

行政院國家科學委員會專題研究計畫成果報告

固態相變之壓力機制

Compression Mechanisms in Solid-State Phase Transitions

計畫編號：NSC 88-2112-M-032-007

執行期限：87年8月1日至88年7月31日

主持人：薛宏中 淡江大學物理系

E-mail: hchsueh@mail.tku.edu.tw

hsueh@gate.sinica.edu.tw

一、中文摘要

在此研究計畫中，我們詳細探討壓力對於一般固態半導體之影響。本報告將著重於層狀半導體(四六族半導體 GeS 及 GeSe)及分子晶體(五族金屬碘化物 AsI₃ 及 SbI₃)對外加靜水壓力之反應，並利用第一原理電子結構計算，展現此類材料之複雜壓力機制(例如鍵長改變、低頻剛體振動模式之破壞、異常電子轉移、等等)。

關鍵詞：層狀半導體、第一原理電子結構計算、分子晶體、低頻剛體振動

Abstract

We examine in detail the effect of hydrostatic pressure on semiconductors which, at ambient conditions, are characterized by the coexistence of both weak and strong cohesive forces. We focus on elucidating the response to compression of the structural, vibrational and electronic properties in quasi-two-dimensional layered semiconductors (IV-VI semiconductors GeS and GeSe) and quasi-molecular solids (Group-V metal triiodides AsI₃ and SbI₃). Using *ab initio* electronic structure simulations, we demonstrate that hydrostatic pressure in this class of material leads to complex compression mechanisms favoring more isotropically bonded phases, to gradual breakdown of low-frequency rigid-layer vibrations and to unusual electron charge transfer effects.

Keywords: Quasi-two-dimensional layered semiconductors, *ab initio* electronic

structure simulations, quasi-molecular solids, low-frequency rigid-layer vibrations,

二、緣由與目的

As a result of considerable advances in experimental high-pressure methods and electronic structure techniques, it has recently become possible to begin detailed study of the hierarchical forces and compression mechanisms of anisotropic solids such as layered and molecular semiconducting materials. Here, both these classes of material are studied by experimental and theoretical methods to examine their response to compression.

In this work, we explore the structural, vibrational, and electronic properties of GeS, GeSe (layered semiconductors), and AsI₃, SbI₃ (molecular crystals) using first principles density functional pseudopotential calculations to compare the experimental result [1-3]. Therefore, we are able to predict the compression mechanisms and get insight into the nature of bonding in anisotropic systems.

三、結果與討論

The structural, vibrational, and electronic properties of three anisotropic materials (GeS, GeSe, AsI₃, and SbI₃) have been extensively investigated using theoretical methods in this work. The following result shows that the pressure response of structure of layered semiconductors and the quasi-molecular crystal can be well accounted for by first-principle calculations.

(a) Layered semiconductors (GeS and GeSe)

Our structural calculated results suggest that the compression occurs by individual layer distortion and reduction of adjacent layer separations (see Fig. 1). As a result, the intra-layer non-bonded Ge-chalcogen distance and the inter-layer atomic separation approach the intra-layer bond length leading to a loss of structural anisotropy.

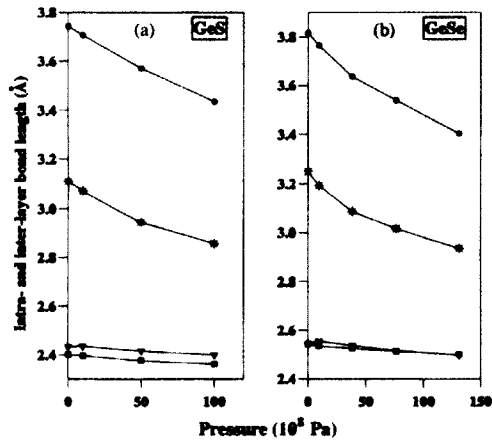


Fig. 1 Pressure dependence of the intra and interlayer bond length of a) GeS b) GeSe. Solid squares and triangles represent the calculated intralayer bond. The calculated shortest intralayer non-bonded Ge-chalcogen distance and interlayer atomic separation are denoted by stars and solid circles.

On the other hand, the pressure dependence of Raman-active GeS phonon (A_g , B_{1g} , B_{2g} , and B_{3g}) frequencies and with the relevant eigenvectors are also studied by our first principles calculation. At low pressure (<3Gpa), the mode-Gruneisen parameter of rigid-layer (RL) A_g , RL B_{3g} , and intralayer bond-stretching B_{3g} mode is 1.68, 1.80, and 0.31, respectively. It is clear that the characteristic low-frequency RL modes are preferentially affected by compression. Meanwhile, we found a pronounced sublinear pressure response of the RL A_g shear mode of GeS up to about 6.5Gpa (shown in Fig 2.). From our calculated eigenvectors, it is attributed to a pressure-enhanced mode mixing of a nearly RL vibration. In addition, the inter/intra-layer force constant ratio $[(v_{RL}^{B_{3g}} / v_{intra-layer}^{B_{3g}})^2]$ increases from 0.083 to 0.13 at 10Gpa. It indicates that the anisotropy of these layered compounds may

lose gradually under hydrostatic pressure. Therefore, the discrepancy between bondlength and the nearest nonbonded separation suggests that the structures of two Ge chalcogenides are still characterised by highly anisotropic bonding under the highest pressure studied here. Considering the lattice dynamics, the pressure-enhanced inter/intra layer force constant ratio and the failure of rigid-layer approximation under compression reveal that the substantial anisotropy of vibrational properties of layered materials decreases much more severe than the structural anisotropy.

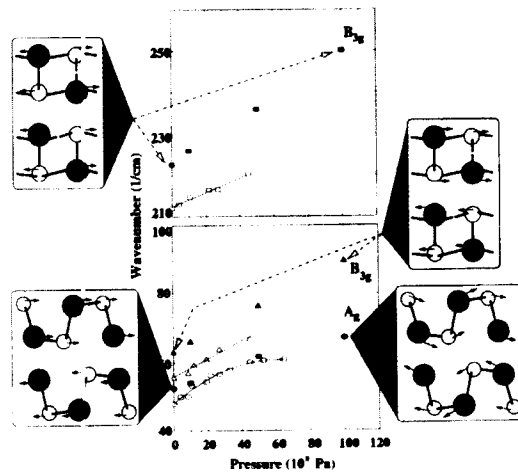


Fig. 2 Observed and calculated frequencies of RL A_g , RL B_{3g} , and intralayer B_{3g} modes of GeS with calculated corresponding eigenvectors as a function of pressure.

(b) Molecular Crystals (AsI_3 and SbI_3)

A pressure-induced molecular-nonmolecular transition has been found and the isostructural high pressure modification is a quasi-two-dimensional layered solid characterised by more-or-less ideal octahedral coordination of cation(As and Sb). This pressure effect can be illustrated clearly in Fig. 3. In the low pressure regime (below the 1st order structural phase transition pressure), both calculated and observed results show that the nearest metal-iodine intra-molecular bondlength increases initially and then decreases while up to modest pressure. This detail unexpected pressure response could be attributed to the anomalous vibrational behaviour.

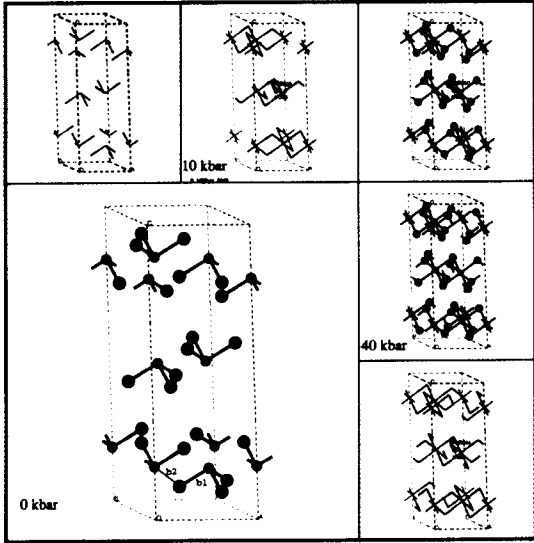


Fig. 3 The schematic calculated structural response of molecular crystal SbI_3 .

Furthermore, the calculated overlap population of intra- and inter-molecular bonds at different pressure (shown in Fig. 4) shows that compression induce intra- to inter-molecular electron transfer accompanied by a pronounced weakening of the intra-molecular bond strength and the formation of a two-dimensional layered solid. Continued compression drives the layers closer together until a three-dimensional network solid of very low symmetry is formed. The gradual migration of electron charge is consistent with the vibrational evidence suggesting that the strength of the intra-molecular bond decreases gradually under compression while stronger inter-molecular bonds are formed. Therefore, the roughly degeneracy of overlap populations under pressure is the evidence for the reduction in the disparity between the stiffness of the intra-molecular and intermolecular bonds. Such non-monotonic pressure variation was also found in H_2O ice in which the turn-over of infrared-active vibrational frequency indicates the molecular-ionic solid transition [4].

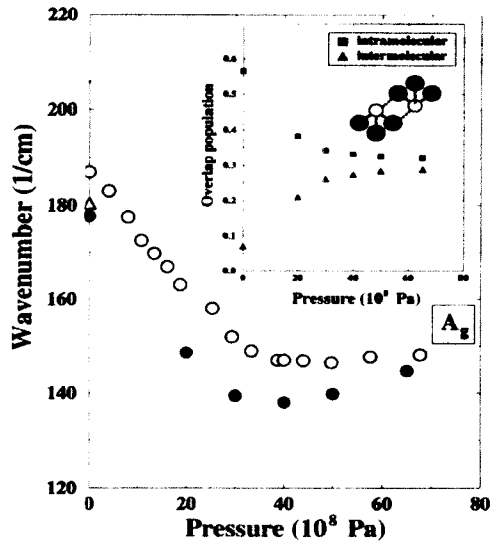


Fig. 4 Frequencies of the intramolecular As-I symmetric stretching A_g mode and overlap populations versus pressure in AsI_3 .

In Fig. 5, we present an example of this unique bonding transformation in SbI_3 is substantially enhanced by more compression perturbation.

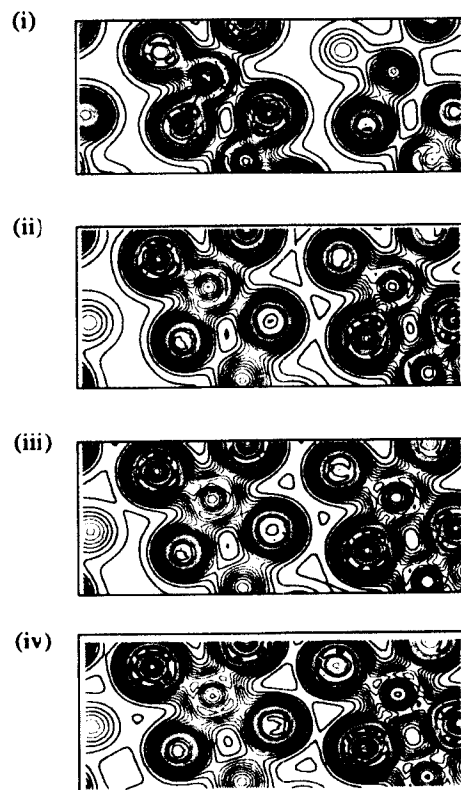


Fig. 5 Charge-density contour plot of the calculated valence charge of SbI_3 at (1) ambient pressure, (2) 5 kbar, (3) 10 kbar, and (4) 20 kbar.

肆、參考文獻

- [1] H. C. Hsueh, M. C. Warren, H. Vass, G. J. Ackland, S. J. Clark, and J. Crain, *Phys. Rev. B*, **53**, 14806 (1996)
- [2] H. C. Hsueh, Roger K. Chen, H. Vass, S. J. Clark, G. J. Ackland, W. C-K. Poon, J. Crain, *Phys. Rev. B*, **58**, 14812 (1998)
- [3] H. C. Hsueh and J. Crain, *Phys. Stat. Sol. (b)*, **211**, 365 (1999)
- [4] A. F. Goncharov, V. V. Struzhkin, M. S. Somayazulu, R. J. Hemely, and H. K. Mao, *Science*, **273**, 218 (1996).