行政院國家科學委員會專題研究計畫　期中進度報告

特殊材料之第一原理多體計算(2/3)

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計畫主持人：薛宏中

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行政院國家科學委員會專題研究計畫成果報告
特殊材料之第一原理多體計算(2/3)
Ab initio many-body calculations on novel materials (2/3)

計畫編號：NSC 93-2112-M-032 -004
執行期限：94 年 08 月 01 日至 95 年 07 月 31 日
主　持　人　：薛宏中 淡江大學物理系　副教授

一、中文摘要

在本計畫之第二階段，首先我們通過第一原理準粒子(quasiparticle)計算法，在**GW**近似之下，得到**InN**之能隙與最近實驗所得相當吻合；另一方面，由自旋極化密度泛函理論計算(spin-polarized DFT)，發現不僅在**III-V**族、**II-VI**族半導體或各種螺旋性質(chirality)之氮化硼奈米管(BNT)中，晶格空缺(vacancy)皆可能導致系統之磁偶極增大，進而造成磁性半導體。此外，我們也分析鈣鈦礦摻雜系統($Pb_{1-x}Ca_xTiO_3$)之電子結構與聲子振動模式，以釐清其相變機制。最後，我們將進行光譜之多體效應GW-BSE測試計算。

關鍵詞：準粒子 **GW** 近似、自旋極化密函、氮化硼奈米管、鈣鈦礦、GW-BSE

Abstract

At the 2nd step of this 3-year project, we perform quasiparticle calculations of InN within a GW approximation. Our spin-polarized DFT calculated electronic structures are in a good agreement with recent observation. On the other hand, our calculations indicate the possibility of vacancy-induced magnetization in not only III-V and II-VI compounds but also BN nanotubes in various chirality symmetries. Furthermore, we calculated the electronic structure and vibrational behavior of a perovskite with doping ($Pb_{1-x}Ca_xTiO_3$) in order to elucidate the mechanism of the doping effects on the structural phase transition. Finally, we start to test the optical spectrum calculation in GW-BSE scheme.

Keywords: quasiparticle, spin–polarized, BN nanotube, perovskite, GW-BSE

I、Introduction

Until recent measurement on MBE-grown wurtzite InN[1], the fundamental gap decreases to about 0.8 eV rather than a wider bandgap of 1.9 eV which has been accepted in last 20 years. In order to resolve this debate, we present *ab initio* quasiparticle band structure calculations for InN within GWA. The detail of this many-body perturbation theory can be found elsewhere [2].

On the other hand, just similar to the defect-induced magnetization in BN and AlN in our 1st year result, we extend this calculation systematically to III-V, II-V semiconductors and BN nanotubes (BNT) with versatile structures. Using spin-polarized DFT calculation taking into account the local geometrical distortion around the vacancy center, we will compare the magnetization corresponding to different compounds.

Furthermore, recent Raman and x-ray data showed a tetragonal→cubic→orthorhombic sequence of phase transition along with the concentration of doping in Ca-modified $PbTiO_3$ [3]. We performed DFT and DFPT calculation to study the structural stability of $Pb_{1-x}Ca_xTiO_3$.

Finally, in order to carry out the optical spectrum including the exciton effects, we will start to perform the GW-BSE calculation in which a 2-particle Green's function is adopted to represent the quasparticles of electron-hole pairs.

II、Result and discussion

As shown in Fig. 1, comparing with negative direct bandgap(-0.02eV) at **Γ** point obtained from LDA, our GWA opens up the LDA bandgap up to 0.9 eV which is in good accord with recent measurements (~0.8 ev).

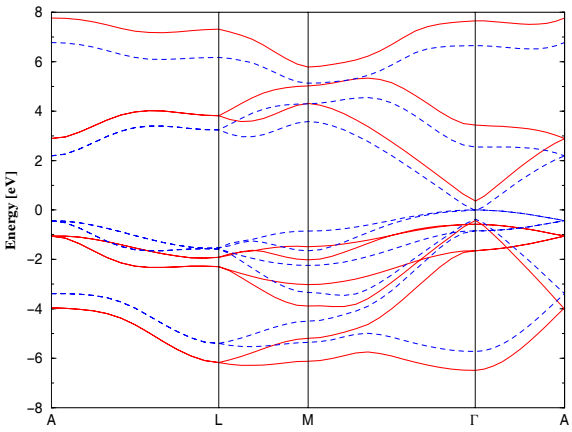
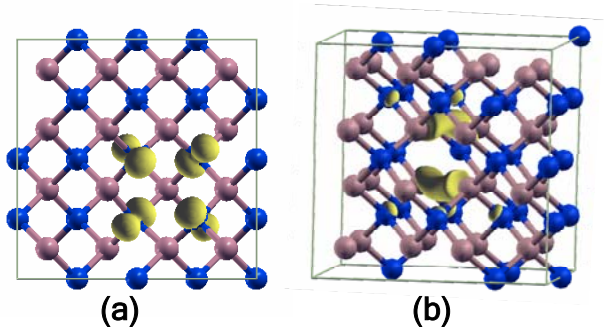


Fig.1. ***Electronic band-structure of wurtzite-InN in (a) LDA (blue dashed curves) and (b) GWA (red solid curves).***

Our spin-polarized calculations also show that a vacancy of Ga and N in cubic GaN induces a nonzero magnetic moment of 3 μ_B and 1 μ_B, respectively (as shown in Fig. 2(a) and (b)). Similar vacancy effect can be found in other III-V and II-VI compounds (as shown in Fig. 2 (c) and Table 1)



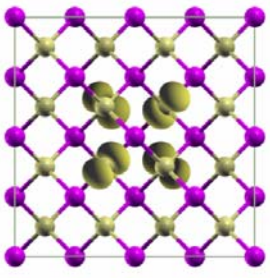


Table 1	μ_B/Defect
BP($\mathbf{V_B}$)	1.0
GaN($\mathbf{V_{Ga}}$)	2.98
GaN($\mathbf{V_N}$)	0.95
ZnS($\mathbf{V_{Zn}}$)	2.1

Fig. 2 ***Electronic spin density around defect center of (a) V_{Ga} in GaN (b) V_N in GaN, and (c) V_{Zn} in ZnS. Corresponding magnetic moments are compiled in Table 1.***

Furthermore, we calculate the zigzag ((5,0)) armchair((5,5)), and chiral ((5,2)) BN nano-tubes with the vacancy of B. As shown in Fig.3., the optimal structures near vacancy center all shows an outward expansion. The vacancy-induced magnetizations are all about 3 μ_B/vacancy.

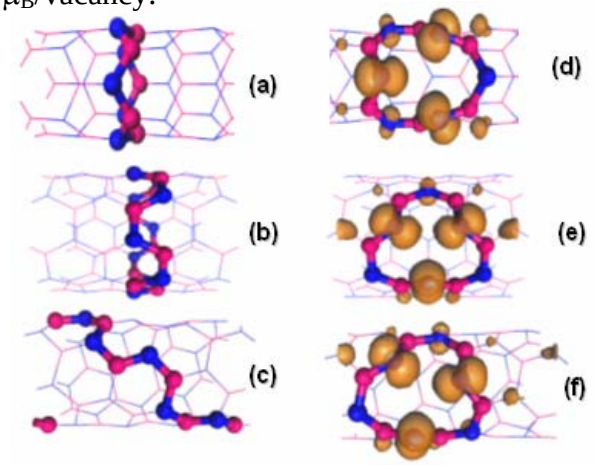


Fig.3. ***Atomic geometry of BN nantube in (a) (5,0) (b) (5,5) (c) (5,2) chiral symmetry. Corresponding optimal structure and spin density with a vacancy of B is shown in (d), (e), and (f), respectively.***

On the other hand, the electronic and vibrational structures of $Pb_{1-x}Ca_xTiO_3$ have been calculated to study the doping effects. Different bonding characters corresponding to different stable structures in x=0.25 and x=0.5 are shown in Fig. 4 (a) and (b).

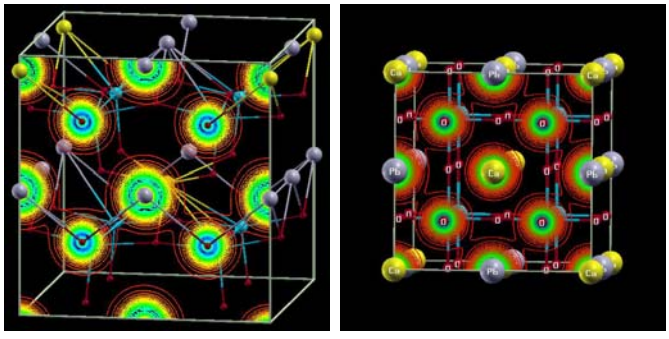


Fig. 4. ***Contour of charge density of (a) tetragonal $Pb_{0.75}Ca_{0.25}TiO_3$ and (b) cubic $Pb_{0.5}Ca_{0.5}TiO_3$. Pb, Ca, Ti, and O atom is denoted by a grey, yellow, light blue, and red sphere, respectively.***

Based on the Density Functional Perturbation Theory (DFPT), we performed the phonon calculation for $Pb_{0.5}Ca_{0.5}TiO_3$. The eigen-vector w.r.t. the softest mode at **Γ** point which dominates the structural instability is shown in Fig. 5. Such vibrational mode indicates the possibility of a stable orthorhombic structure for x>0.5.

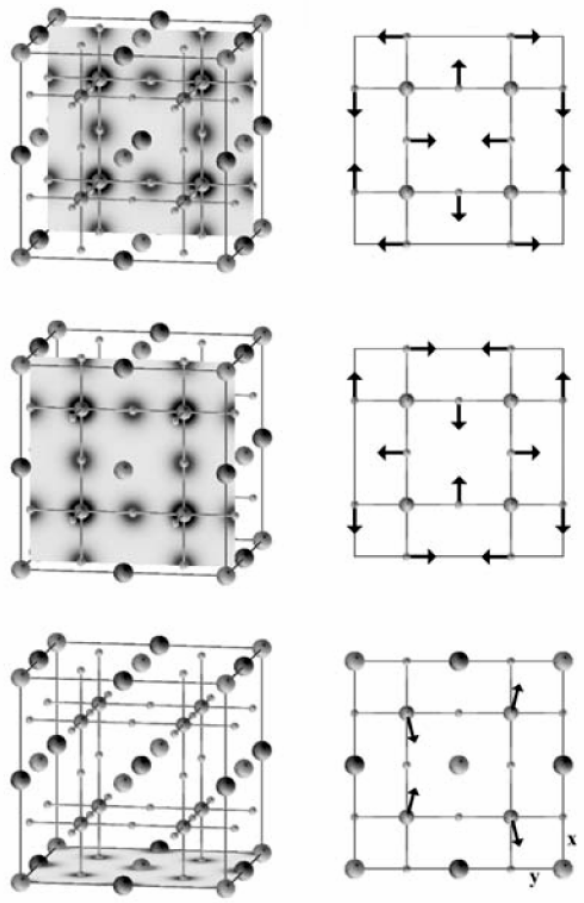


Fig.5. ***Eigenvetors, shown as arrows in arbitrary unit, of the softest mode at Γ point of $Pb_{0.5}Ca_{0.5}TiO_3$.***

III Further work

In order to calculate the optical spectrum with taking into account the electron-hole interaction, we start quasiparticle excitation calculation based on a scheme of 2-particle Green's function of Bathe-Salpeter equation [4]. Our preliminary results of Si, as shown in Fig. 6, represent the effect of electron-hole interaction (exciton) on optical spectrum which does not included in both DFT and the random phase approximation (RPA)-GWA calculation. We will carry out such GW-BSE calculations in other novel materials in our next year project.

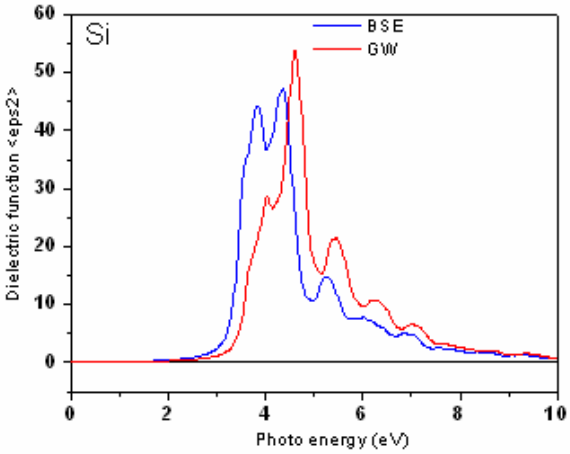


Fig.6 ***The calculated optical spectrum (ε_2) in RPA-GW (red curves) and GW-BSE (blue curves) scheme.***

IV. References

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