PHYSICAL REVIEW B VOLUME 58, NUMBER 17 1 NOVEMBER 1998-I

Pressure-induced phase transitions in solid Si, SiO_2, and Fe: Performance of local-spin-density and generalized-gradient-approximation density functionals

Aleš Zupan
Department of Physical and Organic Chemistry, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

Peter Blaha and Karlheinz Schwarz
Institute for Technical Electrochemistry, Technical University Vienna, Getreidemarkt 9/158, A-1060 Vienna, Austria

John P. Perdew
Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

(Received 24 April 1998)

We focus on a particular shortcoming of the local-spin-density (LSD) approximation for the exchange-correlation energy of a many-electron system: underestimation of the transition pressure p_t at pressure-induced structural phase transitions in solids. We have performed self-consistent full-potential LAPW calculations, with full structure optimization, for three cases—silicon (Si), silica (SiO_2), and iron (Fe). In agreement with previous calculations, we find that gradient corrections to LSD over-correct the equilibrium volumes in Si and SiO_2, but correct or slightly under-correct the volume in Fe and the transition pressures in all three materials. We apply a thermodynamiclike inequality [A. Zupan *et al.*, J. Chem. Phys. **106**, 10 184 (1997)] to our results to explain why the generalized gradient approximation expands the equilibrium volume and increases the value of p_t over LSD. In all three cases, gradient corrections to LSD tend to stabilize the low-pressure phase because of its more inhomogeneous electron density. [S0163-1829(98)05241-2]

I. INTRODUCTION

Kohn-Sham (KS) spin-density functional theory[1] is a tool for accurate first-principles calculations of the ground-state structure of many-electron systems.[2] The only term in this formally exact method that must be approximated is the exchange-correlation energy $E_{\mathrm{XC}}[n_\uparrow,n_\downarrow]$. The local-spin-density approximation[1,3] (LSD) for E_{XC} has been used successfully for thirty years in solid-state physics, giving reasonable but imperfect predictions for lattice parameters, elastic and cohesive properties, etc. Recently, generalized gradient approximations[4–11] (GGA's) have improved upon the accuracy of LSD, giving accurate total energies of atoms and atomization energies of molecules,[12] and thus becoming a standard method of quantum chemistry. In solid state physics, GGA's have been catching on only recently, although solid state applications were an early motivation for GGA.[4,13]

Theoretical complication and computational effort increase from LSD to GGA, and the resulting improvement of calculated properties is not uniform for all classes of solid state problems. GGA does improve lattice parameters, elastic constants, and magnetic properties of many metals,[10,14] and also improves the transition pressures for some pressure-induced phase transitions.[15,16] In covalent semiconductors, where LSD gives unusually accurate lattice constants and bulk moduli, GGA sometimes leads to improvement[15] and sometimes to worsening[17–21] via over-correction of LSD.

In this paper we concentrate on one particular shortcoming of LSD, i.e., underestimation of the coexistence or transition pressure for a pressure-induced structural phase transition in a solid. To explain why gradient-corrected functionals expand lattice parameters and increase the transition pressure, we use a thermodynamiclike inequality[22–24] that determines whether the nonlocal correction drives a process forward or not.

As numerical examples, we have chosen (a) silicon (Si), which under pressure transforms from the semiconducting diamond to the metallic β-tin structure (as studied theoretically in Refs. 15, 25, and 26), (b) silica (SiO_2) which transforms from the α-quartz to the stishovite structure (as studied theoretically in Refs. 16, 27–31), and (c) the metal-metal transition of iron (Fe) from the ferromagnetic bcc to the nonmagnetic fcc structure.[32–37] The experimentally observed phase transitions are from α-quartz to coesite and then to stishovite (with a metastable equilibrium between α-quartz and stishovite),[38] and from bcc Fe to hcp Fe.[39] Nevertheless, these examples are useful for an understanding of the underlying physics. We used the LSD parametrization of the exchange-correlation energy by Perdew and Wang,[3] and the most recent parameter-free GGA form by Perdew, Burke, and Ernzerhof (PBE),[9] which is numerically similar to the GGA of Perdew and Wang (PW91).[7]

II. COMPUTATIONAL DETAILS

We calculated the Kohn-Sham[1] total energies self-consistently for all crystal phases within the LSD (Ref. 3) and GGA (Ref. 9) approximations for the exchange-correlation energy. The WIEN97 (Ref. 40) program package that we used employs the solar relativistic full-potential linearized augmented plane wave (LAPW) method. Special attention was paid to convergence of the results, especially for the SiO_2 system for which the LSD energy difference between α-quartz and stishovite is particularly small. For that purpose, we carefully checked the k-mesh (finally using 6 k

TABLE I. Equilibrium structural properties of each phase, and parameters of the diamond to β-tin phase transition of Si, calculated with different approximations for E_{XC}. V_0 is the volume of the primitive unit cell, which contains 2 atoms in each structure. The energy differences ΔE_t between the two phases, as well as their volumes V_t^d and V_t^β, are given at the transition point. For a selection of experimental values, see Ref. 15. (1 GPa=0.01 Mbar=0.0680 mRy/bohr^3.)

Phase		Expt.	LSD	PW91	PBE
Diamond	V_0 (a.u.)	270.1	266.2	276.0	276.3
	B_0 (GPa)	99	97	91	91
	B_0'	4.2[a]	4.0	3.7	3.7
β-tin	V_0 (a.u.)		199.9	208.5	207.0
	c/a	0.552	0.546	0.551	0.547
	B_0 (GPa)		117	106	109
	B_0'		4.3	4.1	4.1
	ΔE_t (mRy)		29	43	37
	V_t^d/V_0^d (expt.)	0.918	0.938	0.928	0.937
	V_t^β/V_0^d (expt.)	0.710	0.704	0.706	0.717
	p_t (GPa)	10.5–12.5	6.7	10.6	9.2

[a] Reference 44.

points in the irreducible wedge of the Brillouin zone in α-quartz and 9 in stishovite), used a large plane-wave cutoff ($R_{\mathrm{mt}}K_{\mathrm{max}}=9.5$), and treated even the Si $2p$ states as band states using the local orbital extension of the LAPW method.[40] For all the phases of the remaining two systems, we used the plane-wave cutoff $R_{\mathrm{mt}}K_{\mathrm{max}}=9.0$. We used 47 k points in Si in the diamond structure and 99 k points in the β-tin structure; for iron we used 286 k points in each structure.

For each crystalline phase, we calculated the total energy of the unit cell for a number of different volumes. For the β-tin phase of silicon and the silica phases, we optimized the c/a ratio for each volume and relaxed all independent internal atomic coordinates until the respective forces were less than 1 mRy/a.u. We fitted the calculated total energies for $0.8V_0<V<1.2V_0$ to the Murnaghan equation of state[41] to obtain the equilibrium volume V_0, bulk modulus at equilibrium B_0, its pressure derivative B_0', and ground-state total energy E_0.

The coexistence pressure was finally calculated from a common tangent (Gibbs) construction to the two energy-versus-volume curves for the diamond and β-tin phases of Si, the α-quartz and stishovite structures of SiO$_2$, and the bcc and fcc phases of Fe.

III. RESULTS AND DISCUSSION

A. Silicon (Si)

The calculated structural parameters for Si in the diamond and β-tin phases are listed in Table I. The reported experimental cell volume and bulk modulus correspond to zero pressure and temperature $T=0$ K. The diamond-structure LSD results are in excellent agreement with experiment, the error in calculated volume being -1.4% and in bulk modulus -2.0%. Gradient corrections (either PW91 or PBE) expand the volume by 3.7% and decrease the bulk modulus by 6.2%, leading to a worsening of the results. The difference between PW91 and PBE values is small and barely noticeable for the structural parameters. We note that convergence is faster for PBE than for PW91, because PBE employs a simpler analytic form for the exchange-correlation potential, which is free from the spurious wiggles in the PW91 potential. PW91 and PBE are otherwise similar, although PW91 was constructed via a real-space cutoff of the exchange-correlation hole, while PBE was constructed by imposing several exact physical constraints on the energy functional. Thus for the other systems (SiO$_2$ and Fe), the only GGA we will consider is PBE.

In the β-tin structure, a similar trend is observed: gradient corrections expand the volume by approximately 4% and reduce the bulk modulus on the average by 8%.

In Table I we also report parameters of the diamond to β-tin phase transition of Si. The coexistence pressure is obtained via the Gibbs common-tangent construction using the energy versus volume plot for the two phases, i.e., $p_t = -(E_t^d - E_t^\beta)/(V_t^d - V_t^\beta)$. The LSD result is significantly lower than the experimental value, whereas the gradient correction increases the transition pressure, leading to a value that is close to the experimental value (PBE) or even within the experimental uncertainty (PW91).

Our results are almost identical to those of Filippi, Singh, and Umrigar[17] (who also used a full-potential LAPW method) for the structural parameters of Si, and compare well to the most recent pseudopotential (PP) calculations by Moll *et al.*[15] using the same approximations for the exchange-correlation energy E_{XC}. For the diamond structure, Moll *et al.* report $V_0=264.2$ a.u. and $B_0=97$ GPa in LSD, and $V_0=273.1$ a.u. and $B_0=92$ GPa in PW91. These and our numbers differ by less than 1%. For the β-tin structure, they report $V_0=197.5$ a.u. and $B_0=115$ GPa in LSD, and $V_0=211.5$ a.u. and $B_0=104$ GPa in PW91. Again their results are close to ours. The largest difference can be seen in the transition pressure, a very sensitive quantity depending not only on the energy but also on its first derivative with respect to volume. They quote $p_t=8.0$ GPa in LSD and $p_t=12.2$ GPa in PW91. Our numbers are 10–15% smaller. The reason for this small discrepancy could be that in the β-tin

TABLE II. Equilibrium structural parameters for two SiO_2 polymorphs, and parameters of the phase transition between them, calculated with LSD and PBE approximations for E_{XC}. V_0 is the volume per SiO_2 formula unit. Symbols u, x, y, and z denote free internal coordinates in units of lattice parameters as defined in Refs. 47 and 48 (space group $P3_221$). Calculated values of B_0 and B_0' are unreliable, due to the small number of fitted energies (5 for LSD, 7 for PBE).

Phase		Expt.	LSD	PBE
α-quartz	V_0 (a.u.)	254.5[a]	244.4	266.0
	c/a	1.099[a]	1.104	1.099
	B_0 (GPa)	38[a]	35	44
	B_0'	6[a]	7.1	3.2
	u	0.4697[a]	0.460	0.474
	x	0.4135[a]	0.409	0.413
	y	0.2669[a]	0.280	0.261
	z	0.1191[a]	0.108	0.123
Stishovite	V_0 (a.u.)	157.3[b]	155.4	163.5
	c/a	0.638[b]	0.642	0.636
	B_0 (GPa)	313[c,b]	303	257
	B_0'	2.8–6.0[c,b]	4.8	4.9
	u	0.306[b]	0.305	0.307
	ΔE_t (mRy)		-6.6[d]	32.7
	$V_t^{\alpha}/V_0^{\alpha}$ (expt.)			0.935
	$V_t^{\mathrm{stis}}/V_0^{\alpha}$ (expt.)			0.628
	p_t (GPa)	7.46[e]		6.2

[a] Reference 49.

[b] Reference 50.

[c] Reference 51.

[d] Difference between the energy minima of both phases.

[e] Reference 46.

structure there is an additional degree of freedom, the c/a ratio, which was not optimized by Moll *et al.*, whereas we optimized it and as a consequence obtained a smaller value for the transition pressure.

Many pseudopotential studies of Si have been made. Our LSD and PBE results for the diamond structure of Si agree closely with those of Lee and Martin.[20] Our LSD results also agree reasonably with those of García *et al.*[42] and Ortiz,[43] who also tested earlier versions of GGA. Yin and Cohen[25] reported the LSD transition pressure to the β-tin phase to be 9.9 GPa, somewhat higher than our LSD value of 6.7 GPa.

B. Silica (SiO_2)

The two phases of silica present the most demanding computational challenge in the present work. These calculations required several months of computation time on a dedicated 6-processor Silicon Graphics Power Challenge. The unit cell of the high-pressure phase stishovite consists of two formula units of SiO_2, while the low-pressure phase α-quartz has three formula units per unit cell. At each volume, two additional parameters must be optimized in stishovite (c/a ratio and one independent internal coordinate), and five in α-quartz (c/a ratio and four independent internal coordinates).

We calculated the energy of the unit cell as a function of volume for both phases using LSD and PBE functionals, converging the forces to less than 1 mRy/a.u. We report the results in Table II. In predicting the equilibrium volume, both approximations deviate from experiment to the same degree. LSD underestimates the equilibrium volume of α-quartz by 4%, and GGA over-corrects this, making the equilibrium volume too big by approximately the same amount. The LSD bulk modulus is very close to the experimental value, while the GGA bulk modulus is too big by 16%. This is in contrast to the usual behavior, where one finds ‘‘softer’’ crystals (smaller B_0) at the larger GGA equilibrium volumes. It should be mentioned that Hamann[16] reports the same anomaly.

Our calculated structural parameters compare well with other theoretical studies,[16,27–31] all using pseudopotentials. Those studies report for α-quartz LSD equilibrium volumes per SiO_2 ranging from 246.9 a.u. (Ref. 16) to 260.2 a.u.[29] Our volume is smaller by 1% than the smaller previous value, and 6.1% from the bigger value. In GGA, Hamann[16] reports 265.6 a.u. using the PW91 exchange-correlation functional; our volume using the similar PBE approximation is only 0.15% bigger. We find similar accord in the calculated structural parameters of stishovite. (Very recent PBE results from Hamann[45] show excellent agreement between his and our calculations. His PBE results are, for α-quartz, $V_0=269.3$ a.u., $B_0=43$ GPa, $B_0'=3.3$, and for stishovite, $V_0=164.7$ a.u., $B_0=249$ GPa, $B_0'=5.0$.)

More interesting is the energy difference between the α-quartz and stishovite phases. Experiment[38,46] reports a difference of 0.51 to 0.54 eV per formula unit, with α-quartz lying lower in energy. Liu *et al.*[28] report 0.07 eV and Hamann[16]

TABLE III. Equilibrium structural parameters for two crystal phases of iron, and parameters of the phase transition between them. V_0 is the volume per atom. At ambient conditions, the bcc ferromagnetic phase is stable.

Phase		Expt.	LSD	PBE
bcc FM	V_0 (a.u.)	79.5[a]	70.5	76.6
	B_0 (GPa)	172[a]	260	200
	B_0'	5.0[b]	4.6	4.5
fcc NM	V_0 (a.u.)		65.1	69.4
	B_0 (GPa)		354	297
	B_0'		4.7	4.5
	ΔE_t (mRy)		-5.1[c]	9.22
	$V_t^{\rm bcc}/V_0^{\rm bcc}$ (expt.)			0.868
	$V_t^{\rm fcc}/V_0^{\rm bcc}$ (expt.)			0.810
	p_t (GPa)			29.4

[a] Reference 39.

[b] Reference 52.

[c] Difference between the energy minima of both phases.

0.02 eV using pseudopotentials and the LSD approximation. Hamann's LSD LAPW calculation favors stishovite, the energy difference between the minima being -0.04 to -0.06 eV per SiO_2. We find very similar results, with an energy difference between the minima of the two phases of -0.09 eV per formula unit in LSD and $+0.51$ eV in the GGA approximation (compared to Hamann's 0.57 eV).

The energy difference between two phases is an essential ingredient to calculate the transition pressure. The LSD energy difference is negative and thus gives no positive transition pressure. On the other hand, GGA favors the more open crystal structure, i.e., the α-quartz structure. We find a GGA transition pressure of 6.2 GPa, which is in good agreement with the experiment,[46] and close to Hamann's 7.0 GPa.

C. Iron (Fe)

We calculated the structural parameters of the bcc ferromagnetic (FM) and fcc nonmagnetic (NM) phases of Fe using the LSD and PBE approximation. We also report the transition pressure p_t between the two phases. The pressure-induced phase transition can occur only in GGA, since LSD predicts a wrong ground state (fcc NM instead of bcc FM phase[32]). In practice, iron under pressure transforms to the hcp NM and not to the fcc NM phase. Nevertheless, these two phases are so close in energy (see, for example, Fig. 4 of Ref. 37) that the phase transition between the bcc FM and fcc NM phase can serve as a model and clearly supports our explanation why GGA functionals increase the transition pressure in pressure-induced phase transitions over LSD.

We report our results for the structural parameters in Table III. We found a number of different experimental values for the volume per atom and the bulk modulus. Experimental volumes for bcc FM range from 78.93 a.u. (Ref. 34) to 79.51 a.u. (Ref. 36), and experimental bulk moduli from 168 GPa (Ref. 35) to 172 GPa.[34] Our LSD result for the equilibrium volume is 11% smaller than the experimental value, but compares well with other theoretical calculations (LAPW:[34,36] 70.7 a.u., LMTO ASA:[33] 70.44 a.u.). The only calculation that differs significantly from ours is by Zhu *et al.*,[35] whose use of pseudopotentials may have caused this discrepancy. The bulk modulus is severely overestimated (in our case by 51%) as a consequence of the too-small equilibrium volume. Similar results were obtained in the above-mentioned studies.

Gradient corrections expand the equilibrium volume of the bcc FM structure by almost 9%, but this volume remains 3.7% smaller than the experimental value. Our GGA volume is in good agreement with that of Stixrude *et al.*[36] A GGA expansion was also observed in Ref. 33, using LM (Ref. 4) and PW86 (Ref. 5) gradient-corrected exchange-correlation functionals.

The fcc NM results can also be compared to other studies. Again, our LSD numbers are in excellent agreement with the results of Stixrude *et al.*[36] ($V_0=65.1$ a.u., $B_0=340$ GPa), but differ from the pseudopotential values of Zhu *et al.*[35] ($V_0=68.0$ a.u., $B_0=334$ GPa).

We find a stable fcc NM phase in the LSD approximation, so no (positive) transition pressure can be calculated. On the other hand, GGA favors the more open crystal structure, i.e., the bcc FM phase, and thus permits a calculation of the transition pressure. Our results are reported in Table III. We explain the effect of the gradient correction on the transition pressure in the next section.

IV. INEQUALITY FOR AVERAGE VALUES OF DENSITY PARAMETERS

The GGA form for the exchange-correlation energy can be cast in the following way (neglecting small $\nabla\zeta$ terms):

$$E_{\rm XC}^{\rm GGA}[n_\uparrow,n_\downarrow]=\int d\mathbf{r}\,n(\mathbf{r})\varepsilon_{\rm X}(r_s)F_{\rm XC}^{\rm GGA}(r_s,\zeta,s), \tag{1}$$

where $\varepsilon_X(r_s)=-(3/4\pi)(9\pi/4)^{1/3}/r_s$ is the exchange energy per electron in the homogeneous electron gas with density $n=(4\pi r_s^3/3)^{-1}$. We use atomic units ($\hbar=e^2=m=1$).

The enhancement factor $F_{\rm XC}^{\rm GGA}(r_s,\zeta,s)$ is a function of three density parameters: the Seitz radius r_s, the relative spin polarization $\zeta=(n_\uparrow-n_\downarrow)/n$, and the reduced density gradient $s=|\nabla n|/2k_F n=(3/2\pi)^{1/3}|\nabla r_s|$, where $k_F=(3\pi^2 n)^{1/3}$ is the local Fermi wave vector. In the present work, we consider only the PBE enhancement factor.[9] Note that, in the case of a uniform density ($s=0$ everywhere), the enhancement factor $F_{\rm XC}^{\rm GGA}(r_s,\zeta,s=0)$ and the exchange-correlation energy $E_{\rm XC}^{\rm GGA}$ in Eq. (1) reduce to the LSD limit.

In order to simplify the interpretation, we replace the continuous values of the density parameters r_s, ζ, and s in Eq. (1) by their averages $\langle r_s\rangle$, $\langle|\zeta|\rangle$, and $\langle s\rangle$,[22–24] which then fix the exchange-correlation energy:

$$E_{\rm XC}=N\varepsilon_{\rm X}(\langle r_s\rangle)F_{\rm XC}(\langle r_s\rangle,\langle|\zeta|\rangle,\langle s\rangle). \tag{2}$$

The averaging of these density parameters is not unique, but we use the definition in Eq. (6) from Ref. 23.

To understand how the gradient correction modifies LSD results in our systems, we focus on the difference between the LSD and GGA total energies. Since $E^{\rm LSD}$ is minimal with respect to variations of $n(\mathbf{r})$, we can usually ignore the small differences between self-consistent LSD and GGA densities,[53] so that $E^{\rm GGA}-E^{\rm LSD}\approx E_{\rm XC}^{\rm GGA}-E_{\rm XC}^{\rm LSD}$. Then the

TABLE IV. Average density parameters for Si diamond and β-tin phases, and a test of the inequality (4) for the volume expansion of each and for the reverse phase transition between them. ''Infinitesimal'' changes of average parameters are obtained by increasing the volume of the primitive unit cell for each phase from V_0-5 a.u. to V_0+5 a.u. For the phase transition process, the average values taken are arithmetic means between two phases, and the difference is obtained as a difference of the density parameters at equilibrium positions. P is 1.119 for the diamond structure, 1.117 for the β-tin structure, and 1.118 for the transition.

	Diamond	β-tin		β-tin→Diamond
$\langle r_s\rangle$	0.3416	0.3413	$\overline{\langle r_s\rangle}$	0.3415
$\langle s\rangle$	0.6396	0.6352	$\overline{\langle s\rangle}$	0.6374
$d\langle r_s\rangle$	2.193×10^{-4}	3.190×10^{-4}	$\Delta\langle r_s\rangle$	3.0×10^{-4}
$d\langle s\rangle$	5.387×10^{-4}	7.930×10^{-4}	$\Delta\langle s\rangle$	4.4×10^{-3}
Ineq. (4)	$8.4\times10^{-4}>3.6\times10^{-4}$	$1.2\times10^{-3}>5.2\times10^{-4}$	Ineq. (4)	$6.9\times10^{-3}>4.9\times10^{-4}$

gradient correction to the energy per electron for an N-electron system with a given density is

$$\Delta=(E_{\mathrm{XC}}^{\mathrm{GGA}}-E_{\mathrm{XC}}^{\mathrm{LSD}})/N\approx\varepsilon_{\mathrm{X}}(\langle r_s\rangle)\times[F_{\mathrm{XC}}(\langle r_s\rangle,\langle|\zeta|\rangle,\langle s\rangle)-F_{\mathrm{XC}}(\langle r_s\rangle,\langle|\zeta|\rangle,0)]. \quad (3)$$

Now consider some process that leads to infinitesimal changes in $\langle r_s\rangle$, $\langle|\zeta|\rangle$, and $\langle s\rangle$. In a typical process such as stretching of a bond, both $\langle r_s\rangle$ and $\langle s\rangle$ increase. The gradient correction will favor this process if $d\Delta<0$. Partial differentiation of Eq. (3) yields

$$\frac{d\langle s\rangle}{\langle s\rangle}>P\,\frac{d\langle r_s\rangle}{2\langle r_s\rangle}+Q d\langle|\zeta|\rangle \quad (d\Delta<0), \quad (4)$$

where

$$P=-\frac{2\langle r_s\rangle}{\langle s\rangle}\,\frac{\partial\Delta/\partial\langle r_s\rangle}{\partial\Delta/\partial\langle s\rangle}, \quad (5)$$

$$Q=-\frac{1}{\langle s\rangle}\,\frac{\partial\Delta/\partial\langle|\zeta|\rangle}{\partial\Delta/\partial\langle s\rangle}. \quad (6)$$

In general, gradient corrections favor density contractions (smaller $\langle r_s\rangle$) as well as density inhomogeneity (larger $\langle s\rangle$), and Eq. (4) shows that the relative increase of inhomogeneity ($d\langle s\rangle/\langle s\rangle$) must be greater than the relative decrease of the density ($d\langle r_s\rangle/2\langle r_s\rangle$) to ensure that gradient corrections should drive a process forward. (Note that P is close to unity, and Q is zero for nonmagnetic systems). If the inequality (4) is not fulfilled, then gradient corrections will disfavor the process. An example of such a disfavored process is bond stretching in the H_2 molecule. In this molecule, the GGA bond length is smaller than the LSD bond length,[12,23] contrary to the usual trend.

The inequality (4) can be applied not only to processes where the changes of the density parameters are infinitesimal (small changes in lattice parameters), but also to processes where the density parameters change by small finite amounts (phase transitions). We test this inequality for phase transitions to explain the effect of gradient corrections on the coexistence (or phase transition) pressure between two crystal structures. (Although the transition pressure p_t is $-\Delta E_t/\Delta V_t$, we note that the gradient corrections have a much larger relative effect on ΔE_t than on ΔV_t.)

In Tables IV, V, and VI, we report average density parameters $\langle r_s\rangle$ and $\langle s\rangle$ for all phases, evaluated with the LSD equilibrium density (and LSD atomic positions). Note that these values do not change qualitatively if a GGA density is used. (See, for example, Fig. 1 in Ref. 54 for a detailed study of the difference between the LSD and GGA values of density parameters $\langle r_s\rangle$, $\langle|\zeta|\rangle$, and $\langle s\rangle$ in the fragmentation of the H_3 transition state). For Si the average Seitz radius $\langle r_s\rangle$ is smaller in the β-tin structure, indicating a bigger average electron density and thus a more compact and also more uniform crystal phase. In fact the β-tin structure has a smaller value of the reduced density gradient $\langle s\rangle$, which can be regarded as a measure of the inhomogeneity of the system (in the sense of how much the system differs on the average from the uniform electron gas, where $\langle s\rangle=0$).

Small changes in the density parameters listed in Tables IV, V, and VI as a consequence of the rearrangement of the atomic positions have been evaluated around the LSD equi-

TABLE V. Average density parameters for SiO_2 α-quartz and stishovite, and a test of the inequality (4) for the volume expansion of each and for the reverse phase transition between them. ''Infinitesimal'' changes of average parameters are obtained by increasing the volume per SiO_2 formula unit for each phase from V_0-5 a.u. to V_0+5 a.u. P is 1.130 for the α-quartz structure, 1.128 for the stishovite structure, and 1.129 for the transition.

	α-quartz	Stishovite		Stishovite→α-quartz
$\langle r_s\rangle$	0.4046	0.4035	$\overline{\langle r_s\rangle}$	0.4041
$\langle s\rangle$	0.6707	0.6631	$\overline{\langle s\rangle}$	0.6669
$d\langle r_s\rangle$	1.073×10^{-4}	9.387×10^{-4}	$\Delta\langle r_s\rangle$	5.637×10^{-4}
$d\langle s\rangle$	4.669×10^{-4}	2.000×10^{-3}	$\Delta\langle s\rangle$	3.848×10^{-3}
Ineq. (4)	$7.0\times10^{-4}>1.5\times10^{-4}$	$3.0\times10^{-3}>1.3\times10^{-3}$	Ineq. (4)	$5.8\times10^{-3}>7.9\times10^{-4}$

TABLE VI. Average density parameters for Fe bcc FM and fcc NM phases, and a test of the inequality (4) for the volume expansion of each and for the reverse phase transition between them. ''Infinitesimal'' changes of average parameters are obtained by increasing the volume per atom for each phase from $V_0 - 5$ a.u. to $V_0 + 5$ a.u. P is 1.0915 for the bcc structure, 1.0913 for the fcc structure, and 1.0914 for the transition; the corresponding values of Q are 2.00×10^{-3}, 0, and 1.04×10^{-3}.

	bcc FM	fcc NM		fcc NM→bcc FM
$\langle r_s\rangle$	0.2316	0.2315	$\overline{\langle r_s\rangle}$	0.23155
$\langle\lvert\zeta\rvert\rangle$	6.523×10^{-2}		$\overline{\langle\lvert\zeta\rvert\rangle}$	3.262×10^{-2}
$\langle s\rangle$	0.5568	0.5559	$\overline{\langle s\rangle}$	0.5564
$d\langle r_s\rangle$	2.835×10^{-4}	3.713×10^{-4}	$\Delta\langle r_s\rangle$	1.200×10^{-4}
$d\langle\lvert\zeta\rvert\rangle$	7.284×10^{-3}		$\Delta\langle\lvert\zeta\rvert\rangle$	6.523×10^{-2}
$d\langle s\rangle$	1.504×10^{-3}	1.789×10^{-3}	$\Delta\langle s\rangle$	9.110×10^{-4}
Ineq. (4)	$2.7\times10^{-3} > 6.8\times10^{-4}$	$3.2\times10^{-3} > 8.7\times10^{-4}$	Ineq. (4)	$1.6\times10^{-3} > 3.5\times10^{-4}$

librium volume, by increasing and decreasing the volume by ±5 a.u. Inequality (4) is then evaluated for expansion from $V_0 - 5$ a.u. to $V_0 + 5$ a.u. and is confirmed for all crystal structures. This implies that the gradient correction to the exchange-correlation energy should favor larger equilibrium volumes, as it actually does (compare calculated LSD and PBE structural parameters in Tables I, II, and III).

Although the inequality (4) was derived for infinitesimally small rearrangements of atomic positions, it can be successfully applied to finite changes. To do so, we replace $\langle r_s\rangle$, $\langle|\zeta|\rangle$, and $\langle s\rangle$ by their mean values taken from the initial and final state, and insert finite changes instead of infinitesimal ones.

We apply the inequality to the reverse phase transitions from the β-tin to the diamond phase in Si, from stishovite to α-quartz in SiO_2, and from the fcc NM to bcc FM phase in Fe. Each reverse transition is one in which inhomogeneity increases and density decreases. The inequality is obeyed in all three cases, and thus gradient corrections favor the diamond phase, the α-quartz phase, and the bcc FM phase, respectively, resulting in a bigger energy difference between the two phases. As a consequence, the transition pressure should increase in the GGA approximation, as indeed it does (see LSD and GGA phase transition parameters in Tables I, II, and III). Thus, for the cases studied here, the energy gain due to the increase of inhomogeneity always dominates the energy loss due to the density expansion during the reverse phase transition. Typically the inhomogeneity effect also dominates the density effect in GGA calculations of bondlengths, surface energies, or transition state barriers.[23,24]

V. CONCLUSIONS

To test the performance of LSD and GGA in solid state physics, we have performed state-of-the art all-electron calculations in two crystal structures for each of three materials. Our results confirm the accuracy of recent all-electron or pseudopotential studies of these systems.

We find that gradient corrections to LSD correct or slightly under-correct the transition pressures in all three materials, and the equilibrium volume in Fe. However, they over-correct the volume in Si and SiO_2. Recent work by Fuchs *et al.*[21] suggests that LSD and GGA errors of lattice constants arise from unreliable descriptions of core-valence interaction. Thus, reliable equilibrium volumes might be attainable in GGA with the help of pseudopotentials constructed for the free atom at a beyond-GGA level.[55–57] Lattice constants aside, GGA seems to perform better than LSD for bulk solids, consistent with the observation that gradient corrections improve the valence-valence exchange energy in Si (Ref. 58) and model solids[59] as well as the valence-valence exchange-correlation energy in Si.[60]

In the cases studied here, gradient corrections expand equilibrium volumes and increase transition pressures from one crystal structure to another. We have shown that this is a consequence of their tendency to stabilize systems with more inhomogeneous electron densities, as surmised in previous work.[15,16]

ACKNOWLEDGMENTS

A.Z. wishes to thank the Austrian Science Foundation (Project No. P10847), the Slovenian Ministry of Science and Technology (Project No. J1-8665), J.P.P. acknowledges the support of the U.S. National Science Foundation under Grant No. DMR 95-21353. A.Z. and J.P.P. were also supported by a U.S.-Slovenia Cooperative Research Grant (NSF-INT-9800968).

---

[1] W. Kohn and L. J. Sham, Phys. Rev. A **140**, A1133 (1965).
[2] *Modern Density Functional Theory: A Tool for Chemistry*, edited by J. M. Seminario and P. Politzer (Elsevier, Amsterdam, 1995).
[3] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[4] D. C. Langreth and M. J. Mehl, Phys. Rev. B **28**, 1809 (1983).
[5] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986); **40**, 3399(E) (1989).
[6] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[7] J. P. Perdew, in *Electronic Structure of Solids' 91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991).
[8] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B **54**, 16 533 (1996); **57**, 14 999(E) (1998).
[9] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396(E) (1997).

[10] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992); **48**, 4978(E) (1993).

[11] K. Burke, J. P. Perdew, and Y. Wang, in *Electronic Density Functional Theory: Recent Progress and New Directions*, edited by J. F. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1998).

[12] B. G. Johnson, P. M. W. Gill, and J. A. Pople, J. Chem. Phys. **98**, 5612 (1993).

[13] D. C. Langreth and J. P. Perdew, Phys. Rev. B **21**, 5469 (1980).

[14] V. Ozolinš and M. Körling, Phys. Rev. B **48**, 18 304 (1993).

[15] N. Moll, M. Bockstedte, M. Fuchs, E. Pehlke, and M. Scheffler, Phys. Rev. B **52**, 2550 (1995), and references therein.

[16] D. R. Hamann, Phys. Rev. Lett. **76**, 660 (1996).

[17] C. Filippi, D. J. Singh, and C. J. Umrigar, Phys. Rev. B **50**, 14 947 (1994).

[18] M. Causà and A. Zupan, Int. J. Quantum Chem. **S28**, 633 (1994).

[19] A. Zupan and M. Causà, Int. J. Quantum Chem. **56**, 337 (1995).

[20] I.-H. Lee and R. M. Martin, Phys. Rev. B **56**, 7197 (1997).

[21] M. Fuchs, M. Bockstedte, E. Pehlke, and M. Scheffler, Phys. Rev. B **57**, 2134 (1998).

[22] A. Zupan, J. P. Perdew, K. Burke, and M. Causà, Int. J. Quantum Chem. **61**, 835 (1997).

[23] A. Zupan, K. Burke, M. Ernzerhof, and J. P. Perdew, J. Chem. Phys. **106**, 10 184 (1997).

[24] J. P. Perdew, M. Ernzerhof, A. Zupan, and K. Burke, J. Chem. Phys. **108**, 1522 (1998).

[25] M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982).

[26] R. Pandey, M. Causà, N. M. Harrison, and M. Seel, J. Phys.: Condens. Matter **8**, 3993 (1996).

[27] N. R. Keskar and J. R. Chelikovsky, Phys. Rev. B **46**, 1 (1992).

[28] F. Liu, S. H. Garofalini, D. King-Smith, and D. Vanderbilt, Phys. Rev. B **49**, 12 528 (1994).

[29] D. M. Teter, G. V. Gibbs, M. B. Boisen, Jr., D. C. Allan, and M. P. Teter, Phys. Rev. B **52**, 8064 (1995).

[30] J. K. Dewhurst, J. E. Lowther, and L. T. Madzwara, Phys. Rev. B **55**, 11 003 (1997).

[31] T. Demuth and J. Hafner (unpublished).

[32] C. S. Wang, B. M. Klein, and H. Krakauer, Phys. Rev. Lett. **54**, 1852 (1985).

[33] P. Bagno, O. Jepsen, and O. Gunnarsson, Phys. Rev. B **40**, 1997 (1989).

[34] D. J. Singh, W. E. Pickett, and H. Krakauer, Phys. Rev. B **43**, 11 628 (1991).

[35] J. Zhu, X. W. Wang, and S. G. Louie, Phys. Rev. B **45**, 8887 (1992).

[36] L. Stixrude, R. E. Cohen, and D. J. Singh, Phys. Rev. B **50**, 6442 (1994).

[37] P. Söderlind, J. A. Moriarty, and J. M. Wills, Phys. Rev. B **53**, 14 063 (1996).

[38] J. L. Holm, O. J. Kleppa, and E. F. Westrum, Jr., Geochim. Cosmochim. Acta **31**, 2289 (1967).

[39] A. P. Jephcoat, H. K. Mao, and P. M. Bell, J. Geophys. Res. **91**, 4677 (1986).

[40] P. Blaha, K. Schwarz, and J. Luitz, WIEN97, Vienna University of Technology 1997. [Improved and updated Unix version of the original copyrighted WIEN code, which was published by P. Blaha, K. Schwarz, P. Sorantin, and S. B. Trickey, Comput. Phys. Commun. **59**, 339 (1990).]

[41] F. D. Murnaghan, Proc. Natl. Acad. Sci. USA **30**, 244 (1944).

[42] A. Garcìa, C. Elsässer, J. Zhu, S. G. Louie, and M. L. Cohen, Phys. Rev. B **46**, 9829 (1992).

[43] G. Ortiz, Phys. Rev. B **45**, 11 328 (1992).

[44] J. Z. Hu, L. D. Merkle, C. S. Menoni, and I. L. Spain, Phys. Rev. B **34**, 4679 (1986).

[45] D. R. Hamann (private communication).

[46] M. Akaogi and A. Navrotsky, Phys. Earth Planet. Inter. **36**, 124 (1984).

[47] J. D. Jorgensen, J. Appl. Phys. **49**, 5473 (1978).

[48] *International Tables for Crystallography* (Kluwer Academic, Dordrecht, 1995), 4th revised edition, Vol. A.

[49] L. Levien, C. T. Prewitt, and D. J. Weidner, Am. Mineral. **65**, 920 (1980).

[50] M. Sugiyama, S. Endo, and K. Koto, Mineral. J. **13**, 455 (1987).

[51] N. L. Ross, J.-F. Shu, R. M. Hazen, and T. Gasparik, Am. Mineral. **75**, 739 (1990).

[52] M. W. Guinan and D. N. Beshers, J. Phys. Chem. Solids **29**, 541 (1968).

[53] L. Fan and T. Ziegler, J. Chem. Phys. **94**, 6057 (1991).

[54] J. P. Perdew, M. Ernzerhof, A. Zupan, and K. Burke, in Advances in Density Functional Theory, edited by J. M. Seminario, special issue of Adv. Quantum Chem. (to be published).

[55] D. M. Bylander and L. Kleinman, Phys. Rev. B **55**, 9432 (1997).

[56] D. Vogel, P. Kruger, and J. Pollmann, Phys. Rev. B **54**, 5495 (1996).

[57] J. P. Perdew, in *Condensed Matter Theories*, edited by J. da Providencia and M. Brajczewska (Nova, New York, 1998), Vol. 13.

[58] M. Städele, J. A. Majewski, P. Vogl, and A. Görling, Phys. Rev. Lett. **79**, 2089 (1997); (unpublished).

[59] M. Springer, P. S. Svendsen, and U. von Barth, Phys. Rev. B **54**, 17 392 (1996).

[60] R. Q. Hood, M. Y. Chou, A. J. Williamson, G. Rajagopal, and R. J. Needs, Phys. Rev. B **57**, 8972 (1998).