

Mechanism for linear and nonlinear optical effects in SrBe_3O_4 crystal

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(Received 16 April 2002; accepted 8 May 2002)

Electronic and band structure calculations of SrBe_3O_4 crystal from first principles are performed based on a plane-wave pseudopotential method for the first time. The linear refractive indices and the static second-harmonic generation (SHG) coefficients are also calculated by the SHG formula improved by our group. The calculated values are in good agreement with the experimental values. A real-space atom-cutting method is adopted to analyze the respective contributions of the cation and anionic groups to the optical response. The results show that the contribution of the (SrO_9) group to the SHG coefficients is more pronounced than that of $(\text{BeO}_3)^{4-}$ and $(\text{BeO}_4)^{6-}$ groups. Because the plane BeO_3 and tetrahedral BeO_4 groups have a little covalent bonding, they only give a tenth of the contribution of the SrO_9 group. © 2002 American Institute of Physics.
[DOI: 10.1063/1.1490335]

INTRODUCTION

The strontium beryllium oxide SrBe_3O_4 crystal belongs to noncentrosymmetric oxide material.¹ Recently, Keszler *et al.* have pay attention to the second harmonic generation (SHG) effect of the SrBe_3O_4 crystal.² The crystal structure of SrBe_3O_4 has been reported by Harris and Yakel.³ They confirmed that the crystal belongs to the $P6_2c$ space group. Its hexagonal unit cell with $a=b=4.5961\text{ Å}$ and $c=8.9300\text{ Å}$ contains two formula weights. In Fig. 1 the unit cell structure is shown. The ninefold coordination of oxygen atoms about a strontium atom forms a trigonal prism with three coordinating oxygen atoms in the prism midplane. The trigonally coordinated beryllium atom is at the center of an equilateral triangle of oxygen atoms with 1.535 Å in length. This value is consistent with previous observation of similar groups in Y_2BeO_4 (mmm space group)⁴ and $\text{Ca}_{12}\text{Be}_{17}\text{O}_{29}$ ($43m$ space group).⁵ The tetrahedra of oxygen atoms about the four-coordinated beryllium atom form end caps on the trigonal prisms of strontium–oxygen coordination polyhedral. These tetrahedra contain three symmetrically equivalent B–O separations of 1.665 Å and one shorter 1.600 Å contact. The short one occurs in a line paralleled with the c axis.

The structure of SrBe_3O_4 crystal shows that it has a platelike morphology and is optically isotropic when viewed normal to the plane faces, but anisometric when viewed in other directions. Harris and Yakel pointed out that a positive uniaxial optic figure was observed for the SeBe_3O_4 crystal and the measured refractive indices are $n_e=1.72\pm0.1$ and $n_o=1.71\pm0.1$, respectively.

In recent years we have developed a method of calculation of linear and nonlinear optical (NLO) coefficients of NLO crystals based on the first-principles energy band calculation.⁶ In our recent review on theoretical calculations

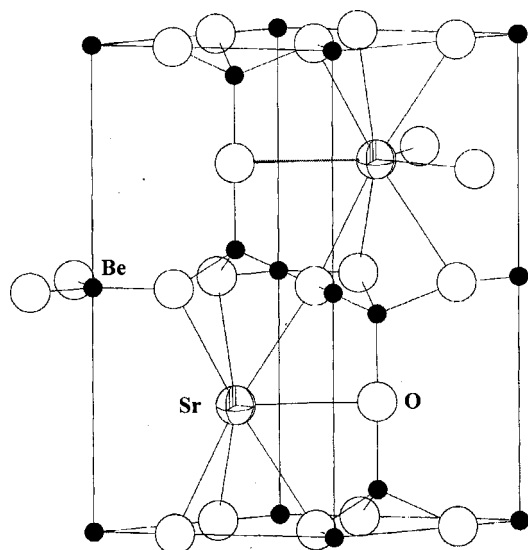
and predictions of NLO coefficients of borate crystals, the computational method and calculated results have been elaborated.⁷ In our calculations the CASTEP,⁸ a plane-wave pseudopotential total energy package, is used for solving the electronic and band structure as well as linear and nonlinear optical properties of the crystals. The theoretical basis of CASTEP is the density functional theory (DFT).⁹ The optimized pseudopotentials in the Kleinman–Bylander form for Sr, Be, and O^{10–12} allows us to use small plane-wave basis set without compromising the accuracy required by our study. Our group and co-workers have reviewed the calculation method for SHG coefficients and given an improved formula.⁶ The static limit of the SHG coefficients plays the most important role in the applications of SHG crystals. We adopt the formula of NLO coefficient

$$\chi^{\alpha\beta\gamma} = \chi^{\alpha\beta\gamma}(\text{VE}) + \chi^{\alpha\beta\gamma}(\text{VH}) + \chi^{\alpha\beta\gamma}(\text{twobands}), \quad (1)$$

where $\chi^{\alpha\beta\gamma}(\text{VE})$ and $\chi^{\alpha\beta\gamma}(\text{VH})$ denote the contributions from virtual-electron processes and virtual-hole processes, respectively, where $\chi^{\alpha\beta\gamma}(\text{twobands})$ gives the contribution to $\chi^{(2)}$ from two band processes. The formulas for calculating $\chi^{\alpha\beta\gamma}(\text{VE})$, $\chi^{\alpha\beta\gamma}(\text{VH})$ and $\chi^{\alpha\beta\gamma}(\text{twobands})$ are given in Ref. 6.

By this method we have successfully calculated the energy bands and optical properties for a number of crystals such as $\beta\text{-BaB}_2\text{O}_4$ (BBO),⁶ LiB_3O_5 (LBO), CsB_3O_5 (CBO) and $\text{CsLiB}_6\text{O}_{10}$ (CLBO),¹³ $\text{KBe}_2\text{BO}_3\text{F}$ (KBBF), $\text{BaAl}_2\text{B}_2\text{O}_7$ (BABO), $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$ (KABO) and BPO_4 (BPO),¹⁴ BiB_3O_6 (BIBO),¹⁵ and NaNO_2 .¹⁶ In these researches by use of atom-cutting method we have given in-depth analysis and thorough explanation of the origins of the SHG effects. In this work we present a theoretical calculation of linear and nonlinear optical coefficients of the SrBe_3O_4 crystal. We believe that these results will help people to recognize the origin of the NLO effect for the SrBe_3O_4 crystal, and will be beneficial to further studies on the optical responses of the crystal.

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FIG. 1. Unit cell of SrBe_3O_4 crystal.

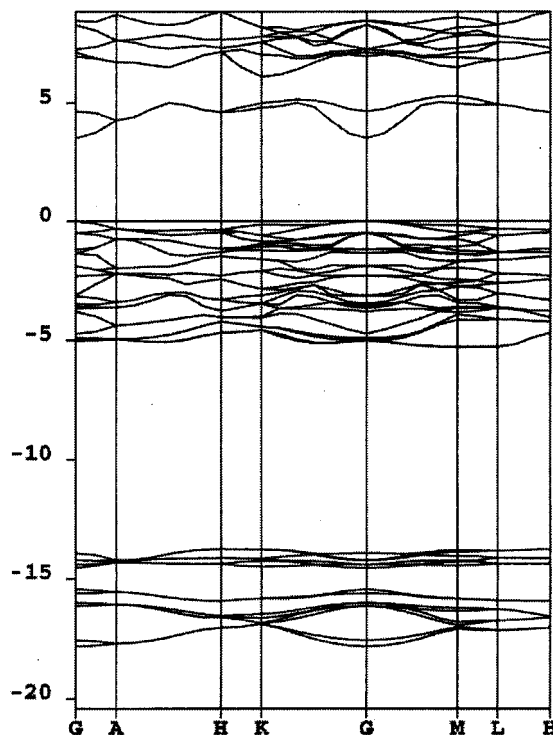
RESULTS AND DISCUSSION

Energy band structure

The calculated energy band structure and the total density of the states (DOS) and atom-resolved partial DOS are given in Figs. 2 and 3, respectively. A directed band gap of 3.52 eV is obtained. In energy band calculations the local density approximation has been adopted, the computed band gaps are usually smaller than corresponding experimental ones. For fitting the measured values people usually use the energy scissors operator to shift up all the conduction bands.^{6,7} In the present work we have used the scissors energy 2.5 eV to obtain the optical responses which are all in good agreement with experimental data. Then the theoretical cutoff wavelength is about 206 nm. Both band structure and DOS figures show that the energy bands can be divided into three regions. The lower region lies below -14 eV. In this region the upper ones are located in -14 to -16 eV, and they are $4p$ and $4s$ orbitals of strontium atom. The ones located below -16 eV consist of $2s$ orbitals of oxygen atoms. The middle region is valence band (VB) from -5 eV to 0 eV. From the DOS figure we can see that the VB is composed of $2p$ orbitals of oxygen atoms. The upper region is the conduction band (CB) which are mainly composed of the valence orbitals of oxygen atoms with a little mixing of the orbitals of the beryllium and strontium atoms.

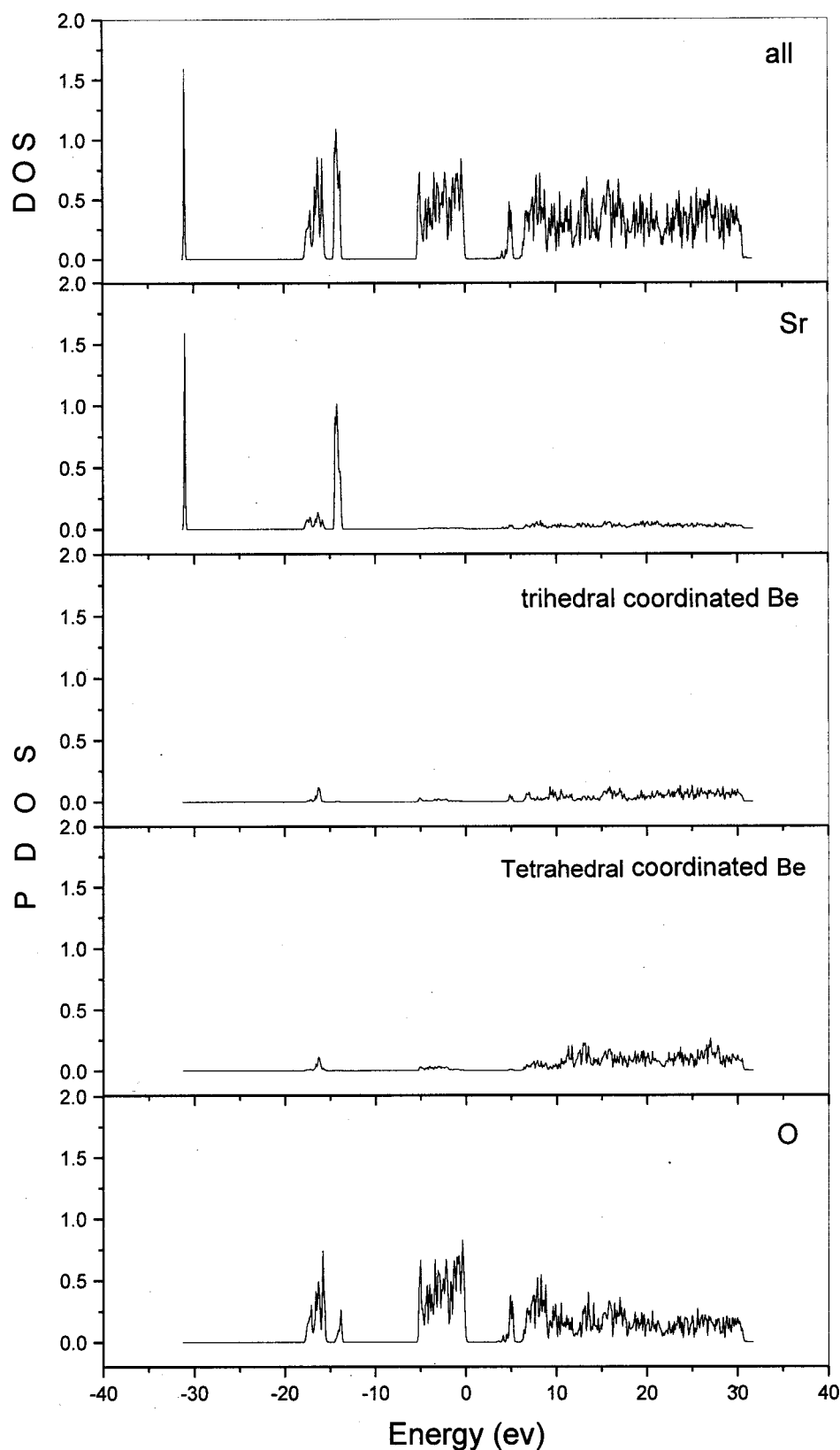
The linear and nonlinear optical coefficients

It is well known that the refractive indices are obtained theoretically from the imaginary part of the dielectric function through the Kromer–Kronig transformation. The imaginary part can be calculated with the matrix elements that describe the electronic transitions between the ground and excited states in the crystal considered. The calculation formulas are given in Ref. 6. For the SrBe_3O_4 crystal the calculated and experimental values of the refractive indices are given in Table I. According to the computational formula given in Ref. 6, the SHG coefficients of the SrBe_3O_4 crystal

FIG. 2. Energy band of SrBe_3O_4 crystal.

have been calculated from the band wave functions and band energies. The theoretical and experimental SHG values are also listed in Table I. Obviously, the calculated linear and nonlinear optical coefficients are all in good agreement with the experimental values.

To investigate the influence of the ions on the optical responses of the SrBe_3O_4 crystal, the real-space atom-cutting method has been used. The method means that if the contribution of ion A to the n th-order polarizability is denoted as $\chi^{(n)}(A)$, we can obtain it by cutting all ions except A from the original wave functions, i.e., $\chi_A^{(n)} = \chi_{\text{All ions expt A}}^{(n)}$. In the previous paper,⁶ it was found that the charge density around cation M is spherical. Figures 4 and 5 show the calculated charge distribution of the SrBe_3O_4 crystal. Figure 4 drawn in the BeO_3 plane shows that there are no apparent overlaps between the orbitals of Be and three O atoms. This fact indicates that in the BeO_3 group the Be–O bonding has a little covalent character. On the other hand, the Fig. 5 drawn in the middle SrO_3 plane shows that there are apparent electron density overlaps between strontium and three oxygen atoms, and this fact indicates the certain covalent character of Sr–O bonding. In our calculations the cutting radii of O, Be, and Sr are 1.10, 0.60, and 1.45 Å, respectively. The cutting analysis results are listed in Table II. These results clearly indicate that: (1) The contributions of BeO_3 , BeO_4 , and SrO_9 groups to the linear optical coefficients are comparable with each other, but SrO_9 group seems slightly important. (2) Theoretical and experimental birefringence are all small. The contribution of the BeO_3 group to the birefringence is a bit larger than that of others. It is well known that the phase-matching conditions are fulfilled only in anisotropic crystals under interaction of differently polar-

FIG. 3. DOS and PDOS plot of SrBe_3O_4 crystal.

ized waves. The small birefringence of the SrBe_3O_4 crystal means that the crystal is difficult to fulfill the phase-matching conditions. (3) Table II shows that the contributions of the SrO_9 group to the SHG coefficients are dominant, i.e., about 90% of total calculated value. For further explanation of

Sr-O group's importance the contribution to the SHG effect of SrO_3^{4-} in the midplane of SrO_9 configuration were calculated to be $d_{22}(\text{SrO}_3) = -0.2665 \text{ pm/V}$ which is about 70% of total contribution of $(\text{SrO}_9)^{16-}$ group. Why is this so? In fact, as is well known, the nonlinear optical susceptibility

TABLE I. Calculated and experimental n and d (in pm/V) of SrBe_3O_4 crystal.

Calculated		Experiment	
n_x	1.7066	n_o^a	1.71 ± 0.01
n_y	1.7066		
n_z	1.7233	n_e^a	1.72 ± 0.01
Δn	0.0167	Δn	0.01
d_{22}	-0.415	d_{eff}^b	0.35

^aReference 3.^bReference 2.

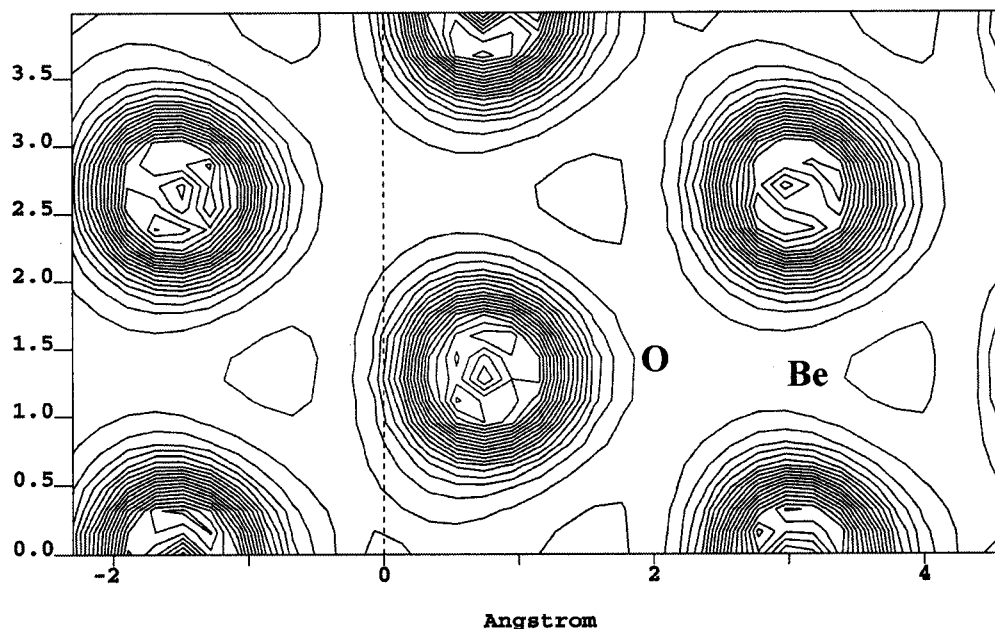
$\chi^{(2)}$ is calculated from the transition matrix elements between the VB and CB. In the above-mentioned band structure we have pointed out that the VB and CB are mainly composed of the $2p$ orbitals of oxygen atoms. This indicates that the oxygen orbitals give a great contribution to the NLO effect. Furthermore, the covalent character of the Sr–O bond is also beneficial to the NLO effect. So the contributions to the nonlinear optical response of the SrO_9 group which contains nine oxygen atoms per group are dominant in the SrBe_3O_4 crystal. On the other hand, the bond of Be and O atoms has more ionic property, so the contributions to the SHG coefficients of BeO_3 and BeO_4 groups are only a tenth of that of the SrO_9 group, and the contribution of BeO_3 has the opposite sign compared with the one of the SrO_9 group. The BeO_3 group is different from the BO_3 group which is mainly a covalent group with a π conjugated orbital. This is the reason why the BO_3 has a larger contribution to the SHG effect than that of BeO_3 group.

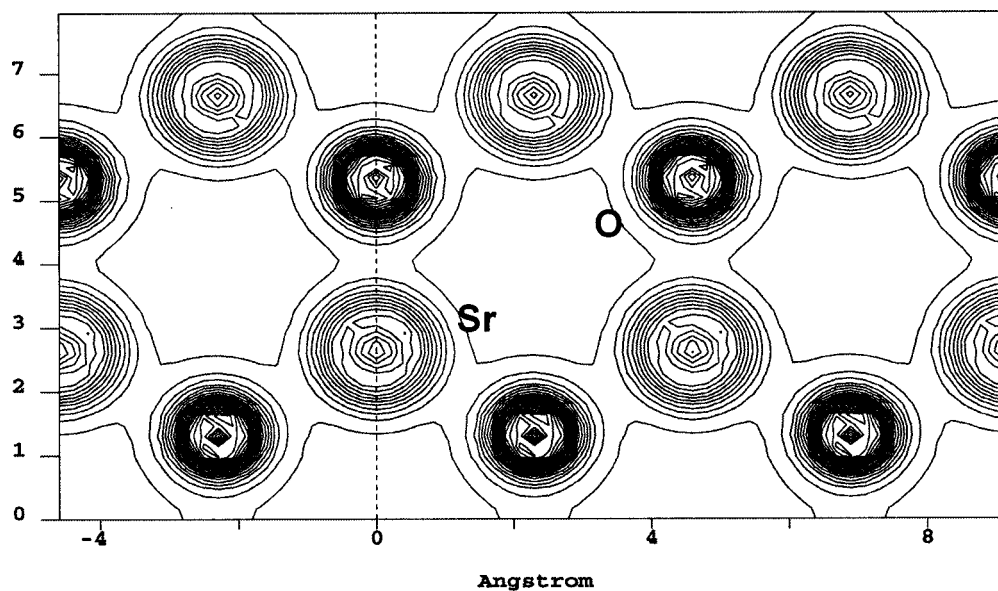
TABLE II. Atom-cutting analysis results of n and d_{ij} for SrBe_3O_4 .

	BeO_3^{4-}	BeO_4^{6-}	SrO_9^{17-}	Total	Original
n_x	1.454	1.570	1.681		1.707
n_y	1.454	1.570	1.681		1.707
n_z	1.428	1.585	1.701		1.723
Δn	-0.026	0.015	0.020	0.009	0.016
d_{22}	0.0423	-0.056	-0.386	-0.400	-0.415

CONCLUSION

In this paper, the band structure and linear and nonlinear optical coefficients have been calculated by means of the first-principles calculations based on the density functional theory. The mechanism of linear and nonlinear optical responses are analyzed by the atom-cutting method. The conclusions are as follows: (1) Both calculated and experimental birefringence of the SeBe_3O_4 crystal are small and it is only about 0.01. So the crystal is difficult to fulfill the phase-matching conditions. (2) The SHG coefficient of the crystal is not large and only about 0.4 pm/V which is approximate to the SHG coefficient of KDP having the birefringence $\Delta n = 0.035$. The SrO_9 group gives the dominant contributions to the SHG effect, and the BeO_3 and BeO_4 groups give only a tenth of that of the SrO_9 . The origin of such situation is that the bond of Be and O atoms has more ionic property. This is very different from the BO_3 group which has a conjugated π orbital and usually gives great contribution to the SHG effect.

FIG. 4. Charge density in the BeO_3 plane.

FIG. 5. Charge density in the SrO_3 plane.

ACKNOWLEDGMENTS

This work was supported by the Chinese National Key Research Project. Support in computing facilities from the Computer Network Information Center is gratefully acknowledged. M.H.L. thanks funding support from NCS-90-2102-M-032-011.

¹P. S. Halasyamani and K. R. Poeppelmeier, *Chem. Mater.* **10**, 2753 (1998).

²D. Keszler, *Laser Focus World* **36**, 13 (2001).

³L. A. Harris and H. L. Yakel, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **B25**, 1647 (1969).

⁴L. A. Harris and H. L. Yakel, *Acta Crystallogr.* **20**, 295 (1966).

⁵L. A. Harris and H. L. Yakel, *Acta Crystallogr.* **22**, 354 (1967).

⁶Z. S. Lin, J. Lin, Z. Z. Wang, Y. C. Wu, C. T. Chen *et al.*, *J. Phys.: Condens. Matter* **13**, R369 (2001).

⁷J. Lin, M. H. Lee, Z. P. Liu, C. T. Chen, and C. J. Pickard, *Phys. Rev. B* **60**, 13380 (1999).

⁸CASTEP 3.5 program developed by Molecular Simulation Inc., 1997.

⁹R. G. Parr and W. T. Yang, *Density Functional Theory of Atom-Molecules* (Oxford University Press, Oxford, 1989).

¹⁰A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, *Phys. Rev. B* **41**, 1227 (1990).

¹¹J. S. Lin, A. Qtseish, M. C. Payne, and V. Heine, *Phys. Rev. B* **47**, 4174 (1993).

¹²M-H. Lee, J-S. Lin, M. C. Payne, V. Heine, V. Milman, and S. Crampin (unpublished).

¹³Z. S. Lin, J. Lin, Z. Z. Wang, C. T. Chen, and M. H. Lee, *Phys. Rev. B* **62**, 1757 (2000).

¹⁴Z. S. Lin, Z. Z. Wang, C. T. Chen, S. K. Chen, and M. H. Lee, *J. Phys. C* (in press).

¹⁵Z. S. Lin, Z. Z. Wang, C. T. Chen, and M. H. Lee, *J. Appl. Phys.* **90**, 5585 (2001).

¹⁶Z. S. Lin, Z. Z. Wang, C. T. Chen, and M-H. Lee, *Acta Phys. Sin.* **50**, 1145 (2001).