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Electronic and structural properties of $CaSi_2$

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Linear augmented-plane-wave calculations of the electronic and structural properties of $CaSi_2$ for three types of stacking of Ca layers and Si double layers are presented. The calculated structural parameters for the two experimentally observed structures are in excellent agreement with experiment. The three different structures contain Ca with sixfold, sevenfold, and eightfold coordination, respectively, with Si. The cohesive energies of the three structures are found to be almost identical and their band structures only weakly dependent on the stacking sequence (or, equivalently, Ca coordination). Although *d* states are not occupied in the Ca atom, these states are found to hybridize strongly with Si *p* states near the Fermi level. The Fermi surface is found to consist of Ca *d*-like electrons and Si *p*-Ca *d*-hybridized holes. Consequences of these results for the $CaSi_2$/Si(111) interface are discussed.

INTRODUCTION

The topic of metal-semiconductor interfaces has long been a subject of both technological and fundamental physical interest. Systems for which ideal, atomically abrupt, and smooth epitaxial interfaces can be grown are of great interest because their relative simplicity allows a close comparison to be made between experimental and theoretical studies and facilitates a clearer analysis of the fundamental characteristics of the interface. In particular, there has been substantial recent interest in ideal metal interfaces with silicon[1-8] and in the effective ballistic transmission of electrons through them[9] in the context of possible metal-base transistors. In the past, only $CoSi_2$ and $NiSi_2$ have provided such ideal interfaces with silicon. Recently,[10] however, high-quality epitaxial $CaSi_2$ films have been grown on Si(111). Cross-sectional electron micrographs of these films have revealed a single-crystal $CaSi_2$/Si interface which is both atomically abrupt and atomically smooth over extended regions. The lattice mismatch between the calcium disilicide and silicon lattices is 0.4%. The electron micrographs indicate that films 150 Å thick grow without a significant number of defects.

For any specific interface, a thorough understanding of the bulk electronic and structural properties of both the semiconductor and the metal involved is clearly a prerequisite for understanding those of the interface. This recent successful epitaxial growth of a smooth, atomically abrupt $CaSi_2$/Si interface has therefore prompted interest in the bulk electronic and structural properties of calcium disilicide. In this paper we will present the results of linear augmented-plane-wave (LAPW) calculations for the band structure and structural properties of bulk calcium disilicide.

Three polymorphs of bulk calcium disilicide have been synthesized:[11,12] two of these consist essentially of (111) double layers of Si alternating with trigonal layers of Ca, and differ only in their stacking sequence [see Figs. 1(a) and 1(b)]; the third form[11] (which will not concern us in the present study) is a more complicated, tetragonal structure with a three-dimensional net of threefold-connected Si atoms. The latter polymorph is denser than the first two and is stable only under pressure. The form of calcium disilicide which occurs in nature and which has been successfully grown in thin-film form on the Si(111) surface, is shown in Fig. 1(a). In this structure (denoted tr6), the stacking of trigonal Ca layers follows an *AABBCC* stacking sequence. Each pair of Ca layers is separated by a Si double layer. The entire structure is hexagonal with a six-layer repeat distance. Each Ca has six Ca nearest neighbors and seven Si nearest neighbors. A second structure (denoted tr3), which has been artificially synthesized,[12] has a three-layer repeat distance, with Ca layers and Si double layers both stacked in an *ABC* sequence, as shown in Fig. 1(b). In this structure, each Ca has six Ca nearest neighbors and eight Si nearest neighbors. For the purposes of this study it is of interest to consider a third structure (denoted h1) similar to tr3 and tr6, which occurs naturally[11] for $CaGe_2$ but not for $CaSi_2$. It has a simple *AA* stacking of alternating

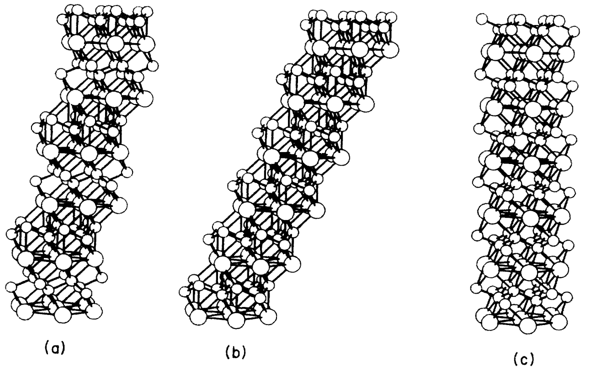

FIG. 1. Six layers of the $CaSi_2$ structure for (a) tr6 stacking, (b) tr3 stacking, and (c) h1 stacking. The larger atoms are Ca and the smaller atoms Si.

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Ca layers and Si double layers, as shown in Fig. 1(c). In this last structure, each Ca atom has six Si nearest neighbors. Thus, the three structures, h1, tr6, and tr3, offer prototypes of sixfold, sevenfold, and eightfold coordination of Ca with Si, with only very minor other changes in structure. By calculating the effects of such coordination changes on the bulk, we can obtain some simple insights into the structural possibilities for the $CaSi_2$/Si(111) interface.

We shall see that the effect of stacking sequence on the band structure is small (especially on the valence bands), and that the Ca-Si interaction in these structures can almost be viewed, to a first approximation, as an interaction of the trigonal Ca layers with only the dangling bonds from the Si double layers. Certainly, it seems to matter little to the band energies whether the Ca is in a tetrahedral site (as in the tr3 structure) or in an hexagonal site (as in the h1 structure) with respect to the Si double layers on either side, or in a tetrahedral site with respect to the double layer on one side and an hexagonal site with respect to the double layer on the other side (as in the tr6 structure). The same is true of the total energies of the structures; the energies for sixfold, sevenfold, and eightfold coordination of Ca with Si are all within approximately 0.01 eV per formula unit of each other. It is then reasonable to expect that different preparation techniques of the $CaSi_2$/Si(111) interface could result in any one of these coordinations of Ca at the interface, with attendant changes in the coefficients for ballistic electron transmission[9] through the interface.

Perhaps the most important and striking result that emerges from an analysis of the band structure and the wave functions is that, although Ca is not a transition element, Ca 3*d* levels hybridize very strongly with Si 3*p* levels at the Fermi level, both contributing about equally to the density of states there and dominating all other contributions. This result was anticipated in the qualitative studies of Refs. 4 and 7. Thus, the physics of electron transport through $CaSi_2$/Si interfaces may bear a greater resemblance to that of $CoSi_2$/Si and $NiSi_2$/Si interfaces[9] than might have been expected intuitively. However, the different position of the nonbonding Ca *d* states (above the Fermi level) in $CaSi_2$, compared to that in $CoSi_2$ and $NiSi_2$ (at or below the Fermi level), may give rise to substantial differences. These results are not in any way sensitive to the stacking of the layers.

STRUCTURES

The tr6 structure [see Fig. 1(a)] has a trigonal-rhombohedral crystal lattice.[11] The stacking of Ca trigonal layers repeats after six layers (hence the notation "tr6"). The space group is D_{3d}^5 ($R\bar{3}m$). In the usual hexagonal classification, the unit cell contains six equivalent Ca atoms in positions 6*c*: $(0,0,z)$, $(0,0,-z)$, $(\frac{1}{3},\frac{2}{3},\frac{2}{3}+z)$, $(\frac{1}{3},\frac{2}{3},\frac{2}{3}-z)$, $(\frac{2}{3},\frac{1}{3},\frac{2}{3}+z)$, and $(\frac{2}{3},\frac{1}{3},\frac{2}{3}-z)$, with $z=0.083$; six Si atoms in positions 6*c* with $z=0.183$; and six Si atoms in positions 6*c* with $z=0.350$. The in-plane lattice constant *a* equals the Ca-Ca nearest-neighbor distance, 3.855 ± 0.005 Å, and out-of-plane lattice constant *c* equals the six-layer repeat distance, 30.6 ± 0.1 Å. The structure is completely specified by the two lattice constants, *a* and *c*, and three internal atom displacement parameters. It has a rhombohedral primitive unit cell with two Ca and four Si atoms in the basis. All Ca sites are equivalent, but there are two inequivalent types of Si site, one in Si double layers between two Ca layers of the same type (*A*, *B*, or *C*), and the other between two Ca layers of different type (*BC*, *CA*, or *AB*). In the real material the two crystallographically inequivalent Si double layers prove to be very similar, both having bond lengths of 2.44 Å (slightly longer than the 2.35-Å bond length in silicon) and Si—Si bond angles of 104° (smaller than the ideal tetrahedral bond angle of 109.47°). Each Ca is sevenfold coordinated with Si, having six Si neighbors at 3.03 Å and one at 3.06 Å. The Ca-Ca nearest-neighbor distance of 3.855 Å is somewhat smaller than that in metallic Ca, where its value is 3.95 Å.

The tr3 structure[12] [see Fig. 1(b)] has a trigonal-rhombohedral crystal lattice in which the stacking of Ca trigonal layers repeats after three layers. It has a rhombohedral primitive unit cell with one Ca and two Si atoms in the basis and the space group is D_{3d}^5. The in-plane lattice constant, $a=3.82$ Å, is approximately 1% smaller than that for the tr6 structure and the out-of-plane lattice constant, $c=15.98$ Å, gives an interlayer separation approximately 0.5% larger than in the tr6 structure. The hexagonal unit cell contains three Ca atoms in positions 3*a*: (0,0,0), $(\frac{1}{3},\frac{2}{3},\frac{2}{3})$, and $(\frac{2}{3},\frac{1}{3},\frac{2}{3})$; and six Si in positions 6*c* with $z=0.197$. Each Ca is eightfold coordinated with Si, with six neighbors at 3.10 Å and two at 3.15 Å. The bond angle in the Si double layers is 105° and the bond length 2.41 Å.

The h1 structure in Fig. 1(c) has an hexagonal primitive unit cell with one Ca at (0,0,0) and two Si atoms at $(\frac{1}{3},\frac{2}{3},z)$ and $(\frac{2}{3},\frac{1}{3},-z)$ in the basis and the space group is D_{3d}^3 ($p\bar{3}m1$). Each Ca atom has six Si and six Ca nearest neighbors. This structure has not been experimentally observed, but we have included it in the present calculation to better elucidate the effects of stacking on the band structure and structural energy of bulk $CaSi_2$ and also to obtain a rough estimate of the energy cost of sixfold Ca-Si coordination at stacking faults in bulk $CaSi_2$ or at the $CaSi_2$/Si(111) interface.

Electron micrographs[10] have shown that the tr6 structure is the form of $CaSi_2$ which has been grown epitaxially on Si(111). This is probably partly due to the greater ease with which the bulk tr6 structure is grown compared to the tr3 structure. However, a second reason is that the lattice mismatch between the tr3 structure and silicon is somewhat larger than for the tr6 structure (-0.6% compared to $+0.4\%$). These two factors make growth of the tr3 modification of $CaSi_2$ on Si(111) more difficult than for the tr6 form.

CALCULATION AND RESULTS

We have calculated structural and electronic properties of the two experimentally observed polymorphs of $CaSi_2$, the tr6 and tr3 structures, and of the third, hypothetical structure, h1. The band-structure and total-energy calculations were performed using the LAPW method as described in detail by Mattheiss and Hamann.[13] Energy cutoffs of 8.0 and 50.0 a.u. for the plane-wave representation of the wave functions and charge, respectively, in the interstitial regions were used. In the Ca muffin tins (radius 3.0 a.u.) the wave functions are expanded in spherical harmonics up to $l = 8$ and the charge up to $l = 6$. In the Si muffin tins (radius 2.0 a.u.) the wave functions are expanded up to $l = 6$ and the charge up to $l = 4$. The Wigner form[14] was used for the exchange-correlation energy. For structural relaxation of the internal parameters and lattice constants, five **k** points in the irreducible Brillouin zone were used for both the tr3 and tr6 structures and six **k** points for the h1 structure. However, for a comparison of the (very small) energy differences between the relaxed h1, tr3, and tr6 structures, sets of 40, 38, and 19 **k** points, respectively, in an irreducible portion of the first Brillouin zone were used. These latter sets were chosen to be equivalent in the sense that the lattices of **k** points generated from them in the extended-zone scheme for the three structures are identical when the interlayer spacing and in-layer lattice constants are the same. The use of such equivalent sets of **k** points in the different structures minimizes the effects of finite **k** point sampling in comparing the total energies of structures.

For the tr3 structure we have performed a full minimization of the total energy with respect the two lattice constants, a and c, and the internal displacement parameter z. The values so obtained are $a = 3.84$ Å, $c = 16.00$ Å, and $z = 0.1975$. All are in excellent agreement with experiment and clearly demonstrate the quantitative reliability of the method in describing these Ca/Si-based systems. The Si—Si bond length equals 2.43 Å and the bond angle is 104.6°. Each Ca atom has six Si neighbors at 3.10 Å and two at 3.16 Å.

Because of the greater complexity of the tr6 structure, we have not minimized the energy with respect to all five structural parameters. Rather, we have kept the two lattice constants fixed at their experimentally determined values and varied the three internal atomic parameters. Variation of the atomic parameters causes a much greater change in the total energy than a comparable percentage variation in the lattice constants, so it was much more important to vary them in comparing the energies of the relaxed tr3, tr6, and h1 structures. Moreover, the experimental uncertainty is greater for the internal atomic parameters than for the lattice constants. In excellent agreement with experiment, we find the Ca in the $6c$ position with $z = 0.081$, Si in $6c$ with $z = 0.348$, and another Si in $6c$ with $z = 0.183$. With these values of the internal structural parameters, the Si—Si bond length in the double layers between Ca layers of the same type (A, B, or C in the stacking sequence) is 2.40 Å and the bond angle is 107.1°. In the double layers between Ca layers of different type, the Si—Si bond length is 2.43 Å and the bond angle 105.0°. Each Ca atom has six Si neighbors at 3.10 Å and one at 3.13 Å.

In the h1 structure we have kept the a lattice constant and the separation between Ca layers the same as in the tr3 structure and have minimized the energy with respect to the internal displacement of the Si atom. The minimum energy occurs for a value of $z = 0.587$. Each Ca then has six Si neighbors at 3.12 Å. The Si—Si bond length is 2.39 Å and the bond angle is 105.9°.

The structural total energies of the relaxed tr6, tr3, and h1 structures are almost identical, the tr6 structure being approximately 10 meV per formula unit more stable than the tr3 structure, which differs in energy from the h1 structure by less than 1 meV per formula unit. This latter difference is beyond the accuracy of calculation, and, when factors such as the zero-point motion of the lattice and approximations in the LAPW calculations are taken into account, even the difference between the tr6 and tr3 structures is not reliably estimated. However, we

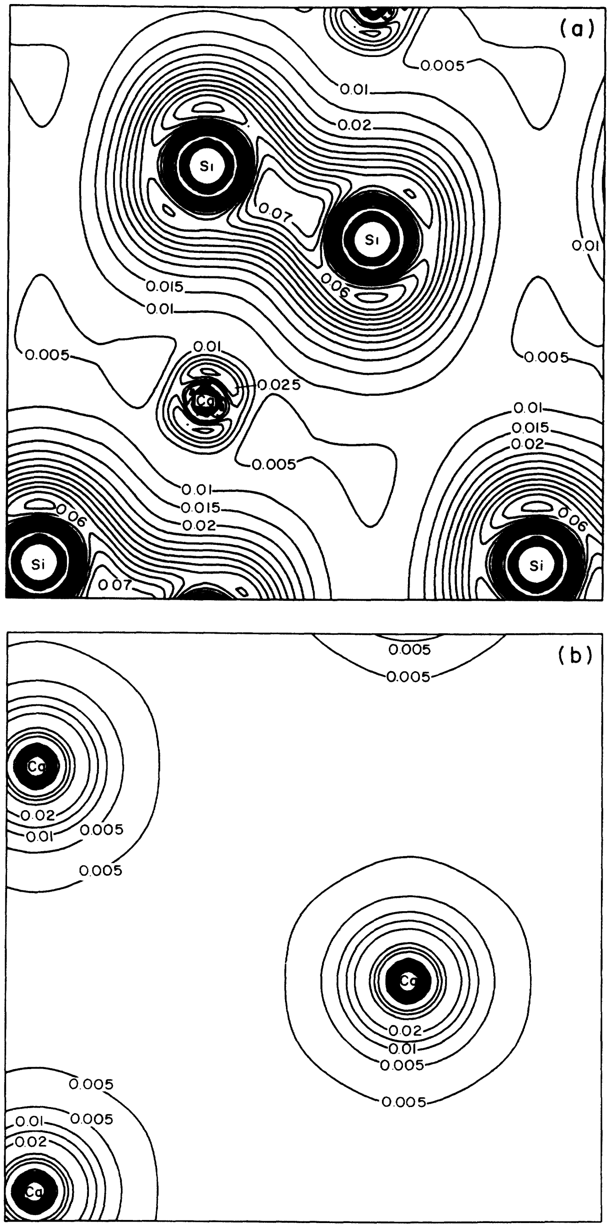

FIG. 2. Charge-density contour plot for the tr3 structure (a) in a plane containing a Ca atom and a Si—Si bond, and (b) in the plane of the Ca layer. The contours are at intervals of 0.005 a.u.

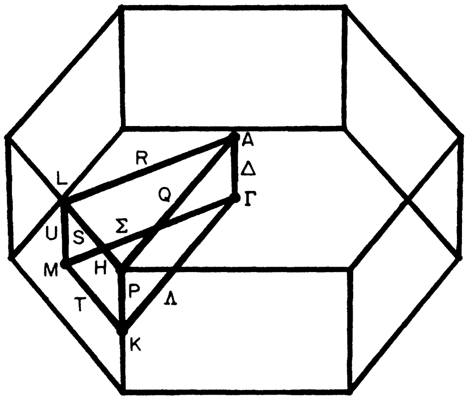

FIG. 3. Brillouin zone of the h1 structure.

can conclude that the energy differences between the three stackings are no more than about 0.01 eV per formula unit. Thus, whether the coordination of Ca with Si is six, seven, or eight affects the structural energy very little. This is in accord with the fact that both tr6 and tr3 structures have been synthesized, although the h1 structure has not been observed for $CaSi_2$.

Morar and Wittmer[10] have recently argued against eightfold coordination of Ca with Si at the $CaSi_2$/Si interface, partly on the basis of an assumed energetic unfavorability of this coordination compared to an alternative interface structure with a stacking fault of Si double layers relative to a continuation of the silicon bulk stacking in which the last double layer in Si is rotated 180° compared to its ideal bulk position. We see from the present calculation that this aspect of their argument is not valid; the energy differences between sixfold, sevenfold, and eightfold coordination of Ca with Si are no larger than the Si stacking-fault energy.[15] Although their arguments based on electron micrographs quite convincingly demonstrate their assignment of the interface structure in the samples they have grown, it is possible that a different sample preparation could lead to sixfold or eightfold coordination of Ca with Si at the interface.

Shown in Fig. 2(a) is a contour plot of the valence charge density in a plane containing a Ca atom and a Si—Si bond in the tr3 structure (the vertical direction is along the *c* axis). Figure 2(b) is a similar plot for the plane of the Ca layer. The Si—Si bond charge is relatively unchanged compared with silicon[16] and a Si dangling-bond charge points from the Si atom to the nearest Ca layer. In view of the very small effect of Ca coordination number with Si on the structural energy, it is not surprising that there is no sign of a clear bond charge between the Ca and Si atoms in Fig. 2(a). There is some polarization in the *c* direction of the charge near the Ca atom due to hybridization and partial occupation of the Ca *d* levels, but Fig. 2(b) reveals an almost circularly symmetric Ca atom in the basal plane. Radial oscillations of the charge density about the Ca atoms are due the nodal structure of the Ca 4*s* atomic wave functions.

In order to facilitate comparison of the band structures of the three structures, h1, tr3, and tr6, we have calculated the bands for **k** points along selected symmetry lines in the Brillouin zone of the h1 structure (see Fig. 3). In Figs. 4, 5, and 6 are plotted the bands for the h1, tr3, and tr6 structures, respectively, each labeled according to the corresponding h1 **k** points. In the tr6 structure there are two formula units in the primitive unit cell and the cell has twice the length in the *c* direction as the h1 and tr3 unit cells, and so the bands in the tr6 structure with $k_z=0$ correspond to states in the h1 and tr3 structures with $k_z=0$ and with $k_z=\pi/c$. This gives rise to the doubling of many bands in Fig. 6.

The effects of stacking sequence (or, equivalently, Ca coordination with Si) on the six lowest (i.e., the five valence and first conduction) bands are generally small. There is some sensitivity to stacking in the first conduction band near the *P* and *U* lines of the Brillouin zone. The position of the Fermi level is sensitive to small changes in dispersion near the *U* line due to the presence of an electron pocket there. The details of the higher conduction bands are somewhat more sensitive to stack-

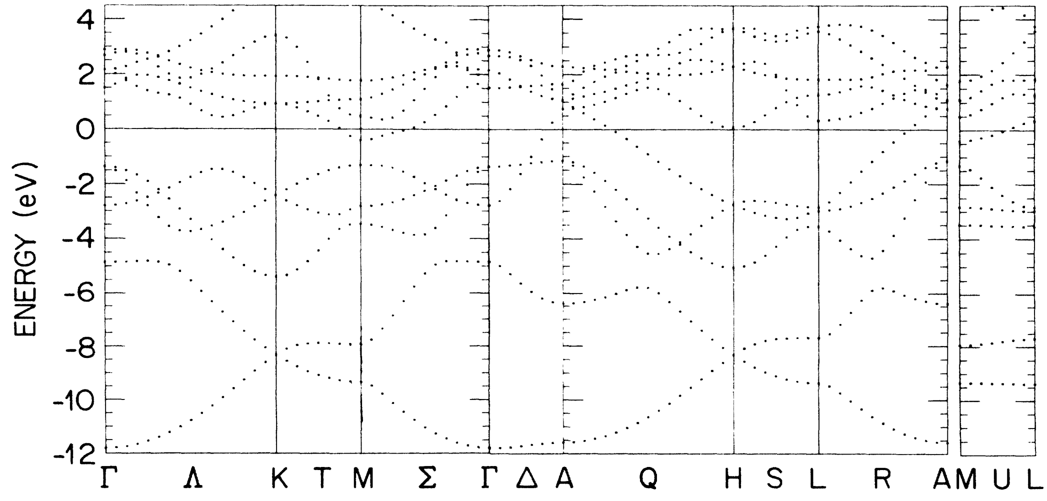

FIG. 4. Band structure of the h1 structure along symmetry lines. The zero of energy is at the Fermi level.

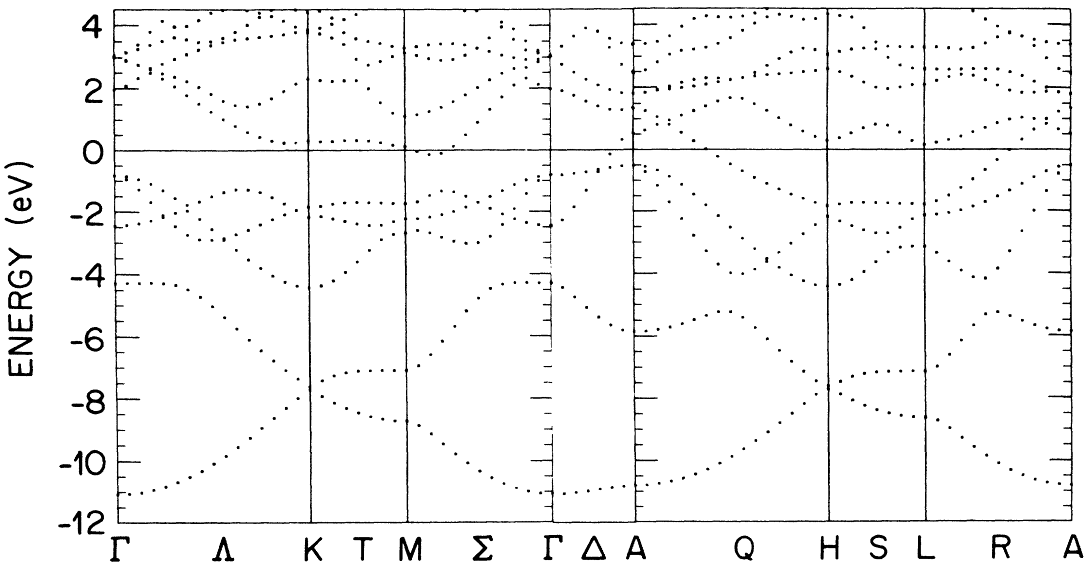

FIG. 5. Band structure of the tr3 structure. The points are labeled according to the corresponding points in the h1 Brillouin zone.

ing, but these bands, which are composed principally of Ca 3*d* levels, have rather small dispersion throughout the Brillouin zone in any case.

The valence bands are largely made up of bonding states of the Si double layers and of Ca 4*s* levels. The Si dangling-bond state hybridizes strongly with Ca 3*d* and 4*s* levels with a substantial dispersion both parallel and normal to the layers. This hybridization gives rise to a bonding combination of the Si*p*–Ca*d* states which disperses across the Fermi level (along lines *Q* and *R*) and an antibonding combination which is entirely unoccupied.[17] A mainly Ca *d* state above the Fermi level at point *A* disperses along line Δ to a mainly Ca *s* state below the Fermi level at point Γ. Along lines *Q* and *R*, the pure Si *p* state at point *A* hybridizes strongly with Ca *d* levels. We do not find any evidence of Ca 3*p* states near the Fermi level. It is doubtful then, especially in view of the insensitivity of our results to stacking sequence, that the Ca 3*p* state could be shifted to the Fermi level at the CaSi$_2$/Si(111) interface, as suggested by the empirical tight-binding results of Ref. 7.

The Fermi surface in CaSi$_2$ (for any one of the three stackings considered here) consists of a hole pocket centered around point *A* and smaller pockets of heavier electrons near the *U* line (from point *L* to point *M*). The shape of the hole part of the Fermi surface shows little dependence on the layer-stacking sequence and is approximately ellipsoidal. Its area is altered by changes in the Fermi level due to changes in dispersion affecting the electron part of the Fermi surface. The shape of the electron part depends very sensitively on the dispersion of the bands near the *U* line in the Brillouin zone, varying more with differences in layer stacking, and gives rise to a change in the position of the Fermi level relative to the valence bands for the h1 structure. The hole states exhibit strong Ca*d*–Si*p* hybridization at the Fermi surface, while the electron states are primarily Ca *d* in character. It is worth noting that for ballistic transmission of electrons through the CaSi$_2$/Si(111) interface it is the states near the electron part of the Fermi surface of CaSi$_2$ which are relevant, since these states lie in the same part of the surface Brillouin zone as the conduction-band minimum in silicon.

In conclusion, we have studied the electronic and

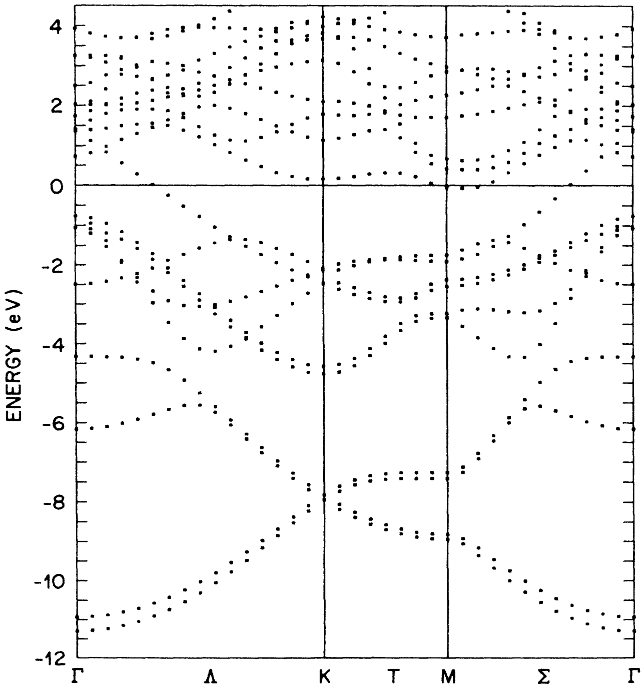

FIG. 6. Band structure of the tr6 structure. The points are labeled according to the corresponding points (see text) in the h1 Brillouin zone.

structural properties of $CaSi_2$ for three different stacking sequences. The values of the structural parameters calculated are in excellent agreement with experimental data, where available. We find that the band structure depends only weakly on the stacking sequence (and the resulting changes in Ca-Si coordination) and that the structural energies of the three stacking sequences are essentially indistinguishable. This supports a picture of the Ca-Si interaction in these systems in which the Ca layers interact mainly with the dangling bonds of the Si double layers, with only minor further interaction between Ca and Si. The 3*d* states of the Ca atom are found to play a crucial role in the electronic structure of this material at the Fermi level. These states hybridize strongly with the dangling-bond states of the Si double layers to form a band which crosses the Fermi level and gives rise to a holelike part of the Fermi surface. An electronlike part of the Fermi surface consists primarily of Ca *d* states. The predominance of the Ca *d* states near the Fermi level in this material suggests that although Ca is not a transition metal, there may be stronger similarities of the electron transport through the $CaSi_2$/Si(111) interface to that through the transition-metal silicide, $CoSi_2$ and $NiSi_2$, interfaces with Si than was naively expected from atomic arguments.

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