

Brief Reports

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Comparison of adamantane and fluorite NiSi₂

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It has recently been proposed that surface-stabilized layers of adamantane NiSi₂ as thick as 180 Å may exist on Si(100). We calculate the adamantane structure to have 1.54 eV less cohesive energy than the fluorite and conclude such thick layers cannot exist. Comparisons of the energy bands, projected densities of states, and charge densities give some insight into why fluorite is the preferred structure.

Ion channeling experiments¹ indicate that low coverages of Ni deposited on Si(100) disperse into the tetrahedral interstitial voids of the Si lattice at room temperature. Chang and Erskin,^{2,3} based on photoemission data and a (200) transmission-electron diffraction (TED) spot,⁴ observed after annealing at temperatures below which cubic NiSi₂ ordinarily forms, concluded that a thin ordered diffusion layer of NiSi₂ (adamantane structure⁵) exists between the Ni₂Si or NiSi and the silicon. For Ni films that were not too thick, 25–50 Å, an 800°C anneal resulted in 90–180 Å of NiSi₂ covered by a thin layer of 2×1 reconstructed Si. Because the NiSi₂ diffused below the Si, they speculated that fairly thick layers of surface-stabilized adamantane NiSi₂ exist in spite of the inability of their TED data to distinguish between the adamantane and fluorite structures.

Using a semiempirical approach, Bisi, Chiao, and Tu⁶ calculated partial densities of states for adamantane interstitials and ordered structures and concluded there was evidence for the existence of both interfacial phases containing Ni interstitials in an adamantane geometry and epitaxial silicon-silicide interfaces. Hamann and Mattheiss⁷ found the adamantane NiSi₂ 1.33 eV less stable than the fluorite and concluded the thick surface-stabilized adamantane film does not exist. They also compared adamantane and fluorite monolayers on two-layer hydrogen terminated Si(111) films but we are not convinced that conclusions about (100) diffusion layers between silicon and silicides can be drawn from these results. In this Brief Report we compare both the electronic structure and the energetics of the two struc-

tures using the linear combination of Gaussian-orbitals method.

We discovered that in our previous fluorite NiSi₂ calculations⁸ we had misweighted a few of the points in our 74 point sample⁹ of the irreducible wedge of the Brillouin zone (BZ). With that correction and the addition of $xyze^{-ar^2}$ fitting functions¹⁰ to the adamantane Ni, the self-consistent calculation here is identical to that of Ref. 8. We used the Si lattice constant of 5.429 Å for the adamantane structure and $a = 5.395$ Å for the fluorite.⁸ These are confirmed by Ref. 7 to be very close to the equilibrium lattice constants. The total energy per unit cell (in Ry) is given by

$$E_T = \sum_{\mathbf{k} \text{ occ}} \int \psi_{\mathbf{k}}^* (-\nabla^2 + \epsilon_{xc} - \frac{1}{2} V_{\text{Coul.}}) \psi_{\mathbf{k}} d^3r + \frac{1}{2} \sum_i Z_i V'_{\text{Coul.}}(\mathbf{R}_i) . \quad (1)$$

Here $V_{\text{Coul.}}$ is the total Coulomb potential¹¹ and $V'_{\text{Coul.}}(\mathbf{R}_i)$ is the Coulomb potential at the i th nucleus due to the electrons and all other nuclei in the crystal. $\epsilon_{xc} = (-0.916/r_s) - 0.88/(r_s + 7.79)$ is the exchange-correlation density functional and Z_i is the i th nuclear charge. It is well known^{12,13} that because it is variational, E_T will be quite insensitive to small errors in the input potential from which $\psi_{\mathbf{k}}$ and ρ , the charge density (upon which ϵ_{xc} and the Coulomb potentials depend), are calculated. The self-consistent input potential was calculated by extrapolating the charge density calculated at 16 points of the $\frac{1}{48}$ th irreducible wedge of the BZ to 74 points at which eigenvalues were obtained.⁸ In Table I we

TABLE I. The total energy (in Ry) per unit cell of both NiSi₂ structures calculated with 6, 16, and 74 point samples of the BZ irreducible wedge. The column labeled 74* has a more tightly packed set of fitting Gaussians on atomic sites; 74** has, in addition, Gaussians on empty sites.

Points	6	16	74	74*	74**
Adamantane	-4161.801 73	-4161.818 89	-4161.820 11	-4161.839 96	-4161.841 77
Fluorite	-4161.936 56	-4161.947 47	-4161.948 11	-4161.953 71	-4161.955 19
Difference	1.834 eV	1.749 eV	1.741 eV	1.548 eV	1.543 eV

list E_T calculated from 6, 16, and 74 point irreducible wedge samples.¹⁴ The fluorite E_T is 0.95 eV more negative than our original⁸ result, of which 0.11 eV can be attributed to using a full 74 point sample and the remainder to correcting the weighting of the points.

In determining E_T we fit ϵ_{xc} and ρ , from which $V_{Coul.}$ is obtained without further fitting. This is the main disadvantage of the linear combination of Gaussian-orbitals method compared to the linear augmented plane-wave method used by Hamann and Mattheiss.⁷ Again, because of the variational nature of E_T , errors introduced by fitting the self-consistent input potential should have a negligible effect on E_T but errors in ϵ_{xc} and $V_{Coul.}$ may have a large effect. We therefore chose an entirely new set of fitting Gaussians which were packed slightly more tightly and then, in addition, put Gaussians in the empty sites symmetrically equivalent to the Ni sites with the results shown in the last two columns of Table I. It is interesting to note that even though there is no variational principle at work, every improvement in the fit resulted in the total energy becoming more negative.¹⁵ We doubt that there is another 0.21-eV reduction in the adamantane-fluorite energy difference to be obtained by improved fitting and the small discrepancy between our result and Ref. 7 is unresolved. A comparison of the individual crystal energies is not possible because theirs is a rigid core calculation whereas ours is all electron. Subtracting E_T from the spin-polarized atomic energies we previously obtained¹⁶ yields 16.72 eV cohesive energy for NiSi₂. This is 2.06 eV larger than the experimental value,¹⁷ which is not atypical for transition metal silicides and can be compared with the 3.16-eV deviation from experiment obtained¹⁶ for Ni₃Si.

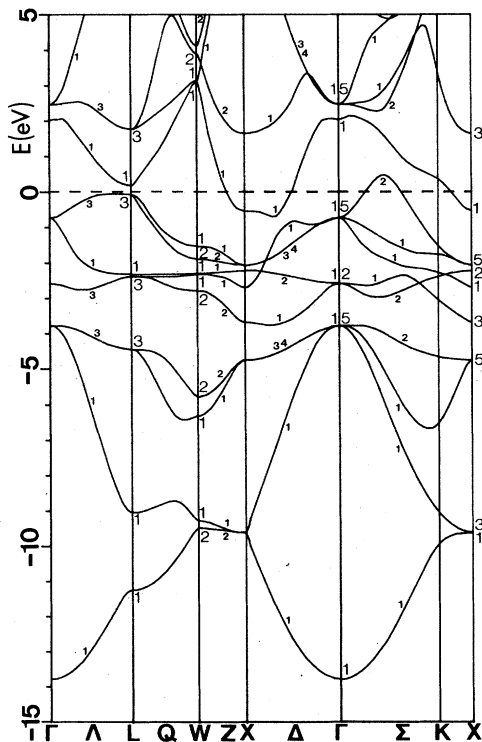


FIG. 1. Energy bands of adamantane NiSi₂ in eV from the Fermi energy.

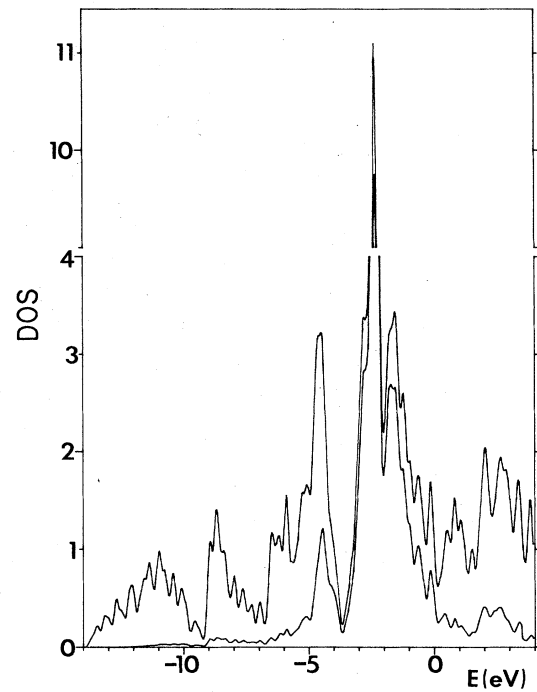


FIG. 2. Projected Ni *d* and total DOS in units of electrons per unit cell per eV.

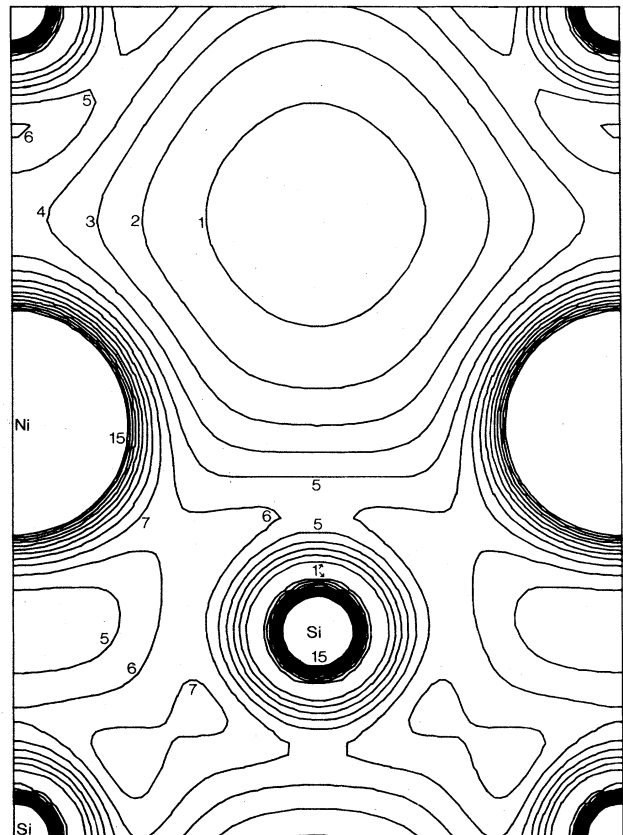


FIG. 3. Contours of constant valence-charge density in units of hundredths of an electron per cubic bohr in the (110) plane. Contours greater than 15 in the atomic cores are not plotted.

We consider the 1.54 eV higher energy of the adamantane structure to be convincing evidence that it does not exist in the thick surface-stabilized films proposed by Chang and Erskine.^{2,3} Whether very thin ordered adamantane diffusion layers exist between silicon and silicides remains an open question, as does the stoichiometry of the layers if they exist. That isolated Ni impurities live in Si adamantane cages is almost certainly the case.¹ A comparison of the adamantane and fluorite electronic structures yields some insight into the total energy difference. Correcting our BZ weighting error caused negligible changes in the fluorite band structure and density of states (DOS) and we refer to Ref. 8 for those figures. In Fig. 1 we display the adamantane energy bands. Note the gap at the top of what looks like the Si valence bands. A Löwdin¹⁸ projection indicates that the Γ_{15} level at the top of these bands has 68% nickel d character compared with 70% for the corresponding fluorite Γ_{25} level. The fluorite level lies 1.51 eV lower relative to the Fermi energy, however. The Γ_{12} levels are 92% and 94% Ni d with the fluorite lying 0.97 eV lower. The Γ_{15} just below E_F is only 7.4% Ni d . The Γ_{15} lying 1.72 eV above E_F which is 35% Ni corresponds to the fluorite Γ_{25} , 2.44 eV above E_F which is 43% Ni d . (We use three Ni d radial basis functions. That the projected d character adds to more than one, implies some $4d$ character in the high-lying

states.) Thus we conclude that the reduced adamantane cohesive energy arises more from having occupied d levels lying closer to E_F than from reduced hybridization. Figure 2 compares the total DOS and the Ni d DOS, confirming the results based on Γ levels only. The total projected Ni d charge is 9.09 electrons compared with the fluorite 9.08; however, the total Ni Löwdin projected charge is 10.50 electrons compared with the fluorite 11.12. The Si with (without) Ni near neighbors has 3.80 (3.70) electrons. Thus the adamantane structure also appears to have a much reduced ionic contribution to the bonding. Figure 3 is a plot of contours of constant charge density. In the adamantane structure there are four Ni—Si and four Si—Si bonds of length $\sqrt{3}a/4$, whereas the fluorite structure has eight Ni—Si bonds of the same length. If the covalent bond strength is assumed to be proportional to the bond charge density minimum, we see that the adamantane Si—Si bonds are about the same strength as the fluorite bonds but the adamantane Ni—Si bonds are slightly weaker. The Si—Si bonds are, however, much weaker than they are in silicon.¹⁹

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³Y.-J. Chang and J. L. Erskine, Phys. Rev. B **28**, 5766 (1983).

⁴This reflection is forbidden in the diamond structure.

⁵This structure consists of three interpenetrating fcc lattices with Si at (000) and $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ and Ni at $(\frac{1}{2}00)$.

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⁹We mistakenly included the $(\frac{11}{12}\frac{7}{12}\frac{1}{12})$ point which lies outside the BZ. This is equivalent to double weighting the $(\frac{1}{12}\frac{5}{12}\frac{11}{12})$ point.

The pair of points $(\frac{1}{6}\frac{1}{3}1)$ and $(\frac{5}{6}\frac{2}{3}0)$ are equivalent, and together occur 24 times in the BZ. We gave each a weighting of 24 previously. The same error was made with the $(\frac{1}{6}\frac{2}{3}\frac{2}{3})(\frac{5}{6}\frac{1}{3}\frac{1}{3})$ pair.

¹⁰These functions are used on the Si which is at a tetrahedral site for both crystal structures but not on the fluorite Ni which is at a cubic site.

¹¹We use the textbook convention for the sign of the Coulomb potential. When we wrote this equation elsewhere, we absorbed the sign of the electronic charge in V_{Coul} , which may have caused

some confusion.

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¹³B. K. Bhattacharyya, D. M. Bylander, and L. Kleinman, Phys. Rev. B **31**, 2049 (1985).

¹⁴ E_T and ρ are always consistent, i.e., calculated from identical sampling schemes. We also calculated E_T for the fluorite structure using the 16–74 point extrapolation and obtained $E_T = -4161.93988$ Ry. This lies close to the 6 point result rather than between the 16 and 74 point results which we had expected.

¹⁵More Gaussians alone do not insure a better fit. For example, when we included a very short-range Gaussian on the empty site, the density of points at which the charge density was calculated in that region was sufficiently sparse that its coefficient could not be properly determined. In this case the inclusion of an extra Gaussian resulted in an 0.19 eV increase in E_T .

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¹⁷The experimental value was obtained by adding the NiSi₂ heat of formation and twice the Si cohesive energy used in Ref. 7 to the Ni cohesive energy listed in C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976), p. 74.

¹⁸P. O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

¹⁹A. Zunger, Phys. Rev. B **21**, 4785 (1980), see Fig. 3.