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Bulk modulus calculations based on perturbation self-consistency

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Abstract. We propose a method for bulk modulus calculations of solids based on perturbation self-consistency within the local density functional. The essential assumption is that a finite scaling is applied to the one-electron wavefunction when the solid adjusts to a new distorted structure under pressure. Thus the one-electron potential of a deformed structure near equilibrium can be obtained by performing a scaling transformation to charge density directly. The method is formulated within the linear muffin-tin orbital method in the atomic sphere approximation and applied to the calculation of bulk moduli of β -SiC, FCC Al, BCC Li, $L1_2$ Al₃Li and an ordered FCC Al₇Li superlattice. The bulk modulus calculated from a single self-consistency is in reasonably good agreement with that of a full self-consistent calculation. Our results for Al–Li systems confirm that the addition of lithium to FCC Al causes the bulk modulus to decrease.

1. Introduction

Density functional theory (DFT), originally formulated in the 1960s [1], has since become the most widely used method for electronic structure and total-energy (TE) calculations. The local-density approximation (LDA) to exchange and correlation has achieved great success in describing the properties of solids. Accurate band-structure calculations make it possible to obtain reliable TEs of a crystal in the ground state. The bulk moduli could in principle be obtained through extensive calculations of the TE versus volume with subsequent fitting and differentiation, but it is time consuming and sometimes difficult to obtain accurate bulk moduli. Recently, the stress theorem which gives analytic expressions for the stress tensor has been derived [2]. The great simplification is that many inequivalent forces can be calculated from a single self-consistent calculation. The determination of equilibrium lattice parameters is straightforward, e.g., a cubic lattice constant.

A general expression for the calculation of elastic constants has been derived by Fuchs and Peng [3] with the help of the self-consistent field 50 years ago. In spite of its mathematical beauty, it is difficult to apply to realistic solids. In this paper we suggest a method for bulk modulus calculations based on perturbation self-consistency. Only one kind of perturbation is considered, i.e. homogeneous and isotropic strains (compression or tension). The scheme is formulated within the linear muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA) [11]. After the self-consistent calculation of a system, the electronic charge density of the system with a small deformation can be constructed from the scaling transformation of valence wave-functions. Then, according to the LDA, a new starting single-particle potential is obtained. In this way the sum of the

perturbation potential and the original potential is obtained. This is somewhat different from the traditional perturbation self-consistent theory [4]. Through the scaling of wavefunctions, the calculation of bulk moduli can be almost directly performed, i.e. by a single self-consistent calculation. As shown below, the direct bulk modulus is close to that of full self-consistency.

To demonstrate our method, we choose the Al–Li systems because of their great technological importance and theoretical interest. The zincblende-structure silicon carbide (β -SiC) is chosen to check the efficiency when our method is applied to non-metallic materials. It has recently been recognized that Al–Li alloys are particularly useful and potential candidates for aerospace materials because of their superior strength-to-weight ratio [5]. Young's modulus Y for Li metal is only about 5–10 GPa, and this value is one order of magnitude smaller than that of Al, i.e. about 66 GPa. However, a small amount of Li addition causes a drastic increase in Young's modulus for Al-based alloys. The explanation of the mechanism of solid-solution hardening and the acquisition of other properties of Al–Li alloys have stimulated strong interest among physicists [6–9]. Our results show that the addition of lithium to FCC aluminium causes the bulk modulus to decrease, in good agreement with [6–8] and experiment [10].

The present paper is organized as follows. In section 2, we will give our perturbation self-consistent method and formulate it within the LMTO ASA method. In section 3, the results on the bulk moduli of β -SiC, FCC aluminium, BCC lithium, the $L1_2$ phase of Al_3Li and an ordered FCC Al_7Li supercell are presented, and some discussion is given. Finally, we give a brief summary in section 4.

2. Theoretical method

We restrict ourselves to the DFT within the LDA. The many-particle problem is transformed into a single-particle problem. The Schrödinger equation is expressed as (in Rydberg atomic units)

$$\left[-\nabla^2 + V_{eff}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r}) \quad (1)$$

where $V_{eff}(\mathbf{r})$ is the effective single-particle potential composed of a Coulomb term and an exchange–correlation term:

$$V_{eff}(\mathbf{r}) = \phi(\mathbf{r}) + V_{xc}(\mathbf{r}). \quad (2)$$

In the LDA, the potential is uniquely determined by the charge density which is obtained by summing over occupied states:

$$\rho(\mathbf{r}) = \sum_j^{occ} |\varphi_j(\mathbf{r})|^2. \quad (3)$$

The Coulomb term includes the attraction of fixed nuclei and the electron–electron repulsion:

$$\phi(\mathbf{r}) = V(\mathbf{r}) \int \frac{2\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}. \quad (4)$$

We use a form of the Hedin–Lundqvist [12] or the Slater [13] $X\alpha$ for the LDA. In order to obtain the single-particle potential of the system with deformation, we make the following scaling transformation to the valence wavefunction. For a small homogeneous deformation, the particle coordinates are transformed as

$$r_{i\alpha} \rightarrow r_{i\alpha} + \sum_{\beta} \epsilon_{\alpha\beta} r_{i\beta} \quad (5)$$

where $\epsilon_{\alpha\beta}$ is a symmetric (i.e. rotation-free) strain tensor. The wavefunction is ‘stretched’ as

$$\varphi_\epsilon(\mathbf{r}) = \det(\mathbf{I} + \epsilon)^{-1/2} \varphi((\mathbf{I} + \epsilon)^{-1} \cdot \mathbf{r}) \quad (6)$$

where the pre-factor preserves the normalization of φ_ϵ . Only isotropic strain is considered in the calculation of bulk moduli.

In our practical calculation of bulk moduli, the scaling transformation of the wavefunction is performed separately. The part near the nuclei is maintained while the outer part is transformed as mentioned above. The wavefunction with perturbation is obtained through subsequent smooth joining and normalization. With the core wavefunction unchanged, the new charge density can be obtained by summing over occupied states (assuming that the occupations of corresponding states are maintained). Then the new starting potential for self-consistent iterations can be constructed from (2). Supposing that the self-consistent calculation of a system has been accomplished, the pressure of the system with a small compression or tension can be obtained from further iteration. As the calculations show, the starting potential constructed in this way is quite close to that of self-consistency. The bulk modulus can be calculated almost directly assuming that the pressure is calculated in a direct way.

Applying the present scheme to the LMTO ASA method, we consider only homogeneous and isotropic strain which can be regarded as a scalar. Because the electronic number density is the sum of the occupied states, a scaling transformation can be performed on the charge density directly. The one-electron potential in the l th ($l = 0$) cell inside the j 'th atomic sphere is expressed as

$$\begin{aligned} V_{j'}(\mathbf{r}) = & \frac{2}{r} \int_0^r 4\pi r'^2 \rho_{j'}(r') dr' + \int_r^{R_{MT,j'}} 8\pi r' \rho_{j'} dr' - \frac{2Z_{j'}}{r} \\ & + \int_{R_{MT,j'}}^\infty 8\pi r' \rho(r') dr + (-1) \sum_{j+l}^l \frac{2Z_j}{r_{j+l}} + V_{exc} \end{aligned} \quad (7)$$

where the first three terms denote the contributions of the nucleus and electrons inside the atomic sphere, and the fourth and fifth terms are the potential of the charged environment, i.e. the Madelung potential, which is readily obtained by the application of Ewald summing technology. The last term is the exchange–correlation potential, which is approximated with the LDA. In this way, the sum of the perturbation and the original potential is obtained. For self-consistent calculation, potential parameters are required by the LMTO method. By solving the Schrödinger or Dirac equation at the energy reference point of the equilibrium state inside an atomic sphere, the four potential parameters can be obtained readily. There are eigenvalue shifts due to perturbation but, for linear method, the small shifts of reference points are not important. Because of the direct calculation of pressures, the bulk modulus can be calculated directly from numerical differentiation. The method presented here is different from a TE calculation, i.e. it needs no parameters to fit the TE. Thus our method could be called a parameter-free method for bulk modulus calculations.

3. Results and discussion

We first use the Hedin–Lundqvist parametrization for exchange–correlation to calculate the bulk moduli of β -SiC, FCC Al, BCC Li, $L1_2$ Al₃Li and ordered Al₇Li in an FCC supercell, which is constructed with twice the lattice spacing needed for one atom, with the coordinates of eight atoms in the Wigner–Seitz cell as follows (in lattice constants): Al (0,1/4,1/4),

(1/4,0,1/4), (1/4,-1/4,0), (1/4,1/4,0), (1/4,0,-1/4), (0,1/4,-1/4), (0,0,0), Li(1/2,0,0). β -SiC has a zincblende structure similar to that of diamond with half of the carbon atoms replaced by silicon atoms. In order to make the ASA rational for β -SiC, two empty atomic spheres with atomic number $Z = 0$ are included in each unit cell positioned in the empty tetrahedral sites. The MTOs up to $l = 2$ are included for Si, Al and Li, while for C we use those up to $l = 1$, and for the empty sphere only that of $l = 0$. The number of k points used for the k -space integration is 89 for FCC, 84 for $L1_2$, 91 for BCC in the one-fortyeighth wedge of the first Brillouin zone. In order to calculate the bulk moduli, we chose the values of ϵ as ± 0.004 . After the self-consistent calculation of a system at equilibrium lattice constant, the one-electron potentials and potential parameters of the two deformed states are constructed as mentioned in the previous section. Three pressures can be obtained from a single self-consistent calculation and then the bulk modulus is calculated from three-point numerical differentiation at the equilibrium point. Three values of pressure give by quadratic interpolation the final lattice constant where the pressure $P = 0$, as well as the bulk modulus from the slope of pressure. We call the bulk moduli obtained in this way as direct bulk moduli. For comparison, we also calculated the two deformed states self-consistently and then obtained the self-consistent bulk moduli. The calculated equilibrium lattice constants a_0 , the direct bulk moduli B_d and the self-consistent moduli B_c are listed in table 1, showing that the direct bulk moduli B_d are in good agreement with the self-consistent moduli B_c . The discrepancies are less than 10%. These results are stimulating. Through the scaling of the charge density, we have almost calculated the bulk moduli directly. There must be some physical mechanism behind the phenomenon. At least it can be concluded that the elastic properties of solids mainly depend on the overlapping of valence electrons. In our calculations within the ASA, the bulk moduli mainly depend on the charge density near the spherical surface. The calculated equilibrium lattice constant for β -SiC is smaller than that of Cheong *et al* [14] (4.361 Å) and that of experiment (4.360 Å), while the bulk modulus is larger than that of Cheong *et al* (212 GPa) and that of experiment (224 GPa). The electronic structure calculation based on the LDA usually tends to underestimate the lattice constant. It is not surprising that the LDA overestimates the bulk modulus.

Table 1. The calculated equilibrium lattice constants a_0 , the direct bulk moduli B_d and the self-consistent moduli B_c .

Systems	a_0 (au)	B_d (GPa)	B_c (GPa)
β -SiC	8.18	272	258
FCC Al	7.49	93.8	99.3
BCC Li	6.33	15.5	15.9
Al ₃ Li	7.40	80.6	82.9
Al ₇ Li	14.88	88.9	90.3

For Al-Li systems, the predicted lattice constants are all smaller than those of experiment. The experiment lattice constants of BCC Li, FCC Al and $L1_2$ Al₃Li are 7.65 au, 6.63 au [15] and 7.5775 au [5], respectively. The error is largest in BCC lithium, where the lattice constant is 4.5% smaller than experiment. The lattice constants of Al and Al₃Li are within about 2% of experiment. While some of this is due to the neglect of zero-point motion and thermal expansion, much of the error, especially in lithium, can be attributed to problems with the LDA and ASA. The bulk moduli are in reasonably good agreement with those in the literature except [9], which claimed that the addition of lithium

to FCC Al causes the bulk modulus to increase, and the enhancement of Young's modulus is correlated with bulk modulus increase. Our calculated bulk moduli are larger than found by other calculations [6–8]. One reason for this may be the choice of $\epsilon = \pm 0.004$ beyond the elastic limit. The results can be improved by choosing more than two deformed states around equilibrium, e.g. the bulk modulus can be obtained from five-point numerical differentiation by choosing four deformed states. According to the scaling transformation in the previous section, a little effort is needed. From direct bulk moduli and full self-consistent moduli, it can be concluded that the bulk modulus decreases with increasing lithium concentration, and that the increase in Young's modulus is due to the anisotropy introduced by the addition of lithium. Poisson's ratio decreases from 0.32 in Al to 0.26 in Al₇Li [7].

Table 2. The calculate equilibrium lattice constants a_0 , the direct bulk moduli B_d and the self-consistent moduli B_c using Slater's $X\alpha$ approximation to exchange–correlation.

Systems	a_0 (au)	B_d (GPa)	B_c (GPa)
FCC Al	7.650	75.0	80.0
BCC Li	6.630	11.3	11.7
Al ₃ Li	7.577	66.3	68.7
Al ₇ Li	15.227	73.2	73.8

Considering that the LDA is in any case an approximation, then we choose the Slater $X\alpha$ form to approximate the exchange–correlation functional. The α -values for Al and Li are adjusted so that the pure metal lattice constants could be correctly reproduced. This gives us $\alpha_{Al} = 0.676$ and $\alpha_{Li} = 0.660$, quite close to the value for a free-electron gas. In electronic structure calculations for Al₃Li and Al₇Li, the same α_{Al} and α_{Li} are used in the atomic spheres of Al and Li, respectively. The calculated equilibrium lattice constants a_0 , the direct bulk moduli B_d and the full self-consistent moduli B_c are listed in table 2. The lattice constant of Al₃Li is reproduced quite well, while that of Al₇Li lies in a reasonable region between Al and Al₃Li. The bulk moduli of Al₇Li and Al₃Li are still smaller than that of pure aluminium. The same in the change in the trend bulk moduli for Al–Li systems can be found from the direct bulk moduli, which also confirms that the addition of lithium to FCC aluminium causes the bulk modulus to decrease.

The equilibrium lattice constants and bulk moduli could in principle be obtained through extensive calculations of the TE versus volume by fitting the energy curve with an assumed equation of state and subsequent differentiation. The quality of the results relies on the accuracy of the TE and the form of the assumed equation of state. We would like to emphasize that the quality of the values obtained for the pressure is of the same order of accuracy as the quality of the band-structure calculations in the framework of the LMTO ASA approach and that, at the same time, the results of TE calculations are much less accurate. Bulk modulus calculations from pressure differentiation are more reliable than the TE fitting and differentiation. The results of [9] are doubtful because they were obtained from TE fitting using the augmented spherical wave method which is not sufficiently accurate. In our bulk modulus calculations, the agreement between the direct bulk moduli and the full self-consistent moduli reveals interesting information on how electrons respond to macroscopic strain. Owing to the agreement between B_d and B_c , it can be concluded that the electronic charge scaling transformation proposed reflects the real response of electrons to compression. The pressure of a system with deformation obtained from one cycle converges that of self-consistency to within 10^{-3} GPa. At least dramatic gains in efficiency are

achieved in the calculations of bulk moduli with the present method.

4. Summary

We have presented here a method by which the bulk modulus can be calculated directly, at least efficiently. The bulk moduli of β -SiC, FCC Al, BCC Li, $L1_2$ Al_3Li and supercell Al_7Li have been presented. The direct bulk moduli are in good agreement with those of full self-consistency; the discrepancies are less than 10%. This implies that the elastic properties of solids mainly depend on the overlapping of valence electrons. The method can be applied to non-metallic materials as well as metallic materials. Our results confirm that the addition of lithium to FCC Al causes the bulk modulus to decrease. It should be pointed out that both direct and full self-consistent bulk moduli show the same trend of a decrease on the addition of lithium. The method presented here can be applied to new material designing.

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References

- [1] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
- [2] Nielsen O H and Martin R M 1983 *Phys. Rev. Lett.* **50** 697; 1985 *Phys. Rev. B* **32** 3708
- [3] Fucks K and Peng H W 1942 *Proc. R. Soc. A* **180** 451
- [4] Baroni S, Giannozzi P and Testa A 1987 *Phys. Rev. Lett.* **58** 1861
- [5] Lavernia E J and Grant N J 1987 *J. Mater. Sci.* **22** 1251 and references therein
- [6] Podloucky R, Jansen H J F, Guo X Q and Freeman A J 1988 *Phys. Rev. B* **37** 5478
- [7] Mehl M J 1993 *Phys. Rev. B* **47** 2493 and references therein
- [8] Guo X Q, Podloucky R, Xu Jian-hua and Freeman A J 1990 *Phys. Rev. B* **41** 12432
Guo X Q, Podloucky R and Freeman A J 1990 *Phys. Rev. B* **42** 10912
- [9] Masuda-Jindo K and Terakura K 1989 *Phys. Rev. B* **39** 7509
- [10] Müller W, Bubeck E and Gerald V 1986 *Aluminum-Lithium Alloys III* ed C Baker, P J Gregson, S J Harris and C J Peel (London: Institute of Metals) p 435
- [11] Skriver H L 1984 *The LMTO Method* (New York: Springer)
- [12] Hedin L and Lundqvist B I 1971 *J. Phys. C: Solid State Phys.* **4** 2064
- [13] Slater J C 1974 *Quantum Theory of Molecules and Solids* vol 4 (New York: McGraw-Hill) ch 1
- [14] Cheong B H, Chang K J and Cohen M L 1991 *Phys. Rev. B* **44** 1053
- [15] Donohue J 1974 *The Structure of the Elements* (New York: Wiley)