

## Application of generalized gradient approximations: The diamond- $\beta$ -tin phase transition in Si and Ge

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Generalized gradient approximations (GGA) for the exchange-correlation energy have been suggested to improve upon the local-density approximation (LDA) in density-functional theory. It has been demonstrated by various authors that the gradient correction suggested by Becke for the exchange functional and Perdew for the correlation energy, as well as the recent GGA by Perdew and Wang (1991), yield improved cohesive energies for solids, correcting for the overbinding in LDA. In this paper we focus on a structural phase transition of Si, which under pressure transforms from the diamond structure to the  $\beta$ -tin structure. The coexistence pressure calculated within the LDA is 80 kbar, smaller than the experimental values (103 – 125 kbar). Both gradient-corrected schemes yield a coexistence pressure which is larger than the LDA value (146 kbar for the Becke-Perdew and 122 kbar for the Perdew-Wang exchange-correlation functional). Ge undergoes a similar transition at around 105 kbar. The LDA result for the coexistence pressure is 73 kbar, it amounts to 118 kbar when calculated within the Becke-Perdew GGA, and 98 kbar within the Perdew-Wang GGA.

### I. INTRODUCTION

Density-functional theory<sup>1,2</sup> (DFT) provides an exact description of the ground state of an interacting electron system, with the complications of the quantum-mechanical many-particle system combined into an exchange-correlation (XC) functional of which the explicit form is not known. The local-density approximation<sup>3</sup> (LDA) to this functional has proven to be amazingly successful in yielding quantitatively reliable predictions for ground state properties. However, there are some well-known difficulties where inhomogeneity corrections become important: The cohesive energy is generally overestimated by LDA, and in many cases equilibrium lattice constants come out too small.<sup>4-7</sup> In this paper we focus on another apparent “failure of the LDA,” the underestimation of the coexistence pressure for a structural phase transition in silicon<sup>8,9</sup> and germanium.<sup>10</sup>

On compression, silicon undergoes a series of phase transitions that have found widespread interest both experimentally<sup>11-17</sup> and theoretically.<sup>8,9,18-20</sup> On compression, Si transforms from the diamond structure to the  $\beta$ -tin structure (see Fig. 1). This transition is accompanied by a change from a semiconducting to a metallic state. The phase transition is of first order, and there is a large hysteresis since, on lowering the pressure, the material does not return to the diamond structure, but transforms to a metastable fourfold coordinated structure with a body-centered-cubic unit cell (BC8).

The experimental value for the coexistence pressure for Si in the diamond and the  $\beta$ -tin phases appears to be uncertain. McMahon and Nelmes<sup>16</sup> measured a value of 103 kbar. In an x-ray diffraction study, Hu and Spain<sup>13</sup> found the transition to initiate at 112 kbar and that the two phases coexist up to 125 kbar. Under nonhydrostatic stress, however, Si can transform at pressures lower than

in the hydrostatic case.<sup>11,17</sup> Knowledge of the temperature dependence of the coexistence pressure  $p_t(T)$  for Si in the diamond and  $\beta$ -tin structures is rather vague, making an extrapolation of the experimental results measured at room temperature to zero Kelvin very unreliable,<sup>12</sup> and thus we will not attempt such a correction. However, we estimate from the experimental phase diagram<sup>12</sup> that the coexistence pressure at least should not decrease by more than 10 kbar.

The coexistence pressure for the diamond to  $\beta$ -tin transition in Si derived within DFT-LDA (computational details will be given below) turns out to be 80 kbar, which is in agreement with other recent LDA calculations.<sup>10,18,21</sup> Even though the experimental values do scatter, we find the LDA pressure to be significantly below the range of experimental values. In this paper we will argue that this is due to the insufficient description of inhomogeneous systems within the LDA.

A similar transformation from a diamond to a  $\beta$ -tin phase also occurs for the two heavier group IVA elements Ge and Sn in the periodic system. The transition pres-

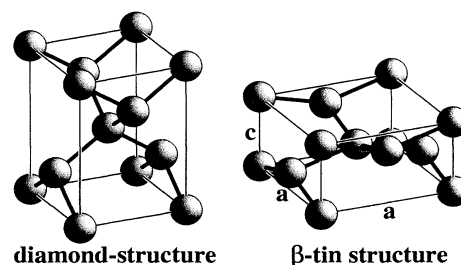


FIG. 1. Comparison of the diamond structure (left) and the  $\beta$ -tin structure (right). The  $\beta$ -tin structure can be regarded as a tetragonally distorted diamond structure with lattice constants  $a$  and  $c$ .

sure becomes increasingly smaller; it is around 105 kbar<sup>22</sup> – 107 kbar<sup>23</sup> for Ge, and in the case of Sn<sup>24</sup> the transition (driven by temperature change) already occurs at ambient pressure. In view of the close similarity of Si and Ge, and to look for “chemical trends,” we also calculate how well the LDA performs for Ge, and compare to our findings for Si.

To improve upon the local-density approximation in density-functional total-energy calculations, various generalized gradient approximations (GGA) for the exchange-correlation energy functional have been suggested in literature.<sup>25–30</sup> Their general form is

$$E_{XC}[n] = \int \epsilon_{XC}(n(\mathbf{r}), \nabla n(\mathbf{r}))n(\mathbf{r})d^3\mathbf{r}, \quad (1)$$

the difference with respect to LDA being the additional local dependence of the integrand on the gradient of the electron density  $n(\mathbf{r})$ . In this paper we apply two GGA’s, the semiempirical exchange functional proposed by Becke<sup>26</sup> in combination with a correlation functional by Perdew<sup>28</sup> (BP), and Perdew’s more recent GGA-II (Refs. 29 and 30) (PW91). These functionals are more refined than the original functional proposed by Langreth and Mehl.<sup>25</sup> The Langreth-Mehl expression for the exchange energy still resembles the form of the gradient expansion, and is less accurate than Perdew and Wang’s functional.<sup>27</sup> As noted by Perdew,<sup>28</sup> the correlation part of the Langreth-Mehl functional does not go beyond the random-phase approximation for the correlation energy, and it does not recover the gradient expansion in the limit of slowly varying densities. The more recent XC functionals (BP, PW91) have been improved with respect to these shortcomings. The PW91 XC functional is based on a parameter-free correlation energy functional and a refined Becke exchange functional. For small values of the scaled density gradient typical for a solid, Perdew’s modified Becke exchange is very similar to the 1986 version of the Perdew-Wang exchange,<sup>27</sup> which is based on the gradient expansion of the exchange hole combined with a real-space cutoff to assure that the hole is negative everywhere and obeys the sum rule that it integrates to  $-1$  electron.

Umrigar and Gonze<sup>31</sup> have compared the exchange-correlation potential and the electron density of light atoms calculated within LDA or GGA with the respective exact quantities from quantum Monte-Carlo calculations. However, as all the approximate XC potentials differ drastically from the exact XC potential, it seems to be rather difficult to draw any conclusions regarding to what extent present GGA’s should be superior to LDA. Therefore, to judge the usefulness of the GGA’s in “real-life” total-energy calculations, a vast amount of test calculations for atoms, molecules, and solids has to be carried out. Such calculations for solids using the BP functional<sup>5,6</sup> and the PW91 functional<sup>4,7</sup> reveal that lattice constants are not consistently improved by GGA, being often too small in LDA but overcorrected by GGA. The static dielectric constant for Si calculated at the experimental lattice spacing comes out smaller in BP-GGA than in LDA, thereby decreasing the difference

from experiment by  $\approx 1/3$  of the LDA error; however, this improvement is practically lost when the calculations are carried out at the respective theoretical lattice constants.<sup>32</sup> On the other hand, in general the cohesive energy, which is overestimated in LDA, is improved significantly by the BP and PW91 GGA.<sup>4–7</sup> This is due to the fact that by introducing the GGA the total energy of the more inhomogeneous atom is lowered by a larger amount than the total energy of the solid.<sup>33</sup> Another area where GGA proved to be of importance is the calculation of activation energy barriers<sup>34</sup> and barriers of adsorption: For example, the dissociation barrier for H<sub>2</sub> on a Cu(111) surface turns out to be almost absent in the LDA calculation, while it is large (0.73 eV) when calculated within the PW91 GGA, and only the GGA result conforms with experiment.<sup>35</sup> Furthermore, Lee *et al.*<sup>36</sup> used the BP GGA to study the equations of state for different phases of ice. They found that gradient corrections have to be included in order to describe the hydrogen bond properly.

We suspect that gradient corrections might be useful for yet another class of problems, certain structural phase transitions in solids. To corroborate this view, we take the diamond to  $\beta$ -tin transformation in Si and Ge as an example and investigate how well this phase transition is described by modern GGAs, as compared to the standard LDA description.

## II. COMPUTATIONAL DETAILS

We have carried out DFT total-energy calculations for Si and Ge in the diamond and  $\beta$ -tin phase.<sup>37</sup> For the LDA exchange-correlation functional we use Perdew and Zunger’s parametrization<sup>38</sup> of Ceperley and Alder’s data<sup>39</sup> for the correlation energy (henceforth denoted CA). For the GGA calculations, on the other hand, we use either the BP (Refs. 26 and 28) or the PW91 (Ref. 30) form of the exchange-correlation energy.

*Ab initio* norm-conserving pseudopotentials are generated with Hamann’s scheme<sup>40</sup> generalized to include GGA functionals. The cutoff radii for pseudoionization have been chosen equal to 0.56 Å, 0.68 Å, and 0.68 Å for the  $s$ ,  $p$ , and  $d$  pseudo-wave-functions of Si,<sup>41</sup> and equal to 0.71 Å, 0.67 Å, and 0.84 Å for the  $s$ ,  $p$ , and  $d$  pseudo-wave-functions of Ge, respectively. The Ge  $d$  potential was generated from the  $4s^1 4p^1 4d^0$ <sup>25</sup> configuration in order to obtain a well-localized normalizable  $d$  wave function.<sup>42</sup> These potentials are further transformed into fully separable pseudopotentials of the Kleinman-Bylander type.<sup>43</sup> For Si, the  $d$  potential was used as the local potential, while in case of Ge, to improve the transferability of its Kleinman-Bylander pseudopotential, we have chosen the  $p$  potential as the local one. All calculations are performed consistently, i.e., the same expression for  $E_{XC}$  is used in the atomic Kohn-Sham equation, the unscreening of the effective potential of the atom to determine the ionic (LDA or GGA) pseudopotential, and the solid-state calculation. There has been evidence that this consistency is essential when lattice constants are calculated.<sup>6</sup> Furthermore, we have taken

the nonlinearity of the core-valence exchange-correlation energy into account.<sup>44</sup> This nonlinear core-valence (nlcv) interaction is negligible in the case of Si within the LDA, and our results show that it is, in fact, still unimportant for the PW91 GGA calculations. For Ge, on the other hand, the overlap of the core and the valence electron densities becomes significant, and thus the nonlinearity of the exchange-correlation energy (with respect to the core-valence interaction) cannot be neglected anymore.

The plane-wave basis set was defined by an energy cutoff of 20 Ry (50 Ry for calculations including nonlinear core-valence XC), and the electron density was calculated from special  $\mathbf{k}$ -point sets<sup>45</sup> equivalent to 144 and 1024 sampling points in the full Brillouin zone of the tetragonal four-atom cell for the diamond and  $\beta$ -tin structures, respectively. The Fermi surface of the metallic  $\beta$ -tin phase was broadened according to an electron temperature of 0.1 eV, and the total energy extrapolated to zero temperature in the usual way.<sup>46</sup> We expect our numerical values for total energy differences to be accurate within  $\pm 14$  meV per atom, which translates into an error of the coexistence pressure of  $\pm 5$  kbar.

We have calculated the total energy per atom for Si and Ge in the diamond structure for several volumes of the unit cell, varying the lattice constant within about  $\pm 5\%$  of its equilibrium value. These energies were then fitted to Murnaghan's<sup>47</sup> equation of state, which yields the values of the equilibrium lattice constant and the bulk modulus. The  $\beta$ -tin structure is slightly more complicated in that it has an additional degree of freedom, the  $c/a$  ratio of the lattice constants, which, at least in principle, has to be optimized separately for each volume. We have minimized the total energy as a function of  $c/a$  at some fixed volume close to the equilibrium volume of the  $\beta$ -tin phase to get a theoretical estimate, and in comparison with experiment found  $c/a$  to be well reproduced. Furthermore, comparing total energy versus volume curves calculated for several fixed  $c/a$  ratios around this value, we found that there is practically no loss of accuracy when we drop the optimization of  $c/a$  and instead just assume that  $c/a$  is constant and equal to its experimental value. As for the diamond structure, the total energy data are then fitted to Murnaghan's equation of state. The coexistence pressure is finally calculated from a common tangent (Gibbs) construction to the two energy versus volume curves for the diamond and  $\beta$ -tin phases.<sup>8</sup>

### III. RESULTS AND DISCUSSION

#### A. Silicon

The calculated structural parameters of Si in the diamond and  $\beta$ -tin phases are listed in Table I. The experimental lattice constant of the diamond phase corresponds to zero pressure and temperature  $T = 0$  K.<sup>8</sup> The diamond-structure LDA and Becke-Perdew GGA lattice constants ( $c_0^{\text{CA}} = 5.39$  Å,  $c_0^{\text{BP}} = 5.47$  Å) and bulk moduli ( $B_0^{\text{CA}} = 0.97$  Mbar,  $B_0^{\text{BP}} = 0.90$  Mbar) are in excellent agreement with recent theoretical results by Gar-

TABLE I. Structural properties and the diamond to  $\beta$ -tin phase transition of Si calculated within different approximations for the XC functional in comparison to experiment. For a compilation of experimental data, see, e.g., the articles by Yin and Cohen (Ref. 8) and Hu *et al.* (Ref. 14).

Phase	Expt.	CA	BP	PW91
Diamond				
$c_0$ (Å)	5.43	5.39	5.47	5.45
$B_0$ (Mbar)	0.99	0.97	0.90	0.92
$\beta$ -tin				
$c_0$ (Å)		2.60	2.67	2.66
$c/a$	0.552	0.548		0.548
$B_0$ (Mbar)		1.15	0.99	1.04
$\Delta E_0$ (eV)		0.226	0.404	0.341
$V_t^d$	0.918	0.908	0.900	0.909
$V_t^\beta$	0.710	0.692	0.696	0.700
$p_t$ (kbar)	103 <sup>a</sup> 125 <sup>b</sup>	80	146	122

<sup>a</sup>Experimental coexistence pressure from Ref. 16.

<sup>b</sup>Experimental coexistence pressure from Ref. 13.

cia *et al.*<sup>6</sup> ( $c_0^{\text{CA}} = 5.37$  Å,  $c_0^{\text{BP}} = 5.47$  Å,  $B_0^{\text{CA}} = 0.98$  Mbar,  $B_0^{\text{BP}} = 0.88$  Mbar) and Ortiz<sup>5</sup> ( $c_0^{\text{CA}} = 5.37$  Å,  $c_0^{\text{BP}} = 5.49$  Å). In comparison to experiment, the equilibrium lattice constant is underestimated by 0.8% within LDA, but overestimated within both GGA schemes, by 0.8% and 0.4% for BP and PW91, respectively. Correspondingly, the bulk modulus is underestimated by the GGA. However, our PW91 results are distinctly closer to experiment than those calculated by Juan and Kaxiras,<sup>7</sup> who stated a large overestimate of the lattice constant by 3% within PW91. We attribute this difference to the additional smoothing of the pseudopotential close to the origin introduced by these authors, which apparently undermines the quality of their pseudopotential. We conclude that in the case of Si, the overall agreement between theory and experiment is similar for both the CA-LDA and the BP and PW91 GGA schemes.

The optimum  $c/a$  ratio for Si in the  $\beta$ -tin phase is 0.548, which is very close to the experimental ratio of 0.552.<sup>13</sup> Furthermore, the value of  $c/a$  turned out to be practically independent of the choice of  $E_{\text{XC}}$  (CA or PW91). The "equilibrium lattice constant" for the  $\beta$ -tin phase is formally defined by the position of the minimum in the equation of state for this structure. Similarly to the lattice constant in the diamond structure, its GGA values are larger than the corresponding LDA value and the corresponding bulk moduli are smaller.

In Fig. 2 the equation of state for both the  $\beta$ -tin and the diamond phases is shown for different approximations to  $E_{\text{XC}}$ . All configurations corresponding to portions of the equation of state energetically above the common tangent (denoted by a dashed line in Fig. 2) are thermodynamically unstable. In equilibrium, this interval instead corresponds to a region of two-phase coexistence, and the coexistence pressure  $p_t$  is given by the slope of

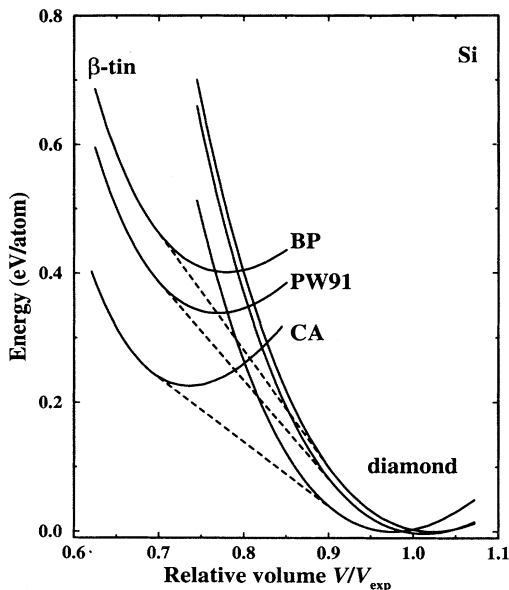


FIG. 2. Total energy per Si atom plotted versus volume. The total energy of Si in the diamond phase at equilibrium has been chosen as a zero-energy reference. The volume is expressed in units of the experimental equilibrium volume. Calculations were based on the Becke-Perdew (BP), Perdew GGA-II (PW91), and Ceperley-Alder LDA (CA) XC energy functional, respectively. The dashed line denotes the common tangent to the equations of state of the diamond and the  $\beta$ -tin structure (Gibbs construction).

the common tangent. In Table I the quantity  $\Delta E_0$  denotes the difference between the energy minima of both phases, and  $V_t^d$  and  $V_t^\beta$  are the volumina of the coexisting diamond and  $\beta$ -tin phases, respectively, in units of the experimental equilibrium volume of the diamond phase. Corrections due to the difference in zero-point energy between both phases have been neglected. For each phase, the contribution to the total energy from zero-point motion could be estimated from the respective Debye temperature  $\Theta_D$ ,  $E_{ZPM} = 9/8k_B\Theta_D$ . For the  $\alpha$  to  $\beta$ -tin transition of Sn  $\Delta E_{ZPM}$  was found to be about 2 meV.<sup>24</sup> We therefore expect this correction to be negligible for Si (and also Ge) in comparison to the value of  $\Delta E_0$ .

Our calculated LDA value of the transition pressure,  $p_t^{CA} = 80$  kbar, is in good agreement with the LDA result of 84 kbar of Boyer *et al.*, and the LDA result of 78 kbar of Needs and Mujica.<sup>9</sup> However, this theoretical value appears to be significantly smaller than the measured one. The coexistence pressure is increased by the GGA schemes. To interpret this finding, we have plotted the distribution of electron densities in Fig. 3. The electron density of the semiconducting diamond phase is much more inhomogeneous than that of the metallic  $\beta$ -tin phase. The GGA lowers the total energies of both phases; however, this energy lowering is larger for the more inhomogeneous diamond phase than for the metallic phase:  $\Delta E_0$  comes out larger in both the BP and PW91 than in the LDA calculations. Therefore, the coexistence pres-

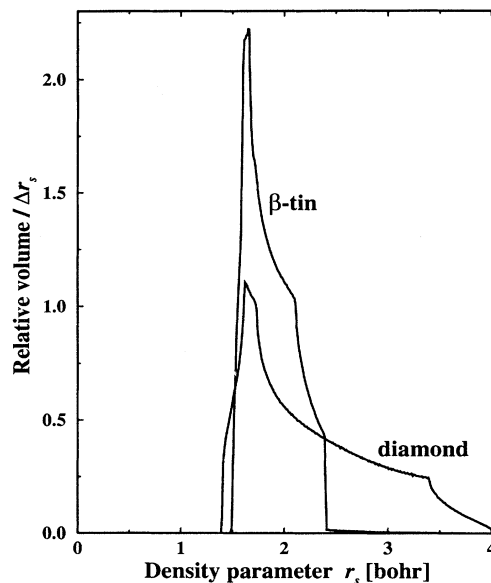


FIG. 3. Distribution of pseudo-electron-densities in the  $\beta$ -tin and diamond phases of Si. The density parameter  $r_s$  is defined by  $r_s = (3/4\pi n)^{1/3}$ , with  $n$  denoting the particle density. The volume of the part of the Wigner-Seitz cell having a density parameter within the interval  $r_s$  and  $r_s + \Delta r_s$ , divided by the experimental equilibrium volume times  $\Delta r_s$ , is plotted versus  $r_s$ .

sure is larger in the GGA than in the LDA. Note that the difference in equilibrium volumes  $V_t^d - V_t^\beta$  (equal to 0.216 for CA, 0.204 for BP, and 0.209 for PW91, all values in units of the experimental equilibrium volume of the diamond structure) depends much less on the choice of the XC functional than  $\Delta E_0$  does (which is increased by 50% when the PW91 XC functional is used instead of the LDA). Thus the change in  $V_t^d - V_t^\beta$  does not affect the above argument. The larger value of  $p_t$  in the GGA is due to a larger energy difference  $\Delta E_0$  between the equation of states of the diamond and  $\beta$ -tin phase, it does not seem to be directly linked to the quality of the prediction of structural parameters (such as  $V_t^d - V_t^\beta$ ).

In Table II we focus on two technical aspects that become important when using GGA pseudopotentials. To check the transferability of our GGA pseudopotentials we have included nonlinear core-valence XC,<sup>44</sup> i.e., we have constructed a pseudocore electron density, which becomes identical to the true core electron density outside a radius of 0.66 Å, and which is continuous with respect to its first and second radial derivatives. The nonlinearity of the exchange-correlation functional is thereby accounted for. In the case of Si, it is well established that the correction due to nlcv XC is negligible for the LDA XC functional. Here we find that this also holds true for the PW91 XC functional (which was not obvious, because this XC functional depends not only on the electron density as in LDA but also on the density gradient and could therefore have transferability properties different from the LDA XC functional).

TABLE II. Comparison of several properties of Si in the diamond and  $\beta$ -tin phase calculated within DFT using the PW91 GGA. The first column corresponds to a self-consistent calculation as described in the text. Incorporating the nonlinear core-valence XC leads to the results of the second column. The third column denotes a calculation in which the LDA pseudopotential was used instead of the correct PW91 pseudopotential.

Phase	PW91	PW91 nlcv	PW91 CA-ps
<b>Diamond</b>			
$c_0$ (Å)	5.45	5.45	5.40
$B_0$ (Mbar)	0.92	0.91	0.94
<b><math>\beta</math>-tin</b>			
$c_0$ (Å)	2.66	2.65	2.64
$B_0$ (Mbar)	1.04	1.05	1.04
$\Delta E_0$ (eV)	0.341	0.335	0.493
$V_t^d$	0.909	0.906	0.845
$V_t^\beta$	0.700	0.697	0.656
$p_t$ (kbar)	122	119	190

Furthermore, it would be convenient if one could simply use the ionic pseudopotential calculated within LDA also for plane-wave total-energy calculations with the PW91 XC functional. However, from the third column in Table II it becomes obvious that such an approach would be invalid, leading, for example, to a dramatic overestimate of the transition pressure. Hence, we consistently have to use the same approximation to  $E_{XC}$  for both the generation of the pseudopotential and the total-energy calculations.

### B. Germanium

We have repeated the calculations described above for Ge, using the CA LDA as well as the BP and PW91 gradient-corrected XC functionals. Our results are summarized in Table III. Nonlinear core-valence interactions have been included, with a pseudocore electron density that becomes identical to the true core electron density outside a radius of 0.63 Å. This was done because, contrary to our findings for Si, the transferability of the Ge pseudopotential with valence XC only turned out to be insufficient in view of the accuracy needed here, as can be judged by comparing the LDA data in the two columns of Table III labeled "CA." Differences in the structural properties of Ge in the diamond phase calculated within the LDA may thus partially be due to inequivalent pseudopotentials and transferability problems with Ge pseudopotentials not accounting for the nlcv XC interaction. Our LDA lattice constant and bulk modulus are  $c_0^{CA}=5.59$  Å and  $B_0^{CA}=0.75$  Mbar. Garcia *et al.*<sup>6</sup> arrived at  $c_0^{CA}=5.55$  Å and  $B_0^{CA}=0.78$  Mbar (valence XC only), and Mujica and Needs<sup>10</sup> calculated  $c_0^{CA}=5.64$  Å and  $B_0^{CA}=0.75$  Mbar, including nlcv XC interactions.

TABLE III. Structural properties and the diamond to  $\beta$ -tin phase transition of Ge calculated within different approximations for the XC functional in comparison to experiment. For a compilation of experimental data, see, e.g., the article by Yin and Cohen (Ref. 8).

Phase	Expt.	CA	CA nlcv	BP nlcv	PW91 nlcv
<b>Diamond</b>					
$c_0$ (Å)	5.65	5.55	5.59	5.74	5.73
$B_0$ (Mbar)	0.77	0.77	0.75	0.62	0.64
<b><math>\beta</math>-tin</b>					
$c_0$ (Å)		2.78	2.78	2.86	2.85
$c/a$	0.551		0.547		
$B_0$ (Mbar)		0.86	0.86	0.67	0.70
$\Delta E_0$ (eV)		0.212	0.182	0.293	0.251
$V_t^d$	0.875	0.863	0.891	0.907	0.921
$V_t^\beta$	0.694	0.700	0.723	0.745	0.752
$p_t$ (kbar)	105 <sup>a</sup> 107 <sup>b</sup>	87	73	118	98

<sup>a</sup>Experimental coexistence pressures from Ref. 22.

<sup>b</sup>Experimental coexistence pressures from Ref. 23.

Our LDA lattice constant is only 1% lower than the experimental value, and the agreement is slightly worsened by both GGA schemes. The lattice constant we have calculated using the BP XC,  $c_0^{BP}=5.74$  Å, is close to the result of Ortiz<sup>5</sup> ( $c_0^{BP}=5.72$  Å). Using the PW91 XC functional, we overestimate the lattice constant by 1.4%, which, however, is still less than the overestimate of 4.7% ( $c_0^{PW91}=5.92$  Å) reported by Juan and Kaxiras.<sup>7</sup> A similar discrepancy for Si is discussed in the preceding subsection.

The equation of state calculated for the experimental  $c/a$  ratio is plotted in Fig. 4, with the dashed line

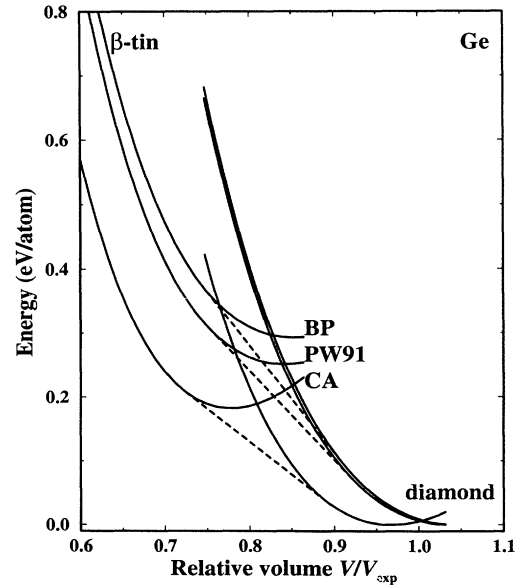


FIG. 4. Same as Fig. 2 for Ge.

marking the diamond and  $\beta$ -tin two-phase coexistence regions. Our transition pressure of 73 kbar calculated within the LDA is in very good agreement with the result of Needs and Mujica<sup>9</sup> ( $p_t = 74$  kbar) and by Kresse and Hafner<sup>48</sup> ( $p_t = 75$  kbar). By the same mechanism as described above the transition pressure becomes larger when the gradient corrections are included. Similarly as in the case of Si, this effect is more pronounced for the BP XC functional: When this scheme is used, the transition pressure for Ge increases to 118 kbar, while the PW91 XC functional leads to a transition pressure of 98 kbar. Comparing these different theoretical results with the experimental values,<sup>22,23</sup> we find that the coexistence pressure is underestimated by 30% within the LDA, while the GGA results are closer to experiment (with a deviation of about 10%).

#### IV. SUMMARY AND CONCLUSION

We have carried out DFT total-energy calculations for the equations of state of bulk Si and Ge, and derived the coexistence pressure for the diamond to  $\beta$ -tin structural phase transition. Comparing with the experimental data, we found that (despite the scatter of the experimental values) the LDA leads to a significant underestimate of the transition pressure. When we use a GGA XC energy functional and thus account for the inhomogeneity of the electron density, the transition pressure increases. While the BP XC functional apparently overestimates this effect, the PW91 XC functional leads to a coexistence pressure very close to the experimental value by Hu and Spain<sup>13</sup> for Si, and also improves agreement with experiment in the case of Ge. The coexistence pressure measured by McMahon and Nelmes for Si lies halfway between the respective LDA and PW91 GGA results.

The difference between our LDA and GGA results for the coexistence pressure of the diamond to  $\beta$ -tin structural phase transition in Si and Ge clearly demonstrates that the calculated pressure does, in fact, sensitively depend on the form of the exchange-correlation functional. Very recently, Seifert *et al.*<sup>49</sup> found a distinct increase of the calculated coexistence pressure as a consequence of the BP gradient correction for a phase transition in Sb.

Thus, when calculating such quantities, special attention has to be paid to choose an exchange-correlation functional that is capable of correctly describing the delicate total-energy difference between the respective phases.

We interpret the increase of the coexistence pressure to be analogous to the well-known effect of "overbinding," i.e., the overestimate of cohesive energies in LDA calculations. In both cases, one is interested in a total-energy difference between two systems that distinctly differ with respect to the homogeneity of their electron density. Atoms, which have an inhomogeneous electron density, bond together to form a solid with a more homogeneous electron density distribution. Similarly, the electron density of Si or Ge in the metallic  $\beta$ -tin phase varies over a much smaller interval (i.e., is more homogeneous) than the electron density in the diamond phase. In comparison to the LDA, the GGA always lowers the total energy; however, this energy decrease is larger for the more inhomogeneous system (i.e., for the atom or the diamond phase, respectively).<sup>33</sup> Thus, cohesive energies come out smaller in GGA than in LDA. Similarly, the energy difference  $\Delta E_0$  becomes larger in GGA. Therefore, the coexistence pressure calculated within the GGA schemes is larger than that calculated within LDA.

This mechanism appears to be rather general. The improvement of the LDA total energy with respect to the exact total energy from quantum Monte-Carlo calculations with increasing "homogeneity" of the system has recently been demonstrated by Mitáš and Martin<sup>50</sup> for the nitrogen atom, molecule, and two types of solid structures. The difference between the LDA errors of the total energies [ $E(\text{LDA}) - E(\text{Monte Carlo})$ ] of the two solid phases are, in principle, analogous to our GGA correction to  $\Delta E_0$ . Hence, we expect the inclusion of electron-density inhomogeneity effects in  $E_{\text{XC}}$  to be of importance also in the case of other structural phase transitions that are accompanied by a substantial change in electron density homogeneity.

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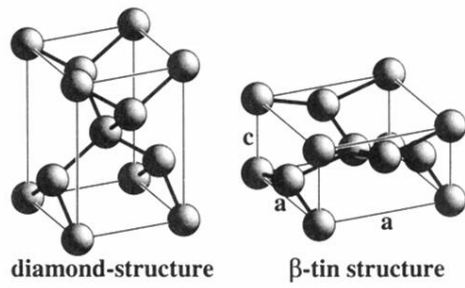


FIG. 1. Comparison of the diamond structure (left) and the  $\beta$ -tin structure (right). The  $\beta$ -tin structure can be regarded as a tetragonally distorted diamond structure with lattice constants  $a$  and  $c$ .