Ground-state properties of $CoSi_2$ determined by a total-energy pseudopotential method

V. Milman
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

M. H. Lee and M. C. Payne
Department of Physics, Cambridge University, Cambridge CB3 0HE, United Kingdom
(Received 14 February 1994)

We calculate the lattice properties and electronic structure of cobalt disilicide using an *ab initio* total-energy method with optimized pseudopotentials. Special attention is paid to the development of a soft robust pseudopotential for the 3*d* element Co. The calculated band structure of $CoSi_2$ agrees well with the results of all-electron studies and the equilibrium lattice constant, bulk modulus, and zone-center phonon frequencies obtained are in good agreement with experimental data.

I. INTRODUCTION

In the last decade transition-metal silicides have received increasing attention because of their practical importance as contact materials in Si electronics.[1–10] Cobalt disilicide crystallizes in the cubic fluorite structure; it has low resistivity and only 1.2% lattice mismatch with silicon,[11,12] so that nearly ideal interfaces are possible in integrated Si matrices. The complicated structures of the $CoSi_2$/Si interfaces were determined only recently using *Z*-contrast electron microscopy technique.[5] Both the (100)- and (111)-oriented interfaces are characterized by complex reconstructions, making these systems intractable for existing *ab initio* techniques based on all-electron formalisms.

An alternative to a completely first-principles investigation is the tight-binding (TB) total-energy study. The TB approach utilizes the electronic structure information from *ab initio* calculations, and it has been shown to describe the lattice properties of the transition-metal silicides rather accurately.[10] This scheme relies not only on the computed band structure but also on the measured lattice properties (the equilibrium lattice constant a_0 and the bulk modulus B) in determining the TB parameters. Usually the experimental data required are readily available, while there might be discrepancies between the band structures calculated using different methods. In the case of cobalt disilicide, however, one encounters an unexpected problem. The band structure of this compound is well established by different authors using various all-electron local-density approximation (LDA) methods.[8–10,3] The adequacy of the first-principles description of the electronic structure has recently been confirmed by positron-annihilation experiments.[3] At the same time, experimental data on the lattice properties of bulk $CoSi_2$ are largely contradictory. The lattice constant is reported as either 5.365 (Ref. 11) or 5.356.[12] The bulk modulus values measured using different techniques vary by as much as 40%. Perhaps the most accurate result, $B=169\pm5$, was obtained from the measurement of ultrasonic wave velocities.[2] The dynamical modulus as estimated from the acoustic-phonon dispersion curves is 187 ± 30 GPa.[6] Finally, an elasticity-theory analysis of the deformation of the $CoSi_2$ film on the Si substrate produces an even higher value of 240 GPa.[4] The only *ab initio* calculation of the bulk modulus gives 190 GPa.[8]

These results suggest that experimental studies of $CoSi_2$ should be continued, particularly including an equation-of-state (EOS) measurement, and that a completely first-principles method could be a preferred way of treating the bulk silicides and the silicon-silicide interfaces. The main contender for such a study is the pseudopotential total-energy method,[13] but its success depends crucially on the availability of transferable robust pseudopotentials for the relevant elements.

The difficulties associated with the construction of the soft norm-conserving pseudopotentials for 3*d* transition metals have become a part of folklore in the electronic-structure community. In our opinion this problem is significantly less severe than commonly suggested. The situation is reminiscent of that with pseudopotential studies of oxides, which are now routinely performed[14] even without invoking the ultrasoft-potential technique. We would like to show in this paper that an optimized potential for Co produces accurate and rapidly convergent results for lattice properties, and it also provides sufficient accuracy in the calculation of the one-electron properties. The importance of the latter issue is related to the main challenge of the future *ab initio* studies of the silicon-silicide interfaces, i.e, the problem of the relation between the local atomic structure and the Schottky barrier height.

We present in this paper an optimization strategy for the generation of the cobalt pseudopotential with an emphasis on its convergence properties. The optimization technique and the transferability of the *d*-only nonlocal pseudopotential from the atomic tests is discussed in Sec. II. Some details of the conjugate-gradient scheme for the total-energy calculation are described in Sec. III, together with the results of the tests for bulk silicon and cobalt. The calculated lattice properties of $CoSi_2$ are analyzed in Sec. IV, where we pay special attention to the finite-basis-set correction.[15] Finally, we compare in Sec. V the calculated band structure and the charge-density distribution to the all-electron calculations results.

II. OPTIMIZED PSEUDOPOTENTIAL

To generate the Co pseudopotential, we have used a kinetic-energy-optimization scheme[16,17] with a number of modifications and enhancements.[18] In our scheme only three spherical Bessel functions are used to expand the pseudo-wave-functions in the core region. The optimal expansion coefficients are obtained under the constraints of norm conservation, and continuity of the pseudo-wave-function and its first derivative at the core radius r_c. The second and higher derivatives of the pseudo-wave-functions are not forced to be continuous in our scheme. This allows a more flexible optimization of the pseudo-wave-functions, and hence a softer pseudopotential can be obtained. The (optimization) cutoff wave vector q_c is used as a kinetic energy filter to fine-tune the character of the pseudo-wave-functions, so that the pseudopotential has the best phase shift over a range of scattering energy which ensures its transferability.

A slightly ionic configuration of $[Ar]3d^7 4s^1 4p^{0.25}$ was used to generate s, p, and d semilocal potentials for Co, with $r_c^s=2.0$, $r_c^p=2.0$, $r_c^d=2.4$, and $q_c^s=2.70$, $q_c^p=4.39$, $q_c^d=5.48$ (all in atomic units).

The advantage of the above strategy is that not only can we generate a very soft d potential for Co, but we can also take advantage of the q_c-tuning procedure to control the shape of the noncritical s and p potentials in such a way that these two potentials become very similar to each other. When a mixture of these potentials is chosen as the local potential, the corresponding nonlocal components become small, and both can be discarded without sacrificing the accuracy of the potential. This provides a significant saving in memory and computation time. Indeed, it has been noticed[19,20] that in order to use Kleinman-Bylander[21] separable nonlocal pseudopotentials for transition metals one must choose the s potential as local, which results in eight projectors to be evaluated (three for p and five for d). In our case of Co, there are only five nonlocal projectors in the potential because we have found a local potential capable of representing both s and p scattering. Detailed discussion of the pseudopotential-generation procedure and test results for a number of transition metals will be published separately.[18]

We have tested three Kerker[22] pseudopotentials for Si that were generated using pd, sp, or s-only nonlocal projectors, with the local components chosen as s, d, and p projectors, respectively. It might seem that the Si potential should not present a problem in this study in view of the variety of successful simulations of Si and Si-containing systems.[23] However, the majority of the previous pseudopotential calculations that utilized the Si potential have been performed for systems composed of sp elements only. Thus, the importance of the correct description of the d scattering for the current investigation remains to be established. The results of calculations for Co, Si, and $CoSi_2$ are given in the following sections.

III. TOTAL-ENERGY PSEUDOPOTENTIAL METHOD

The LDA calculations were performed using the CASTEP (Cambridge Serial Total Energy Package) computer code. The basic idea of the underlying method[13] is to solve the Kohn-Sham equations by minimizing the total-energy functional rather than by diagonalizing the Hamiltonian matrix. We use a plane-wave basis to expand the wave functions; the band-by-band minimization[24] is achieved by the preconditioned conjugate-gradient search in the space of the expansion coefficients.[13] The ion-electron interaction is represented by nonlocal pseudopotentials in Kleinman-Bylander form.[21] The exchange-correlation potential due to Ceperley and Alder is employed as parametrized by Perdew and Zunger.[25] The main features of the method are described extensively by Payne *et al.*,[13] so we address here only those points that are relevant to the particular study and have not received sufficient attention in the review paper.[13]

The Brillouin-zone (BZ) integration is performed in CASTEP using the special points scheme. The quality of the reciprocal-space sampling becomes a secondary consideration in the study of complex systems with hundreds of atoms per supercell because of the small volume of the BZ.[23] Moreover, such calculations are mainly performed for semiconducting systems where sufficient accuracy can be achieved by employing very moderate k-point sets, usually by taking just one k point in the case of the largest systems currently studied using *ab initio* methods. Metallic systems with small unit cells, like the one considered in this paper, have to be treated more carefully by using a denser mesh of k points in the BZ. For example, the all-electron calculations for $CoSi_2$ required from 28 to 505 points in the irreducible part of the BZ, depending on the desired accuracy of the tetrahedron integration scheme.[3,8,9] The conjugate-gradient technique would not be worth using if such a high density of k points were required.

In order to reduce the number of sampling points we use the energy-level smearing technique as suggested by Fu and Ho,[26] and modified by Needs, Martin, and Nielsen.[27] This method has an advantage of introducing the energy functional that is variational with respect to the wave-function coefficients,[27] and converges rapidly with the number of k points used. The only drawback is that the functional depends on the smearing width σ. The usual procedure is to decrease σ in order to estimate the limit of $E_{\rm tot}(\sigma=0)$.[27–30] We employed the so-called entropy correction term to the energy functional[29] that allows the accurate evaluation of the total energy while using the values of σ of order of 1 eV, as compared to the more traditional range of 0.01–0.1 eV.[28,30] This scheme with $\sigma=0.5$ eV produces the total energy of $CoSi_2$ that differs by less than 1 meV from the $E_{\rm tot}(\sigma=0)$. The functional calculated using the entropy correction scheme can be shown to be accurate to at least $O(\sigma^3)$.[29] However, the smearing scheme with the entropy correction introduces an additional contribution to the Hellmann-Feynman forces. For this reason we chose to reduce the smearing width further to 0.1 eV for the frozen-phonon calculations, where we used both the total-energy and ionic forces to evaluate the phonon frequencies. We will show that the entropy-corrected smearing scheme is sufficiently accurate when using ten

($q=4$) or even two ($q=2$) special points in the irreducible part of the BZ of $CoSi_2$, where q is the parameter that determines the number of Monkhorst-Pack special points.[31]

The self-consistent conjugate-gradient minimization includes an additional step in the case of the metallic system as compared to an insulator or a semiconductor. At the end of each self-consistency iteration we use the updated energy eigenvalues to calculate the new Fermi energy. This value of E_F is used to recalculate the occupation numbers and all related properties, e.g., the charge density. Furthermore, it is only at this stage that we symmetrize the charge density.[32] One might expect such a procedure to lead to an instability during the conjugate-gradient steps that change the charge density without preserving its correct symmetry. We find, however, that it is sufficient to introduce mixing of the input and output charge densities at the first few iterations to guarantee stable convergence. No mixing is required when the charge density is reasonably close to the ground-state density.

Finally, we use CASTEP to calculate the band structure at arbitrary points in the BZ using the self-consistent charge density generated using the set of the special k points.[31] The eigenvalues of the states in the conduction band cannot be obtained from a self-consistent CASTEP run, because the empty states do not contribute to the total-energy functional and so cannot be treated variationally. In the spirit of the iterative approach, we find the eigenvalues using the same preconditioned conjugate-gradient scheme as for the total-energy minimization. The difference is that now we minimize the expectation value of the Hamiltonian for the wave function of the given band, i.e., the eigenvalue itself. This results in the different expression for the optimal step along the conjugate-gradient direction, and also simplifies the procedure by eliminating the self-consistency loop. The same constraint of orthogonality of the wave function is used as in the total-energy minimization. The subspace rotation of the wave functions[13] is not, strictly speaking, necessary when using a Gram-Schmidt orthogonalization to the higher bands, but we found that it increases the convergence rate.

Now we will discuss briefly the results for the lattice properties and band-structure calculations for the pure elements Si and Co. The results for the lattice properties of Si computed with three different pseudopotentials are shown in Table I. We performed the total-energy calculations using cutoff energies for the plane-wave expansion E_c between 200 and 500 eV and $q=2$, 4, and 8 sets of special points[31] in the BZ for the primitive unit cell. The calculations for bulk Si are absolutely converged at $E_c=400$ eV and $q=4$, and the results described below were obtained using these values.

All three pseudopotentials describe the ground-state properties of Si reasonably well, with the *sp*-nonlocal pseudopotential performing slightly less satisfactorily than the others. Both the *s*-only nonlocal[23(a),23(c)] and *pd*-nonlocal[23(b)] potentials have been used successfully in *ab initio* states of systems that did not contain *d* elements. We chose the *pd*-nonlocal pseudopotential for $CoSi_2$ expecting that it would represent the *d*-scattering channel in the compound more accurately. All further results were obtained with this potential unless otherwise stated.

The EOS for Si is shown in Fig. 1 for a $\pm 10\%$ range of the volume change. The high degree of convergence is reflected in the smooth character of both the $E(V)$ and $P(V)$ curves, and mainly in the fact that the Murnaghan EOS parameters for these two curves are very close (Table I). The lattice parameter is approximately 1% lower than the experimental value as is often the case in the LDA calculation. The optical-zone-center phonon frequency evaluated using the frozen-phonon approach agrees well with experiment (Table I). The third-order coupling constant γ for this mode was found to be -50.6 eV/Å^3, as compared to the experimental estimate of -47 eV/Å^3 or to the theoretical result of -48.4 eV/Å^3 (both values are taken from Ref. 34, as well as the definition of γ).

The band energies for Si at symmetry points in the BZ are given in Table II. We compare our results to some of the variety of published data on the electronic structure of Si. There is an obvious good agreement between all sets of data, independent of the computational technique employed. The only important difference between all the LDA calculations and the empirical pseudopotential results[40] is that the LDA approach invariably underestimates the energy gap. Analysis of Table II shows that

TABLE I. Lattice properties of silicon calculated with three different pseudopotentials (see text). $\omega_{LTO}(\Gamma)$ is the frequency of the optic mode at the zone center. The results from the Murnaghan EOS fit for the energy and pressure are given separately.

Potential		a_0 (Å)	B (GPa)	dB/dP	$\omega_{LTO}(\Gamma)$ (cm^{-1})
pd nonlocal	From *P-V*	5.378	97.1	4.19	
s local	From *E-V*	5.386	96.3	4.18	498
s-only nonlocal	From *P-V*	5.479	90.2	4.36	
p local	From *E-V*	5.483	89.9	4.30	
sp nonlocal	From *P-V*	5.331	106.4	5.0	
d local	From *E-V*	5.333	105.7	4.8	
Experiment		5.429[a]	100.1[b]	4.23[b]	513[c]

[a]Reference 12, extrapolated to $T=0$ K.
[b]Reference 33, elastic constants were measured at -196 °C.
[c]Reference 34.

TABLE II. Comparison of characteristic high-symmetry states in Si. PP indicates a pseudopotential calculation, including LDA-PP (present work). The energy values are given in eV with respect to $\Gamma_{25'}$.

	LAPW[a]	LCGO[b]	LMTO[c]	OAPW[d]	LDA-PP[e]	Model PP[f]	LDA-PP[g]	Expt.[h]
Γ_1	−12.02	−12.20	−11.87	−11.87	−11.71	−12.36	−12.09	−12.4
$\Gamma_{25'}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Γ_{15}	2.49	2.66	2.59	2.73	2.54	3.42	2.57	
$\Gamma_{2'}$	3.18	3.05	3.11	2.99	3.42	4.10	3.57	
Γ_1	7.46			7.50	7.64	7.69	7.78	
Γ_{12}	7.86				7.79	8.19	7.85	
X_1	−7.84	−8.03	−7.75	−7.77	−7.65	−7.69	−7.85	
X_4	−2.82	−3.11	−2.72	−2.72	−2.77	−2.86	−2.91	−2.9
X_1	0.55	0.79	0.62	0.68	0.53	1.17	0.61	
X_4	10.32	10.11	10.10	9.95	10.07		10.19	
$L_{2'}$	−9.64	−9.86	−9.53	−9.57		−9.55	−9.68	−9.2
L_1	−7.06	−7.25	−6.93	−6.91		−6.96	−7.09	−6.5
$L_{3'}$	−1.16	−1.40	−1.05	−1.16		−1.23	−1.21	−1.2
L_1	1.40	1.46	1.57	1.36		2.23	1.58	
L_3	3.37	3.66	3.51	3.55		4.34	3.32	

[a]Reference 35. LAPW is linear augmented-plane-wave method.
[b]Reference 36. LCGO is linear combination of Gaussian orbitals.
[c]Reference 37. LMTO is linear muffin-tin orbital method (in atomic-sphere approximation).
[d]Reference 38. OAPW is overlapping augmented-plane-wave method.
[e]Reference 39. LDA pseudopotential method with the Hamiltonian diagonalization.
[f]Reference 40. Empirical potential fitted to the experimental data.
[g]Present calculation.
[h]Experimental data from the angle-resolved photoemission, cited from Ref. 36.

our results are in better agreement with the pseudopotential calculation by Needs[39] than with the all-electron data. However, this might be due simply to the fact that the same form of the exchange-correlation potential was used in this work as in Ref. 39. Finally, the calculated band energies are close to the experimental estimates of the valence-band eigenvalues as given in Ref. 36. To summarize, both the lattice and electronic properties of Si are reproduced correctly by the pseudopotential used.

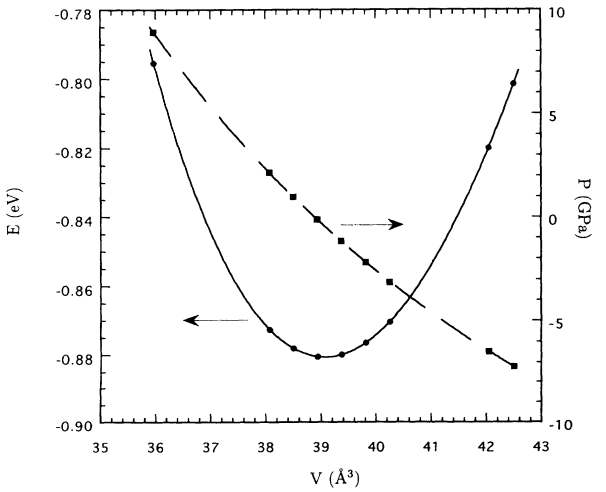

FIG. 1. Equation of state for Si. The total energy is shown by circles, the pressure by squares. Fit is the Murnaghan analytical EOS. The total-energy scale is shifted by an arbitrary constant.

In order to test the Co pseudopotential we calculated the lattice properties of fcc β-Co. This modification is stable at temperature higher than 420 °C and undergoes martensitic transformation into hcp α-Co phase on cooling.[12] The cubic modification was chosen as the test object because in this case the atomic packing is more similar to that in the cubic fluorite structure of $CoSi_2$, and the EOS calculations are simpler than in case of hcp symmetry.

We used $E_c = 500$ eV and the $q = 8$ set of special points in all the calculations described below. The equilibrium lattice properties of β-Co obtained from the Murnaghan fit to the EOS are listed in Table III. The comparison

TABLE III. Lattice properties of fcc β-Co. The results calculated using the Murnaghan fit for the energy and pressure are given separately.

	a_0 (Å)	B (GPa)	dB/dP
From P-V[a]	3.448	297±1	4.7±0.1
From E-V[a]	3.447	295±2	4.3±0.4
LAPW[b]	3.412	284	
Experiment	3.548[c]	212±10[d]	

[a]Present calculation.
[b]Reference 41.
[c]References 12 and 42.
[d]Reference 42.

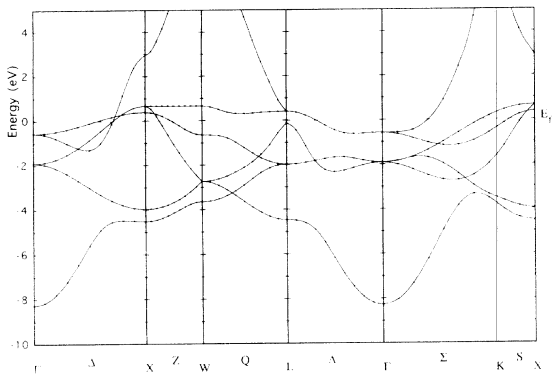

FIG. 2. Band structure of β-Co along high-symmetry directions ($a_0=3.447$ Å).

with experiment might be misleading in this case, taking into account that the fcc phase is metastable. The lattice-constant measurements refer either to temperatures above the transition point[12] or to the $Co_{0.92}Fe_{0.08}$ alloy.[42] The bulk modulus is calculated using the elastic constants measured at room temperature in the neutron-scattering experiments on the $Co_{0.92}Fe_{0.08}$ alloy.[42] Thus, the usual problem of the correspondence between the static and dynamical modulus is compounded by the compositional dependence of B in the alloy. Having this in mind, we expect our results to be in better agreement with another LDA calculation[41] than with the measured data. Indeed, the theoretical lattice constant is substantially shorter than the experimental value and the bulk modulus is overestimated by 35% (Table III), but both of these properties are in good agreement with the calculated results of Moruzzi, Janak, and Williams.[41]

The band structure of β-Co is shown in Fig. 2. It is qualitatively similar to the results of Moruzzi, Janak, and Williams,[41] and the band energies along the high-symmetry directions differ in these two calculations, typically by less than 0.5 eV. We obtained the valence bandwidth that was 0.7 eV lower than in Ref. 41. This discrepancy should be attributed mainly to the difference in the lattice constants (see Table III), and partly to the different choice of the exchange-correlation potential. The bandwidth calculated in this work using the lattice constant $a_0=3.412$ Å from Ref. 41 is 0.4 eV higher than for our calculated equilibrium lattice constant, in better agreement with the results of Moruzzi, Janak, and Williams.[41]

IV. APPLICATION TO COBALT DISILICIDE

The fluorite lattice of $CoSi_2$ contains three atoms in the primitive fcc unit cell, with the Co atom at the origin and two Si atoms at $a_0(\pm\frac{1}{4},\pm\frac{1}{4},\pm\frac{1}{4})$. In our calculations of lattice properties we used an energy cutoff of 500 eV and the $q=4$ set of special points.[31] Further increase of these parameters to 600 eV and $q=8$ changes the total energy by 0.5 meV, and the stress components by at most 0.1 GPa. For all practical purposes this set of parameters, $E_c=500$ eV and $q=4$, corresponds to the fully converged calculation. These low values are unusual for the system containing $3d$ metal, and can be attributed solely to the successful optimization of the Co pseudopotential.

The calculated lattice constant, bulk modulus, and its pressure derivative of $CoSi_2$ are $a_0=5.344$ Å, $B=182$ GPa, and $dB/dP=4.4$ (see Table IV and the corresponding EOS curves, Figs. 3–6). The lattice constant is underestimated by only 0.3%, which could be due to the thermal expansion, taking into account that the experimental values refer to the room-temperature measurements.[11,12] The calculated bulk modulus is in slightly better agreement with the dynamical modulus measured from the inelastic neutron scattering[6] than with the one obtained from ultrasonic experiments.[2] The difference between the theoretical value and these two experimental results is -3% and $+8\%$, respectively, both of them being within the LDA error range. Another LDA result, 190 GPa, was obtained using the linear muffin-tin orbital (LMTO), all-electron method.[8] These data strongly suggest that the value of 240 GPa measured for the $CoSi_2$

TABLE IV. Lattice properties of $CoSi_2$. Results obtained using uncorrected and corrected equations of state for pressure and energy that were calculated using different energy cutoffs and k-point sets are given separately.

E_c (eV)	q	B (GPa)			a_0 (Å)			dB/dP	
		E_{uncorr}	P_{corr}	E_{corr}	E_{uncorr}	P_{corr}	E_{corr}	P_{corr}	E_{corr}
300	4	139±93	230±10	181±23	5.2	5.340	5.24	6.0±1.3	2.4±2.1
400	2	158±33	216±12	187±8	5.33	5.292	5.324	5.3±1.6	6.5±2.8
400	4	187±4	195±2	192±1	5.332	5.325	5.338	4.0±0.3	4.5±0.4
500	4	181.3	181.8	181.3	5.345	5.342	5.345	4.5±0.1	4.4±0.1
			169±5[c]			5.356[b]			
Experiment			187±30[c]			5.365[d]			
			240±5[e]						

[a]Reference 2.
[b]Reference 12.
[c]Reference 6.
[d]Reference 11.
[e]Reference 4.

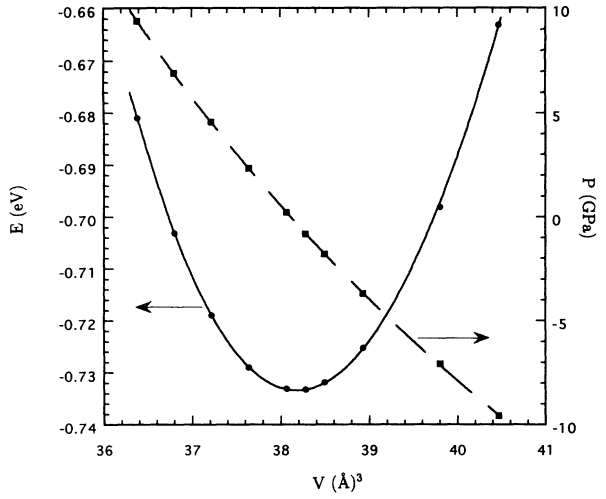

FIG. 3. Equation of state for $CoSi_2$ ($E_c = 500$ eV, $q = 4$). Notations as in Fig. 1.

films[4] cannot be used as the bulk modulus of this compound.

The agreement of the calculated ground-state properties with the experiment becomes worse if we use the *s*-only nonlocal potential for Si. In this case the lattice constant is overestimated by 2%, and the bulk modulus of 205 GPa is too high. The band structure is qualitatively similar to that obtained with the *pd*-potential (see Sec. V), but the valence *s* band is shifted down in energy by 0.2–0.5 eV. These results justify our choice of the *pd*-nonlocal pseudopotential with the *s*-local component for the study of $CoSi_2$.

The importance of the finite-basis-set correction[15] is illustrated by Table IV and Figs. 3–6. This correction accounts not just for the low cutoff energy (and number of plane waves), but more importantly for the finite number of the k points used. In effect, Table IV demonstrates convergence of the lattice properties with respect to both E_c and q. The jagged $E(V)$ curves obtained with the low values of these two parameters are transformed to a sensi-

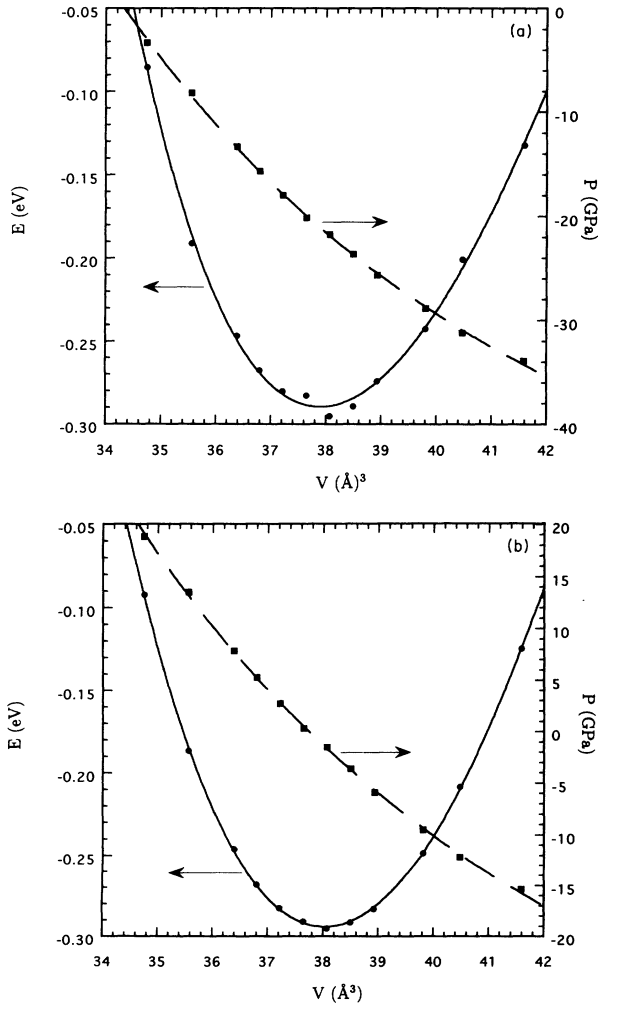

FIG. 4. Equation of state for $CoSi_2$ ($E_c = 400$ eV, $q = 4$), without the finite-basis-set correction (a) and with the correction (b). Notations as in Fig. 1.

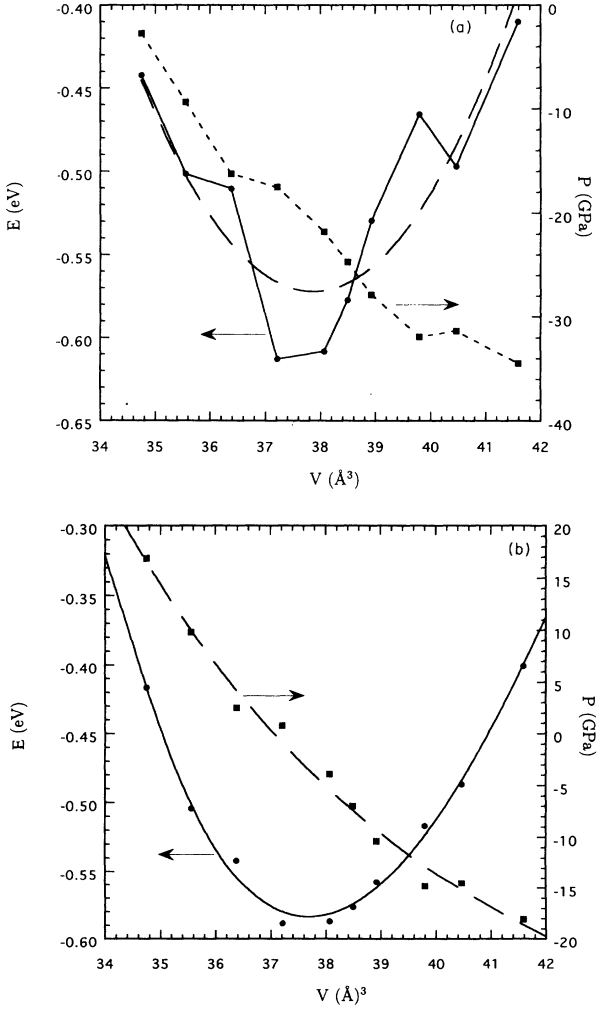

FIG. 5. Equation of state for $CoSi_2$ ($E_c = 400$ eV, $q = 2$). The energy fit in (a) is using quadratic polynomial. Other notations as in Fig. 4.

ble form that can be fitted to the Murnaghan EOS with reasonable accuracy. The uncorrected $E(V)$ curves in Figs. 4(a) and 5(a) can be fitted only using the simple quadratic polynomial, while the corrected curves allow even the accurate determination of the sensitive parameter dB/dP. The consistency between the lattice properties determined from the $E(V)$ and $P(V)$ curves improves with the increase of the cutoff energy, and can be used as a criterion for the convergence of the corrected results. Analysis of these data shows that the $q=2$ set of k points is not sufficient for BZ sampling irrespective of the cutoff used, while the $q=4$ set can be used reliably even with a cutoff energy as low as 400 eV (about 30 Ry).

We also performed the frozen-phonon calculations for two zone-center vibrational modes. The Raman-active phonon involves symmetric counterphase motion of the two Si atoms with the Co atom remaining at rest. The dependence of the total energy and of the ionic force on atomic displacement for this phonon is shown in Fig. 7. The frequency determined from the $E(u)$ and $F(u)$ curves is 268 and 265 cm^{-1}, respectively. The agreement

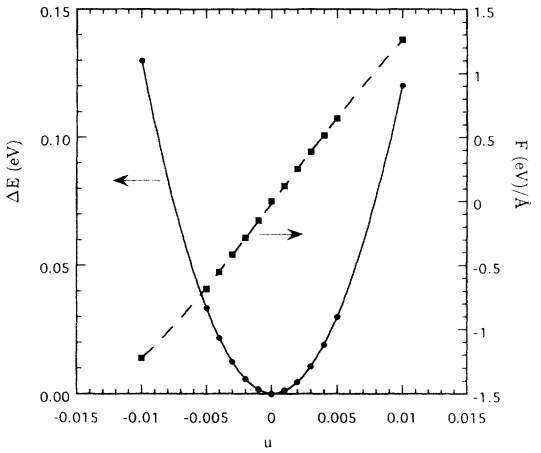

FIG. 7. The total energy and the force on the Si atom as a function of the atomic displacement for the Raman-active zone-center phonon. The energy is shown by circles, force by squares; lines represent polynomial fit. Displacement is in the (111) direction, and u is in units of lattice vectors.

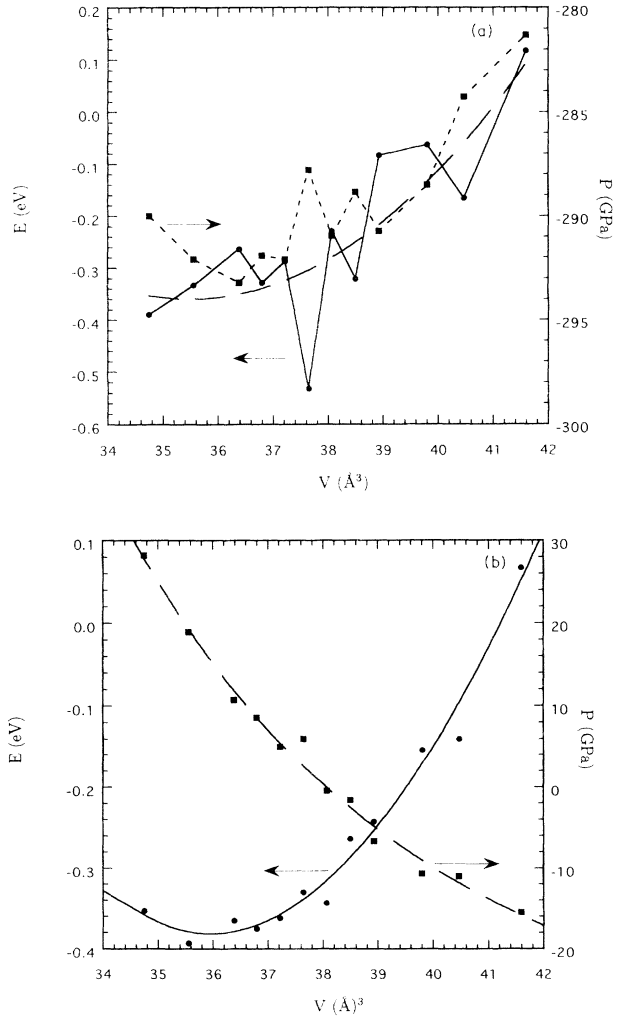

FIG. 6. Equation of state for $CoSi_2$ ($E_c=300$ eV, $q=4$). Notations as in Fig. 5.

between these two values reflects the high level of convergence of the calculation. The Raman spectroscopy shows a single peak for this mode at 267 cm^{-1}.[10] Our data are in excellent agreement with this result, while the TB calculation slightly overestimates the frequency [285 cm^{-1} (Ref. 10)]. The third-order coupling constant defined according to Ref. 10 was obtained from Fig. 7 as -13.8 or -13.2 eV/Å^3 using the $E(u)$ or $F(u)$ curves, respectively. The TB value is -11.15 eV/Å^3,[10] in reasonable agreement with our *ab initio* result. Note that the definition of the third-order coupling constant in Ref. 10 differs from that suggested in Ref. 34 by a factor of 2. Assuming that the bond deformation is twice as large in Si compared to the silicide, one expects $g_{Si}/g_{CoSi_2}\approx 8$.[10] Comparing our results from this section to those from Sec. III we get the ratio of 7.4, which confirms the internal consistency of the results.

Another zone-center phonon is IR active and has a higher frequency. The displacements for this mode are along the ⟨111⟩ direction, and the Si atoms move in phase with each other and counterphase with respect to the Co atom. The relative displacements are determined from the requirement that the center of mass remains at rest. Our frozen-phonon calculation gives the frequency for this mode as 331 cm^{-1}. To the best of our knowledge there are no experimental data available for this mode. The TB calculation produces a higher frequency of 371 cm^{-1},[10] which is consistent with the overestimate of the Raman-active phonon frequency.

V. ELECTRONIC STRUCTURE OF $CoSi_2$

In this section we present the band structure and the charge-density distribution for the $CoSi_2$ compound. There have been several previous calculations of the electronic structure of cobalt disilicide.[3,7–9] The first non-self-consistent calculation by Gupta and Chatterjee[7] used

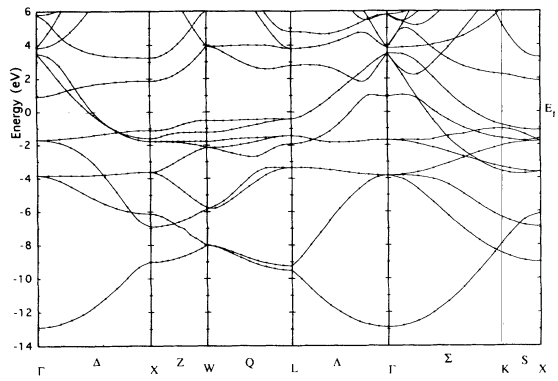

FIG. 8. Band structure of $CoSi_2$ along high-symmetry directions ($a_0 = 5.344$ Å).

a composite wave variational version of the APW (augmented-plane-wave) method, and produced the band structure that was in complete disagreement with the later results. The valence-band width of about 21 eV obtained in Ref. 7 was not confirmed by any of the following studies. On the other hand, the self-consistent results of the linear augmented-plane-wave method (LAPW) or LMTO-ASA (LMTO in the atomic sphere approximation, Refs. 3 and 8) calculations are in very good agreement with each other. The band structure in the present study (Fig. 8) is nearly identical to that calculated by Mattheiss and Hamann using the LAPW method, and it does not differ by more than 0.2 eV from the LMTO results.[3,8] The valence-band width is 13 eV, with the narrow almost-filled *d* band cutting through the wide *sp* band just below the Fermi level. The conclusion is that all the self-consistent calculations predict essentially similar electronic structure, and recent positron-annihilation experiments[3] validate the emerging unanimity in the theoretical description.

This comparison of the band structures calculated using either pseudopotential or all-electron techniques is important in assessing the viability of the projector reduction procedure described in Sec. II. The fact that the states of all symmetries (*s*, *p*, and *d*) are described correctly suggests that the elimination of both *s* and *p* nonlocal projectors by the careful selection of configurations and core radii does not decrease the overall accuracy.

The valence charge density distribution in the (110) plane is shown in Fig. 9. The large circles correspond to Co pseudoatoms, and smaller circles distorted into triangular shapes correspond to Si atoms. The overall charge distribution is quantitatively similar to the LMTO results,[8] with slightly more pronounced covalent bonding between Co and Si in our calculation. This comparison justifies the choice of the relatively high core radius for Co that allows one to obtain a rather soft pseudopotential, and at the same time this does not distort the bonding picture.

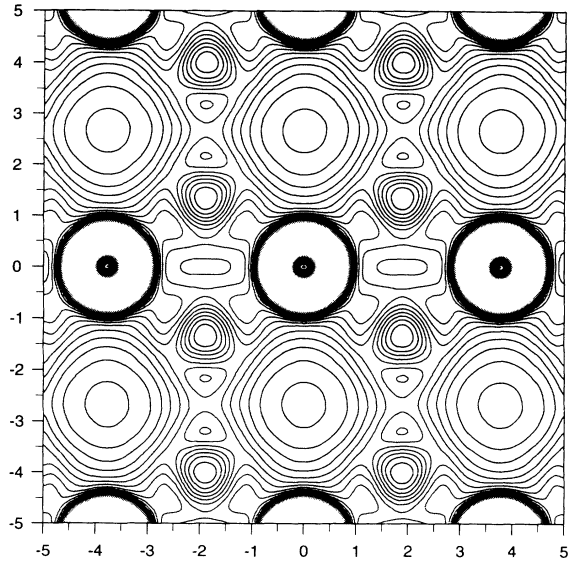

FIG. 9. Charge-density contours in the (110) plane. Axes are marked in Å.

VI. CONCLUSIONS

The total-energy calculations for cobalt disilicide confirm the transferability and robustness of the Co pseudopotential. The calculated lattice properties are in excellent agreement with rather scarce experimental data; in fact the theoretical values of the bulk modulus and its pressure derivative seem to be more reliable than the measured ones. The band structure is in good agreement with previous all-electron self-consistent calculations in the literature. The covalent metal-silicon bonds are found to be slightly more pronounced compared to the LMTO result. To summarize, we presented the method of generating soft and transferable pseudopotentials for the 3*d* transition element Co. This potential was used to create a consistent description of the lattice and electronic properties of cobalt disilicide and should be helpful in future *ab initio* studies of the silicon-silicide systems.

ACKNOWLEDGMENTS

We are pleased to acknowledge many useful conversations with M. F. Chisholm, who drew our attention to the problem of *ab initio* description of bonding in $CoSi_2$. We are grateful to K. Kunc, R. J. Needs, O. H. Nielsen, and R. M. Martin for providing the symmetrization code. The research of V.M. was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Program administered by the Oak Ridge Institute for Science and Education.

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