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LETTER TO THE EDITOR

First-principles study on the lonsdaleite phases of C, Si and Ge

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Abstract

Crystalline C, Si and Ge in a lonsdaleite (hexagonal diamond) structure are studied by plane-wave pseudopotential calculations in the scheme of density-functional theory and the local density approximation. The same calculations with generalized gradient corrections and also for the cubic diamond phases of these elements are also performed for comparison. Our results show that the bulk moduli are quite similar between the diamond and lonsdaleite polytypes of these elements. The theoretical bulk modulus of lonsdaleite C is 0.2–0.3% higher than diamond. It is expected to replace diamond as the hardest material in the world. The LDA result shows lonsdaleite Ge as a semimetal for its zero band gap at its Γ point. Considering the exchange–correlation energy correction, it is estimated that lonsdaleite Ge is a semiconductor with a small direct band gap.

1. Introduction

Diamond is known as the hardest material in the world. However, its position is challenged after the discovery of lonsdaleite, the hexagonal diamond. The lonsdaleite structure is a one-component analogue of the wurtzite structure with the crystallographic symmetry of $P6_3/mmc$. Man-made hexagonal diamond was first synthesized in 1966 [1] and later was also found in meteorite mineral in the Diablo Canyon. The mineral lonsdaleite was named for Kathleen Lonsdale, an English crystallographer. Silicon and germanium in the lonsdaleite structure are also frequently found experimentally in specimens prepared in many ways [2–9]. Due to the crucial fabrication conditions, the available sizes of the lonsdaleite phases of C, Si and Ge are only at nanometre scale in general. This condition prevents researchers from performing directly experimental studies on many mechanical and electronic properties of these solids. On the other hand, the theoretical and technical developments of computational materials science, especially density functional theory (DFT), in recent decades have enabled one to

examine the details of many aspects of the physical properties of materials only by theoretical computations [10, 11]. Despite a few papers on the first-principles studies on lonsdaleite C [12] and lonsdaleite Si [13] having been published, the results of systematic calculations and comprehensive comparisons of their mechanical and electronic properties among these lonsdaleite phases are still lacking.

In this letter, we first optimize the crystallographic configurations of the lonsdaleite C, Si and Ge phases by DFT plane-wave pseudopotential (PWPP) calculation. Their mechanical and electronic properties are then studied within several local-density approximation (LDA) and generalized gradient approximation (GGA) realizations. For comparison, the results from the cubic diamond phases of these elements are also provided.

2. Calculation details

It is well known that the DFT PWPP is one of the most powerful *ab initio* quantum-mechanical modelling methods presently available [14]. Our PWPP calculations are realized using the ABINIT computer code [10]. With regard to the advantages and disadvantages of LDA and GGA, both approximations are used to evaluate the lattice parameters, bulk moduli and energy-band structures of the relevant phases. The LDA pseudopotentials in the present calculations are the Hartwigsen–Goedecker–Hutter (HGH) relativistic separable dual-space Gaussian pseudopotentials [15] and the Troullier–Martins (TM) pseudopotentials [16]. The Perdew–Burke–Ernzerhof (PBE) GGA pseudopotentials [17] in the Hamann scheme [18] are generated using the fhi98PP package [19].

The algorithm of cell geometry optimization is used to obtain the optimal lattice constants for the lonsdaleite C, Si and Ge phases. These optimized parameters are later compared with the lattice data from fitting the Murnaghan equation of state [20] and repeating the whole calculation using the fitted parameters where necessary. Details of the general routines of DFT ground state calculation and energy band structure analyses are described elsewhere [21].

3. Numerical results

3.1. Lattice parameters and bulk moduli

In table 1, we present our results of the equilibrium lattice constants and the bulk moduli for the lonsdaleite phases of C, Si and Ge. We also list the results for their cubic diamond phases for reference. As is well known, LDA generally underestimates, but GGA overestimates, the equilibrium lattice parameter. The rule holds well for all of our theoretical results on the diamond phases of C, Si and Ge. However, the rule breaks down for a few sets of the theoretical data for the lonsdaleite phases. We think it might be due to the difficulty in fabricating larger bulk material, and hence prevented a thorough measurement of the parameters. Overall, it is seen that the fully relativistic HGH pseudopotentials show better results from the other two pseudopotentials in the lattice geometrical study. The two LDA pseudopotentials give better results in the calculation of the theoretical bulk modulus. Their percentage errors are within 6% from the corresponding experimental data, while the GGA calculation may cause an error as large as 25%. The larger errors in the theoretical bulk modulus by GGA realization are also seen in previous studies [25].

We find that the theoretical bulk moduli of lonsdaleite C are a little larger than for the corresponding diamond phase for all of the three pseudopotential realizations. The values are, respectively, 0.3, 0.2 and 0.2% higher for HGH LDA, TM LDA and PBE GGA calculations, implying that lonsdaleite C is harder than diamond. However, the published hardness of lonsdaleite C is only 70–80% of diamond as a result of impurities and poly-crystal composition

Table 1. PWPP results of the equilibrium lattice constant, internal parameter u and bulk modulus B_0 for LD and diamond phases of C, Si and Ge. (The numbers in parentheses after the theoretical data are the percentage errors from the experimental ones.)

Parameter	Method	C	Si	Ge
Lonsdaleite phase				
a_0 (nm)	LDA HGH	0.2483(-1.4)	0.3791(-1.3)	0.3932(-0.7)
	LDA TM	0.2491(-1.2)	0.3802(-1.0)	0.3906(-1.4)
	GGA PBE	0.2504(-0.6)	0.3850(0.2)	0.4083(3.1)
	Experimental	0.252 [1]	0.384 [8]	0.396 [9]
c_0 (nm)	LDA HGH	0.4136(0.4)	0.6263(-0.1)	0.6486(-1.3)
	LDA TM	0.4147(0.7)	0.6280(0.2)	0.6410(-2.4)
	GGA PBE	0.4168(1.2)	0.6355(1.4)	0.6697(1.9)
	Experimental	0.412 [1]	0.627 [8]	0.657 [9]
u	LDA HGH	0.3744	0.3742	0.3745
	LDA TM	0.3744	0.3742	0.3751
	GGA PBE	0.3746	0.3744	0.3756
B_0 (Mbar)	LDA HGH	4.632	0.959	0.710
	LDA TM	4.612	0.962	0.776
	GGA PBE	4.341	0.879	0.556
	Experimental			
B'_0	LDA HGH	3.635	4.183	5.389
	LDA TM	3.656	4.235	3.878
	GGA PBE	3.678	4.266	4.808
Diamond phase				
a_0 (nm)	LDA HGH	0.3532(-0.7)	0.5383(-0.9)	0.5581(-1.4)
	LDA TM	0.3542(-0.4)	0.5398(-0.6)	0.5531(-2.2)
	GGA PBE	0.3560(0.1)	0.5465(0.6)	0.5780(2.2)
	Experimental	0.3556 [24]	0.5431 [24]	0.5658 [24]
B_0 (Mbar)	LDA HGH	4.617(4.2)	0.959(-2.1)	0.733(-2.3)
	LDA TM	4.603(3.9)	0.962(-1.8)	0.794(5.9)
	GGA PBE	4.333(-2.2)	0.879(-10)	0.559(-25)
	Experimental	4.43 [22]	0.98 [23]	0.75 [23]
B'_0	LDA HGH	3.553	4.153	4.678
	LDA TM	3.644	4.243	4.631
	GGA PBE	3.648	4.258	4.837

in specimens available to date. It is expected that the high-quality lonsdaleite C crystal will replace diamond as the hardest material in the world. Our calculations give the same results for the theoretical bulk moduli for lonsdaleite and diamond Si when using each of the three different pseudopotentials. As for germanium, the calculated bulk modulus of diamond Ge is always higher than that of lonsdaleite Ge. Therefore, Si acts as the crossover point for the mechanical properties of the lonsdaleite and diamond structures.

3.2. The energy band structures

Crystallographic symmetry may significantly influence the band structure of solids. Many group III–V wurtzite phases are direct band gap semiconductors, different from the indirect band gap ones of their zincblende counterparts [21]. It is worthwhile checking if the situation occurs for these group IV solids as well.

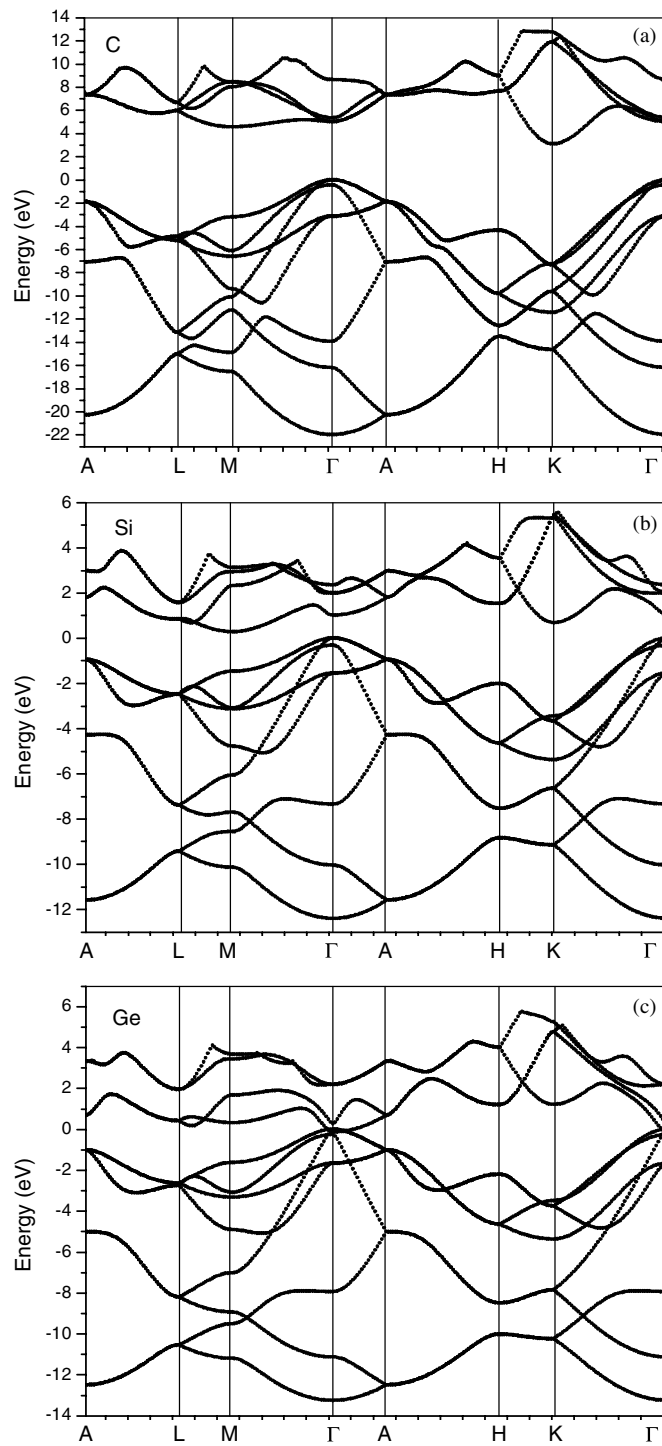


Figure 1. Electron band structures for lonsdaleite C (a), Si (b) and Ge (c) by PWPP calculation using the relativistic LDA HGH pseudopotentials.

The electron energy band structures of C, Si and Ge in lonsdaleite and diamond structures are calculated by using both TM LDA and HGH LDA pseudopotentials. Our results reveal diamond C, Si and Ge as semiconductors of indirect band gap in accordance with experimental measurements. The minimum band gaps are between Γ -X for diamond C and Si, and at Γ_v -L_c for diamond Ge. The LDA energy band structures of C, Si and Ge in the lonsdaleite phase are presented in figure 1, where only the results calculated using LDA HGH pseudopotentials are given for the quite close outcomes by the two LDA realizations. It is seen from figure 1 that lonsdaleite C and Si are indirect band gap semiconductors as well. The minimum band gaps are at Γ_v -K_c and Γ_v -M_c for lonsdaleite C and lonsdaleite Si, respectively. Our LDA results show lonsdaleite Ge as a semimetal for the zero band gap at the Γ point. However, it is known that the band gap from LDA eigenvalues in the Kohn-Sham theory is always underestimated due to the discontinuity of the exchange correlation potential [26–28]. For semiconductors, research experiences from quasiparticle GW calculations suggest that most of the difference between Kohn-Sham eigenvalues and the true excitation energies can be amended by a rigid shift of the conduction band upwards with respect to the valence band [29, 30]. The true minimum gap in the spectrum can be calculated by [28]

$$E_g \approx E_g^{LDA} + \Delta_{xc} \quad (1)$$

where E_g^{LDA} is the band gap from LDA calculations and Δ_{xc} is related to the discontinuity in the functional derivative of the exchange correlation energy to the electron density of a system with a gap. Δ_{xc} is approximately a constant in general [28], which can be calculated by Hedin's GW approximation [31]. It is seen that a rigid upward shift of the conduction band by Δ_{xc} in figure 1(c) gives the typical character of a direct band gap semiconductor for lonsdaleite Ge. Therefore, it is estimated that lonsdaleite Ge is a semiconductor with a small direct band gap.

4. Conclusions

In conclusion, our first-principles calculations indicate some differences in the mechanical and electronic properties of the lonsdaleite and diamond phases. Both LDA and GGA results show that the bulk modulus of lonsdaleite C is higher than for diamond C. The single crystal of lonsdaleite C is estimated as the hardest material in the world. C and Si in the lonsdaleite structure remain indirect band gap semiconductors. However, lonsdaleite Ge becomes a direct band gap semiconductor, different from its cubic counterpart.

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