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Ab initio calculations of the cohesive, elastic, and dynamical properties of $CoSi_2$ by pseudopotential and all-electron techniques

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Ab initio calculations of cohesive properties, elastic constants, and phonon dispersions for $CoSi_2$ were performed by means of the Vienna *ab initio* molecular-dynamics package (VAMP), which makes use of ultrasoft pseudopotentials. In addition, the all-electron full-potential linearized augmented-plane-wave method was used for the calculation of equilibrium properties as well as elastic constants derived from second derivatives of total energies. For both methods, total energies, their derivatives, and related quantities are fully converged with respect to basis sizes and number of **k** points. Our results for C_{44} prove that atomic positions in the strained crystal have to be fully relaxed in order to get quantitatively useful results. The results of both methods obtained within the same type of local-density approximation are in very good agreement between each other. Because elastic constants are very sensitive quantities for an *ab initio* method in general, the reproduction of high-quality all-electron data by VAMP demonstrates the power of suitably constructed pseudopotentials even for systems containing transition elements. VAMP was also applied to calculate elastic constants in two other ways, namely, directly from the stress-strain relations (which yielded the same results as obtained from total-energy derivatives) and from acoustic branches of the phonon dispersion. In this case, however, we only succeeded in getting a useful result for C_{44} whereas for the remaining two elastic constants prohibitively large supercells would be needed. Finally, VAMP calculations were performed within the framework of the generalized gradient approximation to density-functional theory. From that, data were derived which are in very good agreement with experimental values. [S0163-1829(96)12327-4]

I. INTRODUCTION

For materials science $CoSi_2$ is of interest because of potential technological applications as a structural material due to its low specific weight and excellent oxidation behavior.[1] It also got particular attention for microelectronic devices[2] because semiconductor/conductor interfaces can be manufactured by growing the metallic conducting $CoSi_2$ on Si substrates.[3] Recently, the mechanical properties in connections with its color became of interest for some possible applications.[4] Therefore, $CoSi_2$ is a well-suited material to apply computational materials science techniques to bulk, interface, and surface problems.

Ab initio applications require a powerful and reliable numerical method, which is provided by the Vienna *ab initio* molecular-dynamics package (VAMP).[5] For a crucial check of this particular pseudopotential method we applied it for the calculation of cohesive energies and elastic constants for bulk $CoSi_2$ and compared the results to data obtained by a full-potential linearized augmented-plane-wave method (FLAPW).[6] The FLAPW approach, which is an all-electron method and does not require any shape approximations for density and potential, is one of the most precise *ab initio* state-of-the-art methods. It is, however, by construction less fast and versatile than an efficient pseudopotential approach.

Furthermore, we also show that calculations of elastic constants (in particular, for compounds) have to be done carefully from both a numerical and a methodological point of view. Because these quantities are important and sensitive materials properties, the comparison of experimental and *ab initio* elastic constants provides a critical test for the usefulness of *ab initio* methods in the field of materials science in general.

II. METHODS

VAMP (Ref. 5) is based on pseudopotentials that are constructed according to Vanderbilt's recipe for ultrasoft pseudopotentials.[7,8] There—in contrast to standard normconserving pseudopotential methods—the total valence charge density inside suitable atomic spheres is augmented in order to correct for the deviation of the pseudo-charge-density from the correct density, which is described by wave functions with the proper nodal structure. Due to these corrections additional formal complications (for solving Schrödinger's equation as well as for forces) occur compared to standard plane-wave methods. These disadvantages are by far outweighed by a substantial gain in basis size and transferability, which makes the application of pseudopotentials feasible to systems containing 3*d*-transition elements. Therefore, moderate energy cutoffs (e.g., 300 eV for Co and $CoSi_2$) result in fully converged basis sets. For large supercells the energy cutoff was reduced to 200 eV, still yielding converged results. For the actual calculation of ultrasoft pseudopotentials for Co and $CoSi_2$ the atomic cutoff radii were chosen to be 2.7 a.u. for the Co atom (for *s*, *p*, and *d* states), and 2.5 a.u. for Si (*s* and *p* states). The chosen atomic configurations were $3d^8 4s^1 4p^0$ for Co and $3s^2 3p^2$ for Si. Partial core corrections[9] were introduced to enable a proper treatment of the nonlinear dependence of the exchange-correlation functional. In addition to basis set convergence VAMP total energies were also converged concerning the number of **k** points in the irreducible part of the Brillouin zone using a special **k**-point sampling technique.[10,11]

Within FLAPW (Ref. 6) space is divided into nonoverlapping atomic spheres and interstitial space. Inside the spheres the basis functions consist of atomlike functions, which at the sphere boundaries match continuously (by function value and first derivative) onto plane waves. Because of this construction the valence wave functions have the correct nodal structure within the atomic spheres. Since all electronic states are taken into account, core states also, have to be calculated, which is done fully relativistically. According to the space division described above, charge density and potential are expanded in a natural way: in terms of spherical harmonics inside the spheres and into plane waves outside. Due to this mathematically well-defined expansion any shape of charge density and potential can be treated. Usually, in FLAPW basis sizes are smaller than in pseudopotential calculations. However, for the present case for Co and CoSi_2 an extremely large energy cutoff of about 340 eV was chosen resulting in 180 basis functions per atom. This was done to ensure perfect convergency of the total energy. Inside the atomic spheres all spherical harmonics expansions were made up to $l=8$. Particular care was also taken for the total-energy convergence due to **k**-space integration, which in the present case was done by application of the linear tetrahedron method.[12] Although for a moderate to medium number of **k** points this method is less advantageous compared to special **k**-point techniques, it allows an useful extrapolation of the total energy to the limit of an infinite number of **k** points (Jansen and Freeman[6]).

All FLAPW calculations were performed within the local-density approximation (LDA) of Hedin and Lundqvist[13] (HL) for the many-body part of density-functional theory. For the VAMP applications, however, three different types of density-functional approximations have been considered: (i) the HL expression, (ii) the LDA formulation of Ceperly and Alder,[14] and (iii) the generalized gradient approximation (GGA) of Becke and Perdew.[15]

Therefore, when FLAPW and VAMP results are compared they always refer to fully converged total energies within the HL approximation.

III. RESULTS AND DISCUSSION

As a first test we calculated the equilibrium lattice parameter, cohesive energy and bulk modulus for (i) nonmagnetic fcc-Co and for (ii) CoSi_2, which crystallizes in the $Fm3m$ (cubic CaF_2) structure. From Table I for Co we find very good agreement between the two calculated sets of values. The maximum deviation is found for the bulk modulus, which is about 3–4 % larger for the VAMP calculation. For the derivation of the cohesive energies we chose the occupation $(3d\uparrow)^5(3d\downarrow)^{2.897}(4s\uparrow)^1(4s\downarrow)^{0.103}$ (Ref. 16) for the spin-polarized free-atom LDA calculation of Co.

TABLE I. Ground-state properties of nonmagnetic fcc-Co and of CoSi_2 calculated by VAMP and FLAPW. Columns: a_0 (equilibrium lattice spacing), B_0 (bulk modulus at a_0), E_{coh} (cohesive energy at a_0). LDA expression of Hedin und Lundqvist and GGA of Perdew and Becke were applied. Column B_{exp}: bulk moduli calculated at experimental volume. Experimental values: Ref. 27 for CoSi_2.

			a_0/Å	B_0/GPa	B_{exp}/GPa	E_{coh}/eV
fcc-Co	VAMP	LDA	3.387	319.1	180.4	-6.65
	FLAPW	LDA	3.385	310.9	173.0	-6.67
CoSi_2	FLAPW	LDA	5.292	201.8	171.6	-20.38
	VAMP	LDA	5.283	200.2	168.4	-20.69
	VAMP	GGA	5.350	171.5	169.0	
	Experiment		5.365		171.5 ± 3.4	

Also for CoSi_2, FLAPW and VAMP data agree very well between each other. Again, the largest deviations of about 0.5% are found for the bulk modulus at the calculated equilibrium lattice parameters. The lattice parameters agree within 0.2%. Because of the shortcomings of LDA the calculated lattice parameters are smaller by 1.2% than the experimental result. When the bulk moduli are calculated at the experimental volume then we achieve perfect agreement with measured data. It should be noted that the now much larger calculated cohesive energies again agree very well between each other, in particularly when one takes into account that FLAPW and VAMP data are obtained by totally different treatments for the bulk as well as for the free atom. Obviously, the VAMP pseudopotential approach reproduces the ground state results of the FLAPW full-potential all-electron approach quite accurately in distinction to other studies.[17,18]

Elastic constants are important parameters of a material and their *ab initio* calculation requires precise methods. Therefore, the quality of calculated elastic constants provides a critical test for the quality of an *ab initio* method.

The standard way to derive elastic constants from *ab initio* results is to calculate second derivatives of the energy density $U(\delta)$ (which is defined as total energy per volume) as a function of properly chosen lattice distortions δ building up the strain. For a cubic crystal structure there are only three independent elastic constants C_{11}, C_{12}, and C_{44}, for which one needs three independent strains $\epsilon(\delta)$. We have constructed the strains in the following way:

$$\epsilon_{\mathrm{comp}}=\frac{1}{3}\begin{pmatrix}\delta & 0 & 0\\ 0 & \delta & 0\\ 0 & 0 & \delta\end{pmatrix},\quad \epsilon_{\mathrm{tetr}}=\frac{1}{2}\begin{pmatrix}-\delta & 0 & 0\\ 0 & -\delta & 0\\ 0 & 0 & 2\delta\end{pmatrix},$$

$$\epsilon_{\mathrm{trig}}=\begin{pmatrix}\delta^2 & \delta & \delta\\ \delta & \delta^2 & \delta\\ \delta & \delta & \delta^2\end{pmatrix}. \tag{1}$$

The strain ϵ_{comp} describes volume compression whereas ϵ_{tetr} and ϵ_{trig} refer to anisotropic tetragonal and trigonal lat-

TABLE II. Calculated elastic constants of CoSi_2 at calculated equilibrium volume. Elastic constants are derived from second total energy derivatives (E_{tot}), stress-strain relation (stress), and phonon dispersions (phonon). C^0_{44}: values without geometry relaxations. All values in GPa.

	FLAPW E_{tot}	VAMP E_{tot}	VAMP Stress	VAMP Phonon
C_{11}	273.3	273.1	271.5	236.4
C_{12}	166.0	163.7	162.9	140.4
C^0_{44}	168.4	164.1	164.1	
C_{44}	97.4	100.6	100.3	97.7
B	201.8	200.2	199.1	172.4

tice distortions, respectively. Then, the elastic constants (or linear combinations of them) are calculated from the energy density by

$$\frac{\partial^2 U(\epsilon_{\mathrm{comp}})}{\partial \delta^2}=\frac{C_{11}+2C_{12}}{3}=B,$$

$$\frac{\partial^2 U(\epsilon_{\mathrm{tetr}})}{\partial \delta^2}=\frac{3}{2}(C_{11}-C_{12})=3C',$$

$$\frac{\partial^2 U(\epsilon_{\mathrm{trig}})}{\partial \delta^2}=4C_{44}. \tag{2}$$

Particular care was taken to converge the total energies due to the number of **k** points. For the special **k**-point technique of VAMP 84, 550 and 670 **k** points in the irreducible part of the Brillouin zone were sufficient to obtain, correspondingly, B, C', and C_{44} within numerical fluctuations of 1 GPa. For the FLAPW calculation, however, the linear tetrahedron method was applied which is slower convergent but allows the extrapolation to an infinite number of **k** points. There, for the largest set of **k** points of 252, 1162, and 946 for B, C', and C_{44}, correspondingly, one achieves accuracies of 1%, 3%, and 2% when compared to the extrapolated results. Table II compares the values obtained from FLAPW and VAMP calculations (columns E_{tot}) showing very good agreement. The maximum deviation of less than 3% is found for C^0_{44} and C_{44}.

For high-quality calculations of elastic constants it is necessary that internal atomic positions are fully relaxed. This problem arises whenever the chosen strain reduces the symmetry of the undistorted crystal structure in such a way that additional degrees of freedom for the atomic arrangement occur. Such relaxation effects are quite often neglected in related studies. For cubic CoSi_2 the trigonal strain ϵ_{trig} (Eq. 1) leads to Si positions which are not any more located at inversion sites (space group $R\bar{3}m$). Now, one free geometry parameter has to be relaxed along the (111) direction (Fig. 1). Within FLAPW the geometry was optimized by total-energy minimization whereas for the VAMP application atomic forces were minimized by a quasi-Newton-algorithm. The relaxation influences the result for C_{44} drastically as revealed by Table II: the elastic constant C^0_{44} referring to the unrelaxed geometry is 60% larger (64 GPa) than C_{44} for the fully relaxed case. The relaxation gives rise to a softening of C_{44}.

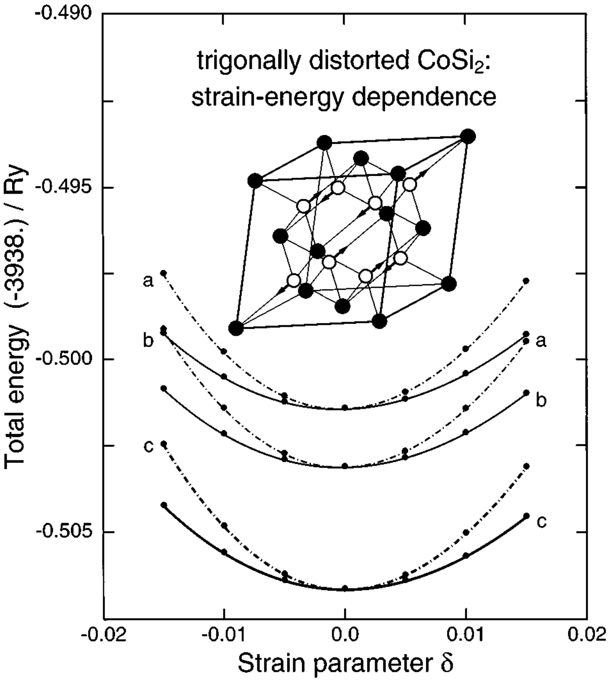

FIG. 1. Trigonal distortion: Crystal structure and strain–total-energy dependence. Atomic relaxation indicated by arrows. Fitted total energies with relaxation (full lines) and without relaxation (dashed-dotted lines) for 525 (a), 946 (b), and extrapolated to an infinite number (c) of **k** points.

According to Kleinman[19] the extent of relaxation may be expressed quantitatively by the internal strain parameter ζ $(0\leqslant\zeta\leqslant 1)$. The value $\zeta=1$ describes the maximal relaxation for which all Co-Si bond lengths remain equal in the strained crystal. For $\zeta=0$ the atoms would follow the macroscopic strain without relaxation. Both *ab initio* methods applying LDA yield the same value $\zeta=0.59$.

The VAMP package was applied for two other exchange-correlation approximations within density-functional theory. The LDA formulation of Ceperley and Alder[14] led to results which were very similar to the tabulated values based on the HL approximation. According to our experience, LDA derived elastic constants calculated at the *experimental* volume agree well with experimental data (for CoSi_2, see Table III).

Applying the GGA,[15] however, changed the equilibrium data significantly, causing a general softening not only of isotropic volume-dependent quantities such as equilibrium lattice parameter and bulk modulus but also of C_{44} (Table III). The internal strain parameter now is found to be $\zeta=0.67$, which is significantly larger than the LDA value given above. As a comparison for pure Si it was found that *ab initio* LDA calculations always gave significantly lower values for ζ (0.53–0.57) than the experimental data (0.65–0.73). A similar trend was also observed for Ge, GaAs, and AlAs.[20]

All GGA results seem now to reproduce in an excellent manner the listed experimental values. However, this perfect agreement might be somewhat misleading. One has to be aware that for the construction of the pseudopotential the

TABLE III. Elastic properties of CoSi_2. LDA: VAMP and FLAPW results for the LDA expression of Hedin and Lundqvist at experimental lattice spacing (a = 5.365 Å). GGA: VAMP calculation applying generalized gradient approximation (Ref. 15) at calculated equilibrium lattice parameter (a_0 = 5.350 Å). Experimental data are taken from Ref. 27. All values in GPa.

	FLAPW (LDA)	VAMP (LDA)	VAMP (GGA)	Experiment
C_{11}	233.8	227.6	225.0	224.7 ± 4.4
C_{12}	140.2	138.4	147.2	144.9 ± 3.9
C_{44}^0	150.3	145.0	150.9	
C_{44}		93.6	85.7	85.0 ± 1.1
B	171.4	168.1	173.1	171.5 ± 3.4

choice of the cutoff radius for the partial core corrections might modify the GGA results.[21] In all our VAMP calculations (for LDA as well as GGA) the cutoff radius was defined at the distance where the valence charge density was equal to the core charge density.

Pursuing a physical argument, one should be careful when comparing the experimental elastic constants, which were measured at room temperature, to the *ab initio* values, which refer to $T=0$ K strictly. Temperature effects generally reduce the size of the elastic constants and therefore C_{44} (for which the GGA has the strongest impact) could be significantly increased at low temperatures. To our knowledge, no experimental data about the temperature dependence of elastic constants for CoSi_2 are available. From a previous *ab initio*[22] and experimental[23] study on $\mathrm{Al}_3\mathrm{Li}$ increases of about 20–30 % for C_{11} and C_{44} were found when comparing measured room temperature values to calculated results. The calculated data, however, were in agreement with the experimental results after extrapolation to $T=0$ K. Summarizing, the better agreement of GGA derived elastic constants—in comparison to LDA results—with experimental data at room temperature is no conclusive proof of the superiority of GGA to LDA, at least for CoSi_2.

The power and flexibility of VAMP made it possible to apply it also for other derivations of elastic constants. In a pure plane-wave description for wave functions and Hamiltonian the stress tensor σ_{ij} can be analytically derived in a straightforward way from the second derivative of the total-energy functional with respect to atomic coordinates (see Kresse[5]). Because of the stress-strain relation $\sigma_{ij}=C_{ijkl}\epsilon_{kl}$ the elastic constants can be directly expressed in terms of stress tensor components by

$$C_{44}=\frac{1}{2}\frac{\partial\sigma_{12}}{\partial\epsilon_{12}}=\frac{1}{2}\frac{\partial\sigma_{21}}{\partial\epsilon_{21}}=\frac{1}{2}\frac{\partial\sigma_{21}}{\partial\delta},$$

$$C'=\frac{\partial\sigma_{11}}{\partial\epsilon_{11}}=-\frac{1}{2}\frac{\partial\sigma_{33}}{\partial\epsilon_{33}}=\frac{\partial\sigma_{11}}{\partial\delta},$$

$$B=\frac{\partial\sigma_{11}}{\partial\epsilon_{11}}=\frac{\partial\sigma_{11}}{\partial\delta}, \tag{3}$$

applying the cubic symmetry to stress and strain. As shown by Table II, the thus-derived VAMP results for the equilibrium volume are in perfect agreement with the results obtained from total-energy derivatives.

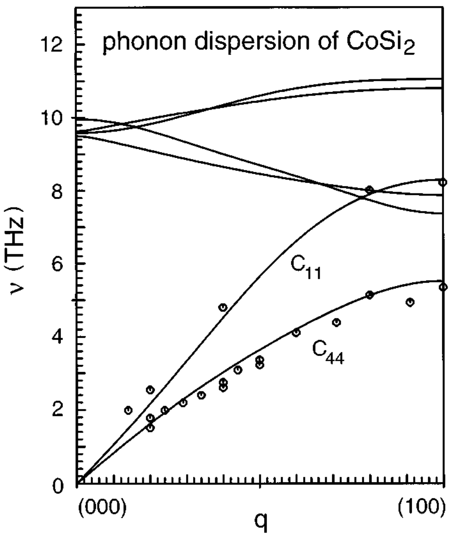

FIG. 2. Phonon dispersion for CoSi_2 calculated by VAMP (full lines) at experimental volume. Experimental data (circles) obtained by neutron scattering (Ref. 26).

Finally, by application of VAMP, dynamical properties in terms of phonon spectra also were calculated. Precise *ab initio* calculations of phonon spectra is still a demanding task, even more so the derivation of elastic constants from the phonon dispersions. For the computation we made use of the force constant[24] approach, which is based on supercells for which all coordinate axes are orthogonal to each other. Within the supercell a single atom is displaced in a particular direction and induces now forces acting on the nuclei in the neighboring shells. For making the computational effort reasonable we oriented the displacement vectors always along main symmetry directions when we calculated the force constant matrix. The applicability of this approach and its accuracy are mainly limited by the size of the supercell box, which depends on the range of the atomic interactions of the studied material. In particular, for CoSi_2, due to the covalent type of bonding we observed rather long-ranged effects caused by the displaced atom. In order to derive elastic constants from phonon dispersions we needed higher precision and for that we made use of the concept of interplanar force constants.[25] In this scheme a tetragonally shaped supercell is constructed by repeating the unit cell along the direction of the chosen wave vector and the atoms in the perpendicular planes are moving rigidly. By such a procedure a wider range of neighboring atoms contributing to the acoustic vibration in question can be treated.

Figure 2 shows the phonon dispersions for CoSi_2 calculated from a tetragonal supercell with 36 atoms having its stretched lattice vector along (100). The agreement with the experimental data[26] is very good although the measured values show some scattering. It should be noted that the acoustic branches close to the Γ point appear perfectly linear without any apparent anomality which makes it — at least in principle — possible to derive the elastic constants from the dispersions.

The elastic constants for a cubic system are extracted from first derivatives of phonon branches $\omega(\mathbf{q})$ by

$$
\begin{aligned}
C_{44} &= \left(\frac{d\omega}{dq}\right)^2 \rho, \quad \mathbf{q}\|(100) \quad \mathbf{u}\perp(100) \\
C_{11} &= \left(\frac{d\omega}{dq}\right)^2 \rho, \quad \mathbf{q}\|(100) \quad \mathbf{u}\|(100) \qquad (4) \\
C' &= \left(\frac{d\omega}{dq}\right)^2 \rho, \quad \mathbf{q}\|(110) \quad \mathbf{u}\perp(110),
\end{aligned}
$$

in which **q** denotes the wave vector and **u** the polarization vector of the vibrations, and ρ is the mass density of the material.

Due to the long-ranged nature of the atomic interactions only for C_{44} (by applying a supercell with 36 atoms) we could obtain a result which is of comparable quality to C_{44} of the previous two derivations. The remaining two constants, C_{11} and C', deviate significantly from the high-precision results, even when supercells of 48 atoms were used. A detailed investigation of the convergence behavior depending on the number of atoms in the supercell showed that the series expansion into planar force constants is very slowly converging for C_{11} and C'. The constant C_{11} is derived from a longitudinal vibration mode. As is well known, longitudinal modes cause perturbations which are more long ranged compared to effects of transversal modes. Due to the construction of a suitable supercell for the calculation of C', the number of planes perpendicular to **q** was lower by a factor of 2 compared to the case for C_{11} and for C_{44}. We did not perform the corresponding very demanding calculations because all the other results already prove the power and precision of an up-to-date *ab initio* method.

IV. SUMMARY

We critically compared one of the most powerful *ab initio* pseudopotential approaches (VAMP) to a high-quality all-electron method (FLAPW) by studying cohesive properties as well as elastic constants of the bulk phase of cubic $CoSi_2$. The outstanding agreement of the data calculated by these totally different methods emphasizes the reliability of the ultrasoft pseudopotential as utilized by VAMP. For applying both methods we took care that total energies and elastic constants are fully converged due to all numerical parameters such as basis sizes and number of **k** points. In particular, we emphasized that for the calculation of elastic constants all atomic positions of the corresponding strained lattice have to be fully relaxed. Our very precise calculations of the elastic constants demonstrate the usefulness of *ab initio* methods for the determination of materials properties. For a proper comparison to experimental data, the elastic constants within LDA have to be calculated at the experimental volume in order to overcome the overbinding problem of LDA. If GGA is applied we achieve almost perfect agreement with experimental data and the elastic constants in particular. However, one should be aware that the measurements were done at room temperature whereas *ab initio* calculations refer to $T=0$ K. By utilization of VAMP we calculated the elastic constants also in two other ways. In addition to deriving the elastic constants directly from the stress-strain relations we also tried to determine them from the phonon dispersions. A precise calculation of C' and C_{11} from proper derivatives of the phonon branches proved to be not feasible because such a task would require very large supercells. Nevertheless, we obtained reliable results for C_{44} as well as the dispersions themselves.

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