^{33,35,70} First, as we have noted, s-nonlocality becomes important because only one p-state cancels the core potential in silicon. However, as we progress down the carbon column from silicon to lead the cancellation becomes more complete and equal (at least at E_F) as the ratio of core s- and p-states becomes closer to unity. This can be verified by an examination of the results of ref. 35. Hence, s-p nonlocality may be important in silicon, but not in, for example, germanium or tin. (It should be mentioned, however, that in the heavier elements, e.g. Pb, nonlocality between s- and p-states can arise from relativistic effects.⁷)

The requirement of a nonlocal d-well in Ge, GaAs and ZnSe, to achieve agreement with experiment, can likewise be understood in an analysis of the core states. In silicon there are no d-core states, but in germanium there are, hence, in Ge a "d-electron" sees a more repulsive d-well than a corresponding "d-electron" in silicon. This manifests itself in the need for a repulsive d-well in germanium, but not in silicon.

Such a result is indeed found by an examination of the Animalu-Heine calculations.³⁵ Further, a study of their results shows a rather interesting trend, namely, that d-nonlocality should become more important in selenium and arsenic than in zinc or gallium. This is contrary to the

suggestion of Pandey and Phillips¹² that the reverse trend should be true, but it agrees with our findings^{11,13,14} that d-nonlocality becomes increasingly important in going across the germanium row from zinc to selenium. A possible explanation for this trend is that the inner s- and p-core states see a less efficiently screened nuclear charge than does the outer d-core state. Therefore, as the nuclear charge increases across the row, the s- and p-states are influenced to a larger degree than the d-states. Consequently the s- and p-core states contract faster than the d-core states. This would result in a much less efficiently cancelled s- and p-potential relative to the d-potential. Hence, with respect to the s- and p-wells we would expect a much less attractive d-well in selenium than in zinc. Therefore, if we correct for this difference of d-well cancellation relative to s-p well cancellation by a repulsive nonlocal d-well, it should grow in magnitude from zinc to selenium which is the case.^{11,13,14}

Finally we shall briefly discuss the energy dependence in silicon, and other semiconductors. Little investigation has been done concerning the energy dependence with the exception of a recent calculation by Chekroun, et al.⁸ However, their calculation involved the use of a local energy dependent potential and, as can be observed in Fig. 1, the s-, p- and d-wells have quite different energy dependent behavior. This would seem to cast doubt on the appropriateness of treating the wells using the same energy dependence as would be the case in a local calculation. In fact it was noted

that while some success was achieved in obtaining an improved valence band density of states, equally successful improved optical transitions were not obtained.⁸

Another calculation which also resulted in an improved valence band density of states involved the use of an effective mass approximation.⁹ That is, m was replaced by an m^* in the hamiltonian and treated as an adjustable parameter. By direct numerical calculation it is found that such a replacement simulates in many respects an energy dependent s-well in its affect on the bottom valence bands. Since the value of m^* deviates increasingly from the free mass, m , in such calculations for the heavier elements,⁹ we might expect to find the energy dependence of the s-well in a Heine-Abarenkov potential to follow this trend. And, indeed, this is observed.⁶⁷

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Table Captions

Table I. Parameters used in the calculations.

Table II. Eigenvalues (in eV) at Γ, X, L symmetry points for local and energy dependent nonlocal pseudopotential calculations.

Table III. Theoretical and experimental reflectivity structure and their identifications including location in the Brillouin zone, energy (in eV) and symmetry of the calculated critical points for Si.

Table IV. Comparison of critical point energies (in eV) as calculated by local and energy dependent nonlocal pseudopotentials and as measured by photoemission experiments.

Table V. Cyclotron mass parameters (see text) and conduction band minimum masses compared to the theoretical values from a local and energy dependent nonlocal pseudopotential. The magnitude and position of the indirect gap along the Δ direction is also given.

Table VI. Fourier coefficients of the valence pseudocharge density (units of e/Ω_c) as calculated by local and energy dependent nonlocal pseudopotentials.

Table I

Si	Form Factors (Ryd)			a_0 (Ryd)	$\partial a_0 / \partial E$	a (A°)
	$V(\sqrt{3})$	$V(\sqrt{8})$	$V(\sqrt{11})$			
Local	-0.2241	0.0551	0.0724	--	--	5.43
Energy Dependent Nonlocal	-0.257	-0.040	0.033	0.55	0.32	5.43

Table II

Point	Level	Local	Energy Dependent Nonlocal
Γ	Γ_1	-12.53	-12.36
	$\Gamma_{25'}$	0.00	0.00
	Γ_{15}	3.43	3.42
	$\Gamma_{2'}$	4.17	4.10
	Γ_1	8.60	7.69
	$\Gamma_{12'}$	7.82	8.19
X	X_1	-8.27	-7.69
	X_4	-2.99	-2.86
	X_1	1.22	1.17
L	$L_{2'}$	-10.17	-9.55
	L_1	-7.24	-6.96
	$L_{3'}$	-1.22	-1.23
	L_1	2.15	2.23
	L_3	4.00	4.34

Table III

Reflectivity Structure				Associated Critical Points		Symmetry		Critical Point	
Theory		Experiment		Location in the Brillouin Zone		of CP		Energy	
Local	Non-local	5°K ^{a)}	80°K ^{b)}	Local	Nonlocal	Local	Non-local	Local	Non-local
3.48	3.49	3.40	3.36	$L_3, -L_1$	$L_3, -L_1$	M_0	M_0	3.37	3.46
		3.45	3.41	$\Gamma_{25}, -\Gamma_{15}$	$\Gamma_{25}, -\Gamma_{15}$	M_0	M_0	3.43	3.42
				Near (0.1, 0.02, 0.02)	Near (0.1, 0.05, 0.05)	M_0	M_0	3.46	3.42
3.75	3.70	3.66	(3.88) ^{c)}	Vol. along Δ	Vol. along Δ	--	--	--	--
4.26	4.15	4.30	4.38	Vol. near (.9, .1, .1)	Vol. near (.9, .1, .1)	--	--	--	--
4.53	4.57	4.57	4.57	Large region near (.5, .25, .25) and $\Sigma_4 - \Sigma_1$	Large region near (.6, .3, .3) and $\Sigma_4 - \Sigma_1$	M_2	M_2	4.53	4.47
						M_2	M_2	4.49	4.60
5.32	5.58	5.48	--	$L_3 - L_3,$ $\Lambda_3 - \Lambda_3, (.4, .4, .4)$	$L_3 - L_3,$ $\Lambda_3 - \Lambda_3, (.45, .45, .45)$	M_0	M_2	5.22	5.56
						M_1	$\sim M_3$	5.25	5.57

a) From ref. 15

b) From ref. 58

c) Inferred from $\epsilon_2(\omega)$ data of ref. 58

Table IV

Energy Level	Theory		Experiment	
	Local	Nonlocal		
Γ_{12}'	8.60 ↓	8.19	8.3 ± 0.1^a	
Γ_1	7.82 ↑	7.69	$\sim 7.6^a$	
Γ_2'	4.17	4.10	4.15 ± 0.05^a	
Γ_1	-12.53	-12.36	$-12.4 \pm 0.6,^b$	-12.5 ± 0.6^c
X_4	-2.99	-2.86	$-2.9,^a$	-2.5 ± 0.3^c
Σ_1^{min}	-4.48	-4.47	$-4.4,^a$	$-4.7 \pm 0.3^{b,c}$
L_3	4.00	4.34	3.9 ± 0.1^a	
L_3'	-1.22	-1.23	-1.2 ± 0.2^a	
L_1	-7.24	-6.96	$-6.4 \pm 0.4,^b$	-6.8 ± 0.2^c
L_2'	-10.17	-9.55	-9.3 ± 0.4^c	

a) See ref. 62

b) See ref. 6

c) See ref. 5

Table IV

Energy Level	Theory		Experiment
	Local	Nonlocal	
Γ_{12}'	8.60 ↓	8.19	8.3 ± 0.1^a
Γ_1	7.82 ↑	7.69	$\sim 7.6^a$
Γ_2'	4.17	4.10	4.15 ± 0.05^a
Γ_1	-12.53	-12.36	$-12.4 \pm 0.6,^b$ -12.5 ± 0.6^c
X_4	-2.99	-2.86	$-2.9,^a$ -2.5 ± 0.3^c
Σ_1^{min}	-4.48	-4.47	$-4.4,^a$ $-4.7 \pm 0.3^{b,c}$
L_3	4.00	4.34	3.9 ± 0.1^a
L_3'	-1.22	-1.23	-1.2 ± 0.2^a
L_1	-7.24	-6.96	$-6.4 \pm 0.4,^b$ -6.8 ± 0.2^c
L_2'	-10.17	-9.55	-9.3 ± 0.4^c

a) See ref. 62

b) See ref. 6

c) See ref. 5

Table V

	Experiment	Theory	
		Local	Nonlocal
F'	-5.04 ^a	-5.11	-5.07
H'	-4.53 ^a	-4.49	-4.23
G'	-0.87 ^a	-0.88	-0.89
$m_0/m_{c\perp}$	5.25 ^b	5.15	5.31
$m_0/m_{c\parallel}$	1.09 ^b	1.21	1.18
$ak_{\min}/2\pi$	0.86 ^c	~0.85	~0.85
E _{ind}	1.15 ^d	1.13	1.05

a) From J. C. Hensel as listed in ref. 16

b) See ref. 63

c) See ref. 64

d) See ref. 65

Table VI

$G(a/2\pi)$	Local	Nonlocal
000	8.00	8.00
111	-1.748	-1.924
220	0.270	0.035
311	0.412	0.345
222	0.481	0.467
400	0.206	0.273
331	0.018	0.015
422	-0.006	-0.033
333	-0.001	-0.032
511	-0.004	-0.022
440	0.007	0.002

Figure Captions

- Fig. 1. Behavior of the Heine-Abarankov well depths, $A_0(E)$, as determined by Animalu (ref. 70).
- Fig. 2. Band structure for Si as determined from a local pseudopotential calculation (dotted line) and an energy dependent nonlocal pseudopotential calculation (solid line).
- Fig. 3. Experimental and theoretical reflectivity derivative spectrum for Si. The experimental results^(a) are from ref. 15. The dotted theoretical curve^(b) was calculated from a local pseudopotential and the solid curve from an energy dependent nonlocal potential.
- Fig. 4. Experimentally^(a) and theoretically^(b) determined electronic density of states for Si. The experimental results are from ref. 5. The dotted theoretical curve is from a local pseudopotential calculation; the solid curve is from an energy dependent nonlocal pseudopotential calculation.
- Fig. 5. The valence charge density as determined by Yang and Coppens (ref. 29) using the X-ray results of ref. 66. The contours are in units of e/Ω_c .
- Fig. 6. The valence pseudocharge density for Si as calculated by a local pseudopotential (a) and by an energy dependent nonlocal pseudopotential (b). The contours are in units of e/Ω_c .
- Fig. 7. The pseudocharge density band by band for Si as calculated by a local pseudopotential. The contours are in units of e/Ω_c .

Fig. 8. The pseudocharge density band by band for Si as calculated by an energy dependent nonlocal pseudopotential. The contours are in units of e/Ω_c .

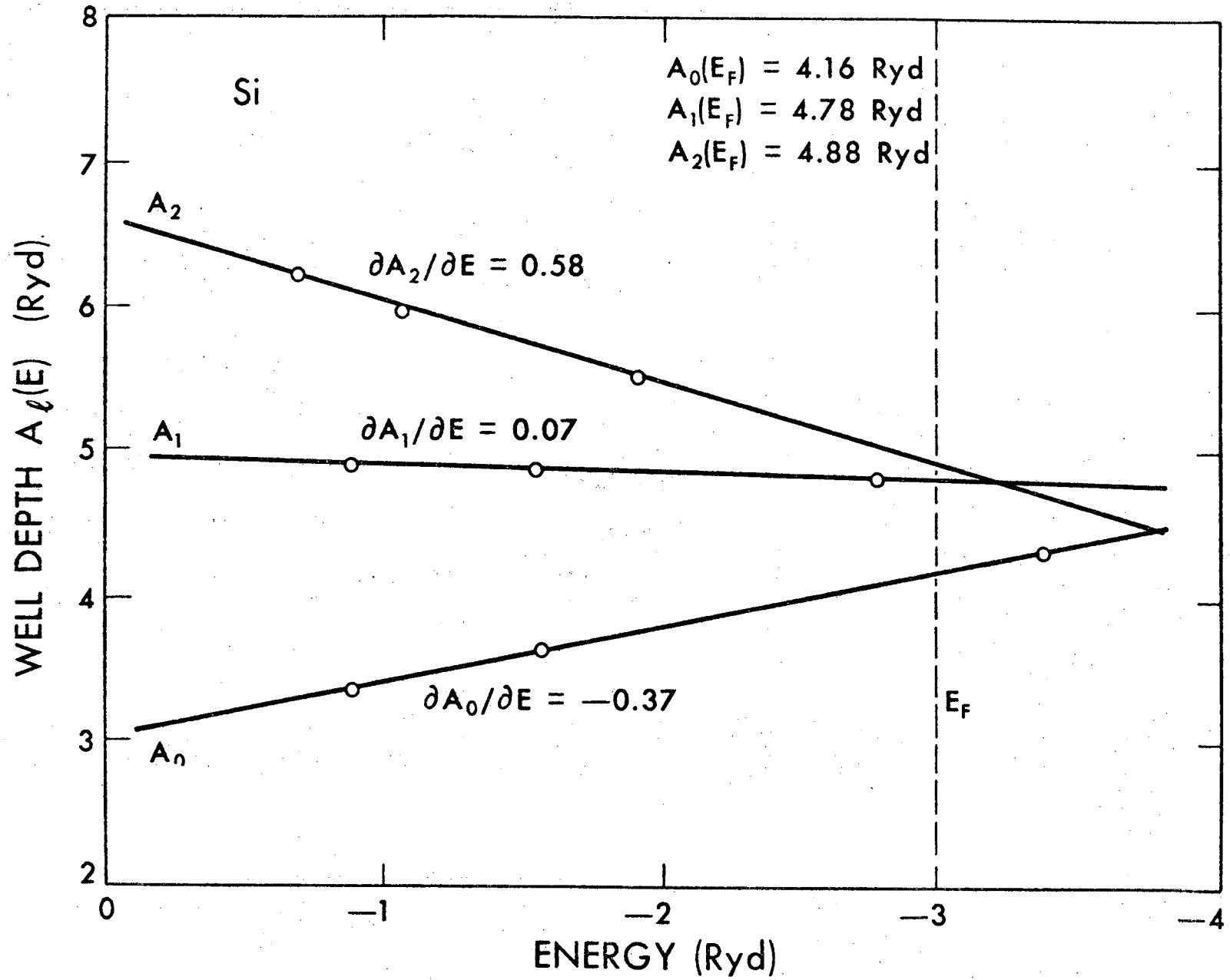


Fig. 1

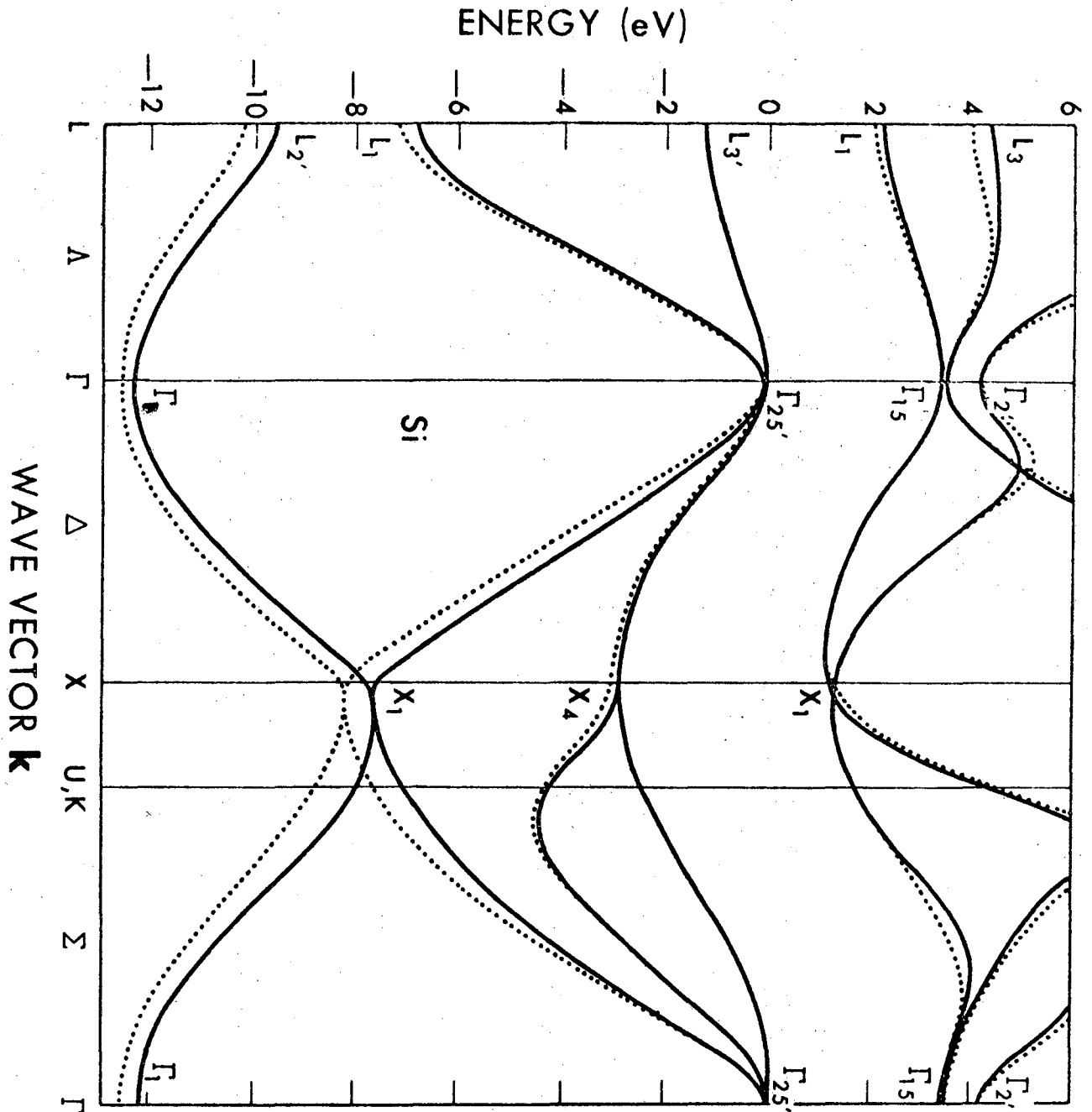


Fig. 2

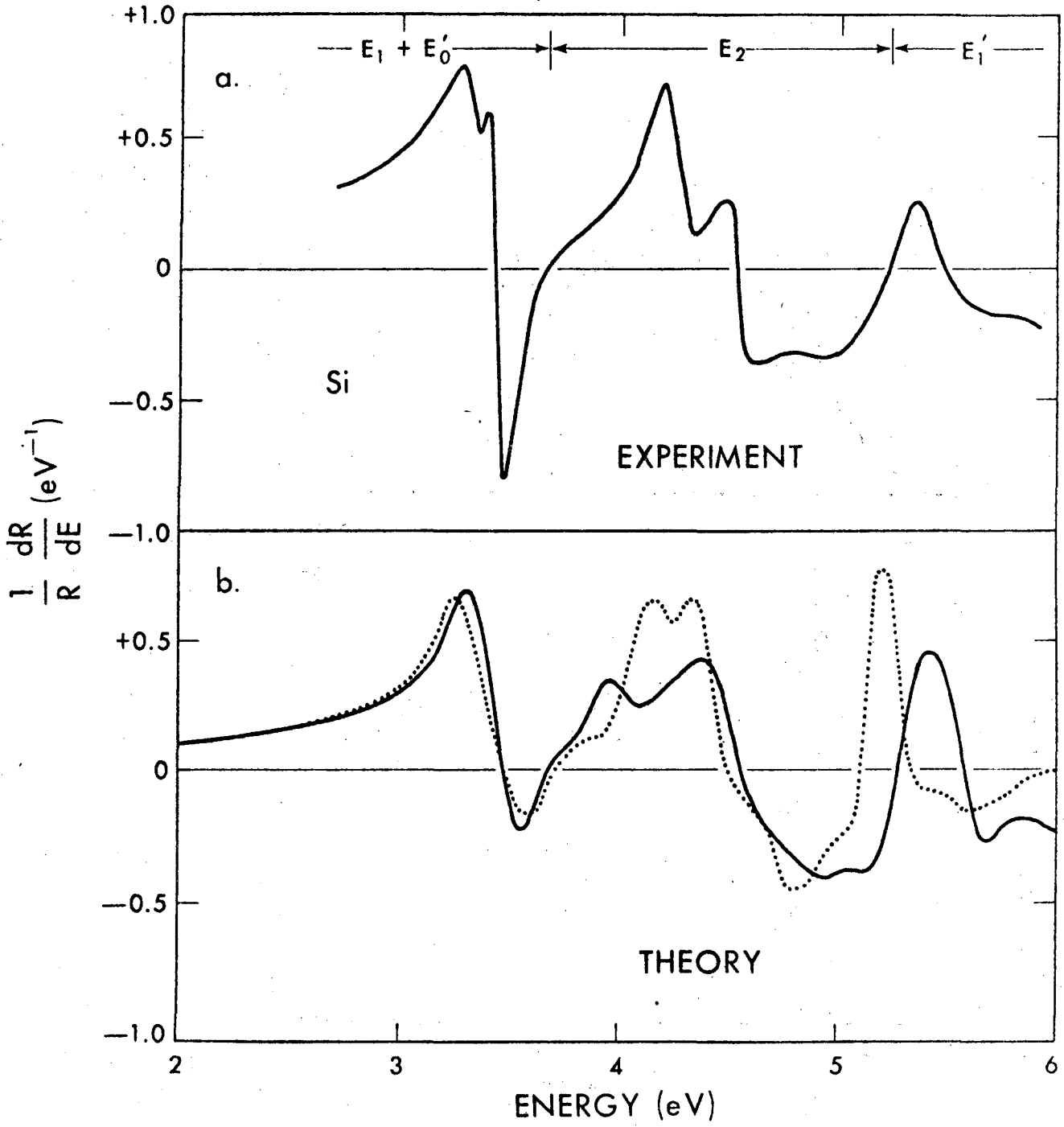


Fig. 3

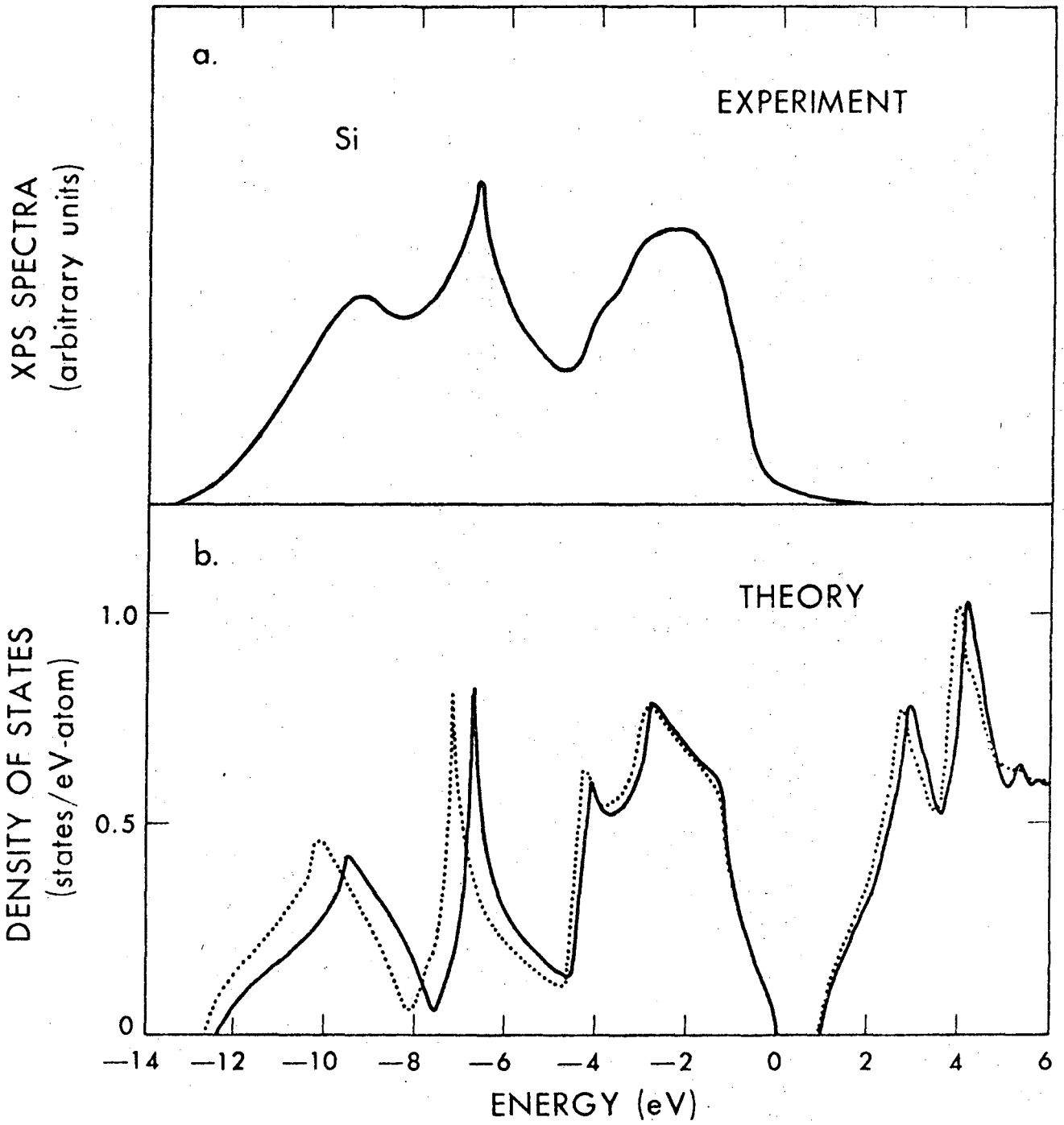


Fig. 4

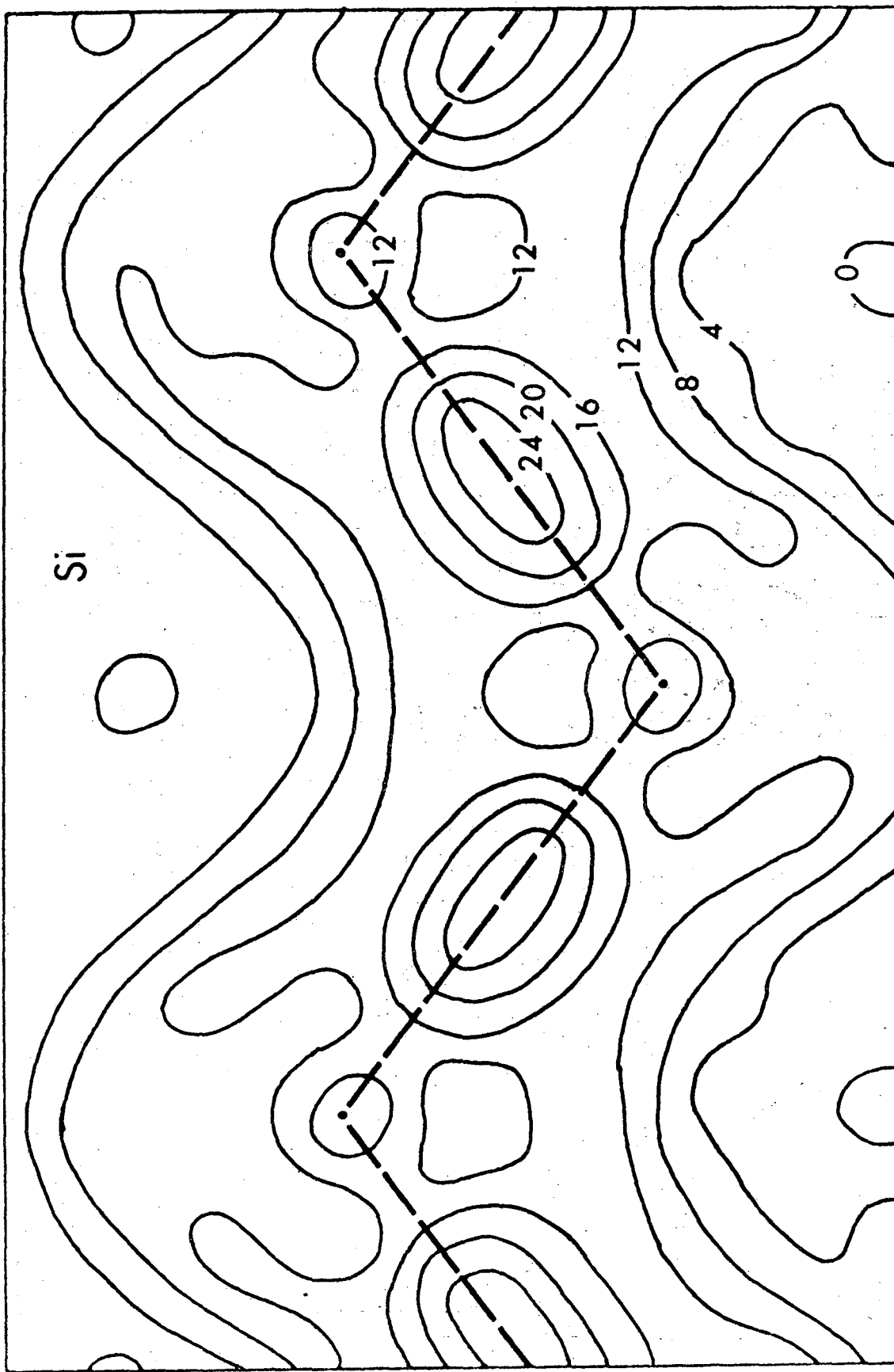


Fig. 5

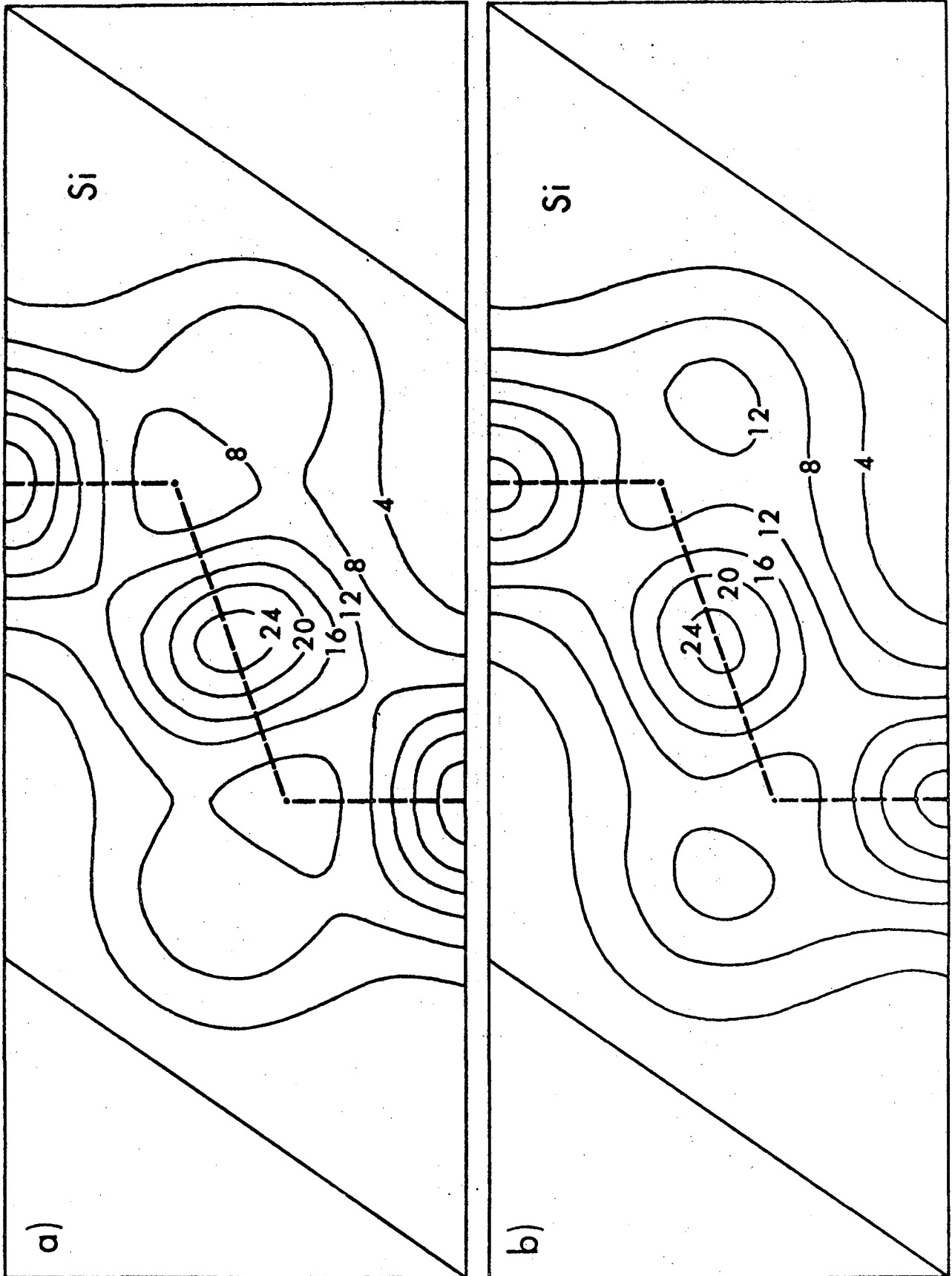


Fig. 6

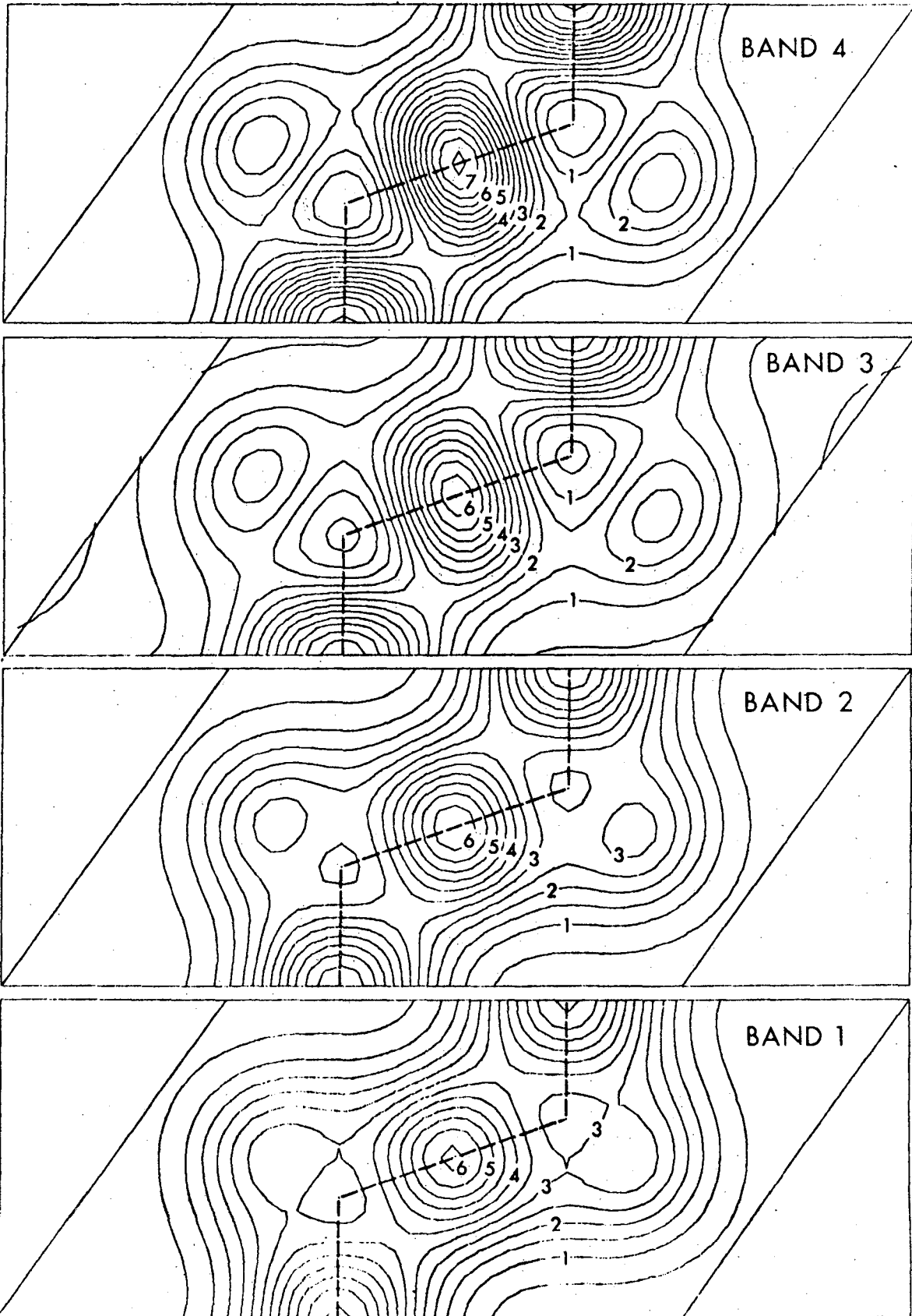


Fig. 7

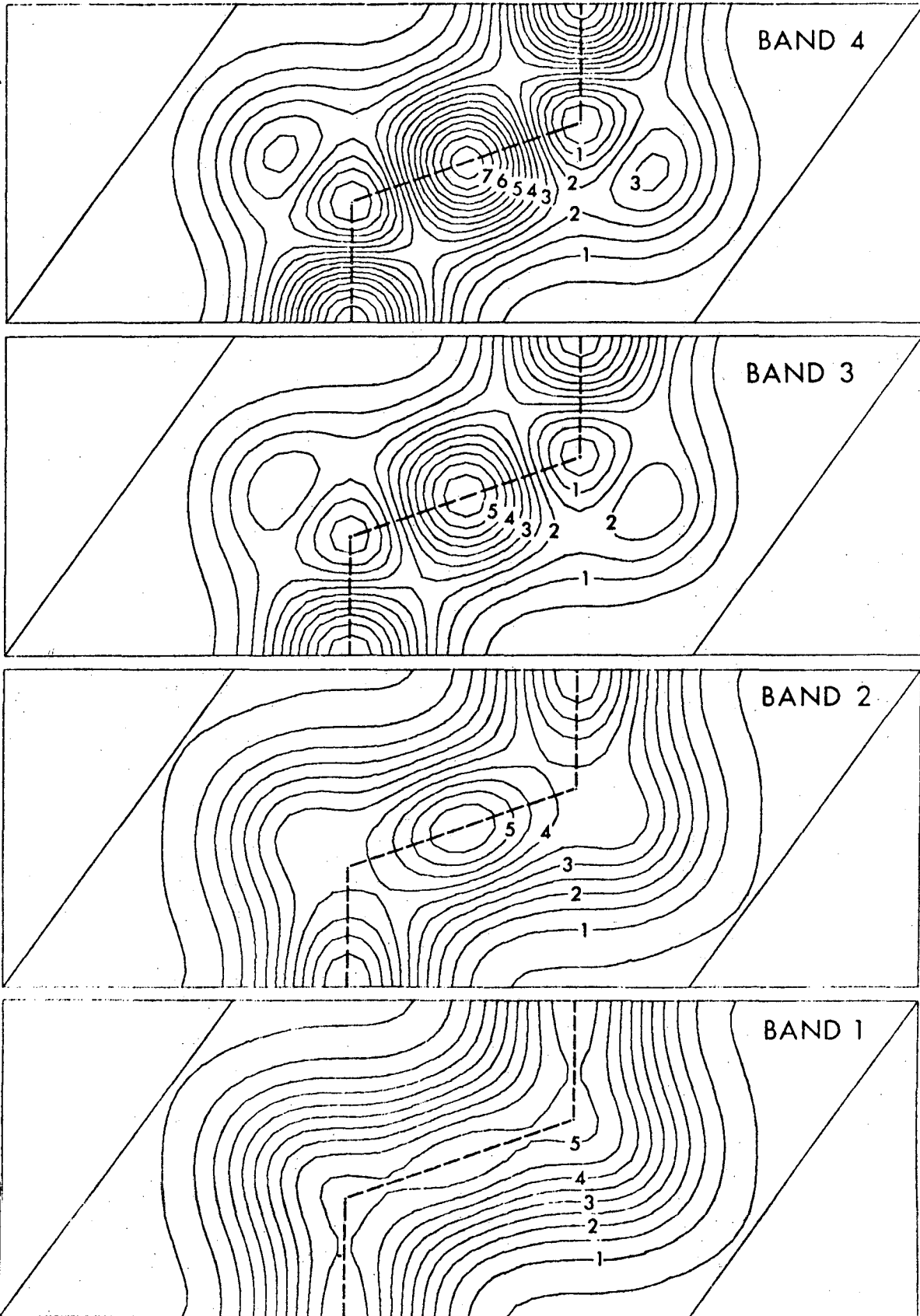


Fig. 8

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