STUDIES OF SHIRAI GROUP

MATERIAL

DYNAMICS DESIGN

DEPT. THEORETICAL NANOTECHNOLOGY, ISIR,
OSAKA UNIVERSITY

21 May 2009

What is dynamics design?

- Materials design utilizing atomic motions
  modification of structures to specific applications

ex.

transform insulator to superconductor

- Control of atomic motions

ex.

control of diffusion of impurities in semiconductors

Material researches by first-principles calculations

Group leader profile

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First-principles method is a method to calculate accurately material properties from fundamental equations of quantum theory only. By using this method, we are able to study not only static properties of materials (crystal structure and band structure), but also dynamic properties such as diffusion and phase transition at finite temperatures, in which most experimentalists are interested. Our study is not limited to study the electronic properties of existing materials. It is our mission to predict unknown or non-existing materials. More-over, it is also important to give guideline to experimentalists how to synthesize such materials.

activities in international

Conferences

Semiconductors physics

29th Int. Conf. Physics of Semiconductors (Brazil, 2008)

2 papers including 1 oral

Defects physics

24th Int. Conf. Defects in Semiconductors (USA. 2007)

3 papers

High Pressure in semiconductors

13th Int. Conf. High-Pressure Semiconductor Physics (Brazil, 2008)

an invited paper

Phonon physics

12th Int. Conf. Phonon Scattering in Condensed Matter (Paris, 2007)

2 papers including 1 oral

Boron materials

16th Int. Symp. Boron, Borides and Related Materials (Matsue, 2008)

three papers including 1 oral

organizing of special session on superconductivity: J. Phys: Conf. Series (in press)

Conversion of semiconductor to superconductor

Highly developed semiconductor technology plus high-speed superconductor technology are put together on a chip.

Adding superconducting properties on a semiconductor chip with highly developed technoglogy yields potential of extremely high-speed and low-power consumption electronic devices.

Usually, semiconductor does not possess superconductivity. Surprisingly, recently, it has been demonstrated that semicon-ductors can exhibit supercon-ductivity by heavy doping. Currently, the critical tempera-ture T_c is at most 10K. However, many researchers believe that this is just the beginning and that it could be possible to raise T_c more than 50 K by further material researches.

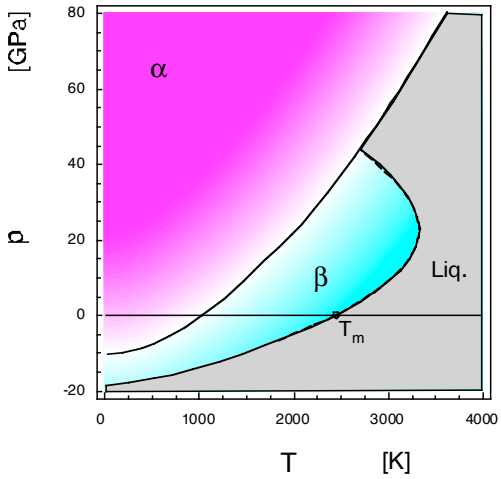


Fig. 1 Prediction of phase diagram of boron

Superconductivity research on boron

Boron is a semiconductor, but it is considered that it could become a superconductor with high T_c, more than 50 K, if appropriate doping is possible.

The primal difficulty is how to dope with a sufficient amount of carriers. One of the ideas is use of high pressure to induce metallic transition. For this purpose, accurate phase diagram is necessary, which were not available for boron before. We have done this prediction as shown in Fig. 1. In fact, it has been demonstrated by experiment that α phase is stable up to 200 GPa and that it undergoes superconductivity transition around 160 GPa.

A. Masago et al., Phys. Rev. B **73** 104102 (2006).
K. Shirai. et al., Phys. Status Solidi (b) **244** (2007), 303

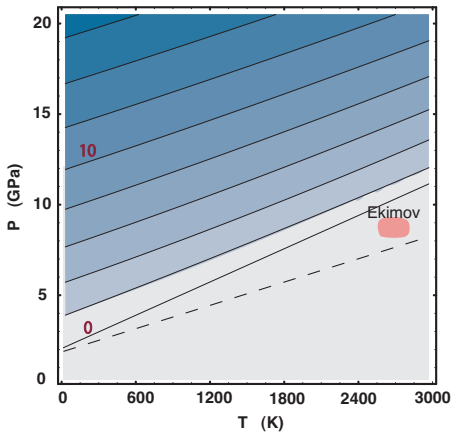


Fig. 2. Prediction of B concentration in diamond by using high-temperature and high-pressure method.

Superconductivity research by B-doped diamond

Diamond is a typical tetrahedrally-coordinated semiconductor, and does not undergo phase transition at high pressure. Recently, it has been demonstrated that it exhibits superconductivity by heavy doping with boron. Currently, the B concentration is several at.% and T_c~10 K. However, many people believe that increase in B concentration leads further increase in T_c. The difficulty is how to dope at such a high concentration. Our proposal of efficient doping method is use of high pressure more than 10 GPa.

K. Shirai, et al., Phys. Status Solidi (b) **246** (2009), 673

Calculation engine underlying materials design

"Osaka2k"

first-principles pseudopotential

Pseudopotential method

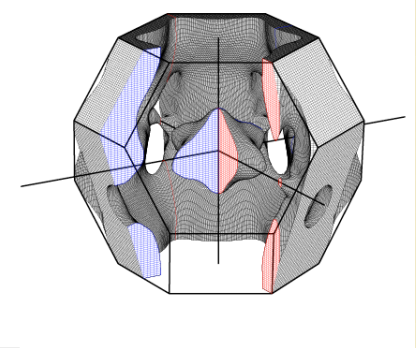
An approach to describe properties of solids by valence electrons of atoms only. With an advantage that forces acting every atoms can be easily obtained, this method is particularly suitable to structural determination and atom dynamics.

Molecular dynamics simulation

Evolution of atomic motion is determined as a function of time by step-by-step approach.

sophisticate algorithms

accurate and high-speed calculation by using crystal symmetry and advanced algorithms.



H. Dekura, et al., J. Comput. Theor. Nanoscience, in press

Further information
http://www.cmp.sanken.osaka-u.ac.jp/~koun/osaka.html

Nanoscale control of defects in semiconductors

Growing demands for miniaturizing devices, while researches of materials to meet for versatile properties

Control of TM impurities

Transition metals (TM) impurities, in particular Cu, have crucial roles in the current technology of Si devices. Increase of its use for wires makes chance of device damage increased. Protection from the metal contamination is a key issue for device miniaturizing.

In order to protect metal contaminations, the gettering method is used: metal impurities are absorbed to gettering centers, which are usually lattice defects intentionally introduced into a part of wafer far from the active area of device. The efficiency of gettering is one of important concerns for the device manufacturers. The materials for gettering center used to be chosen by experience. Now, by using FP method, we are able to design efficient gettering center without help of experiment. Figure 3 shows the situation of Cu gettering by BO_2, which is theoretically predicted as a good candidate for the gettering center.

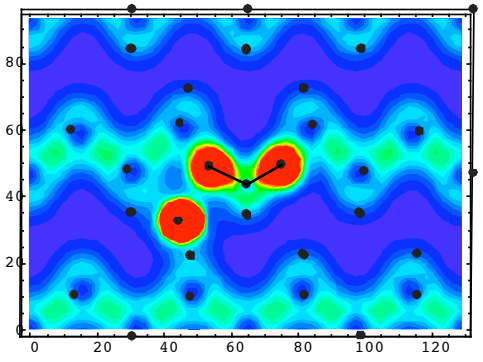


Fig. 3. Cu impurity trapped by BO_2

K. Matsukawa, et al., 29th Int. Conf. Physics of Semiconductors (2008)

It is not always true that TM impurities are detrimental species. In some cases, TM impurities turn out to be useful, when it forms a desirable complex. Cu complex is an example, which can be a luminescence center with high efficiency. Recently, complicated isotope shifts have been demonstrated by experimentalists (Thewalt *et. al.* 2007). We have given a reasonable account for this phenomenon.

K. Shirai, et al., J. Phys.: Condens. Matter **21** 064249 (2009).

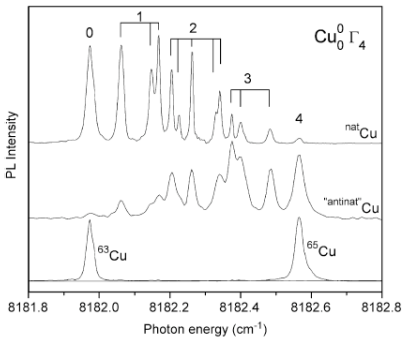
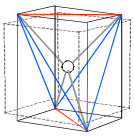


Fig.4 Complex isotope shifts in photoluminescence due to Co complex (Thewalt)

Physics of defects

The vacancy in silicon is one of old subjects, which has been well studied. It is surprising to find a yet unresolved problem related to Jahn-Teller effect.

It has been well known that, when a lattice vacancy is created in Si crystal, the surrounding atoms are displaced in a way of symmetry breaking, *i.e.*, Jahn Teller effect. When atom motions are taken into account, it is found that this distorsion causes interesting effects in the elastic properties.



J. Ishisada, et al., J. Phys.: Conf. Series **92** 012063 (2007).

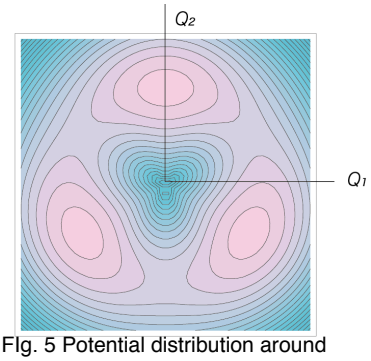


FIg. 5 Potential distribution around the vacancy

Computational materials design workshop

With "Osaka2k", we are the leading members of the computational materials design consortium under conduction of Osaka University. This activity includes a series of regular school (twice of year), special lecture on demand, publication, etc. In the regular school, five-day treaning of program codes including "Osaka2k" is intended for users skill up for computation. Many case studies by experts increases experiences for materials design. Exchange of knowledge of individuals stimulates new ideas of materials design,

- Beginner course
- Advanced course
- Expert course

Schedule of this year

15 th CMD workshop

9/14 (Mon) – 18 (Fri)

Toyonaka Campus, Osaka Univ.

contents of previous workshop

http://www.dyn.ap.eng.osaka-u.ac.jp/CMD14/

Mystery of the ghost line -effects of anharmonicity-

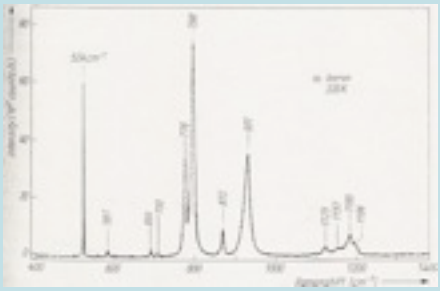
contribution to basic research

One of long-standing problems in α boron is the so-called ghost line in its Raman spectrum. The right figure shows this Raman spectrum. Here, we can see a prominent peak at 524 cm^{-1}. This peak has by far narrowest width. Along with other peculiar properties, the peak used to be called the ghost peak.

The origin of this ghost peak was attributed to a special mode of phonons, that is, librational mode, by Vast in 1997. This discovery was surprising, because it was common that the frequency of librational mode is very low. Why is the boron case an exception? We disclosed that the the mechanism of this low frequency is originated from the large number of angles involved in the mode.

The line width of phonon is determined by anharmonicity. The anharmonicity appears in the pressure dependence of frequency, which is usually recognized as Grüneisen parameter. The Grüneisen parameter of this librational mode is very small. But, this does not necessarily lead to smallness of anharmonicity of this mode.

The true mechanism of this narrow line width is a rather ingenious mechanism of decay process of a specific type, in which the related Bose factors are cancelled out to eliminate the transition rate.



K.Shirai., et al., J. Phys. Soc. Jpn. **67** (1998) 3801.

Control of impurity diffusion

In device manufacturing process, junctions are formed by impurity diffusion at several stages with different temperatures. Thermal diffusion causes degradation of the previously established interfaces. It is a dream of manufactures that diffusion is performed selectively.

One of the ideas for selective diffusion is use of IR excitation, because each impurity has its own vibration mode, so that only resonance-frequency laser can excite the impurity under consideration. The rough idea arose even before. However, the most important problem of the necessity of extremely high power was not seriously considered. Now, we can simulate the effects of IR excitation on impurity vibration, and are able to design experimental setup in order to achieve this.

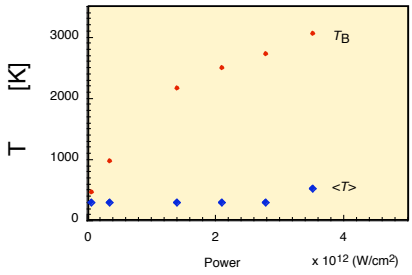


Fig. 6. Effect of raising the local temperature of boron atoms by IR excitation

K.Shirai., et al., Physica B **401-402** (2007) 682

Advent of new materials using electronic excitation

When diamond is subject to high temperature, it is converted to graphite. However, the reverse never happens. By using electronic excitation, it may be possible to convert graphite to diamond without help of high pressure.

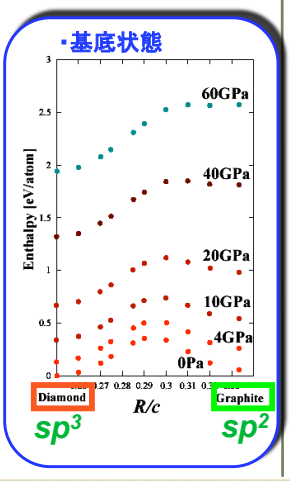
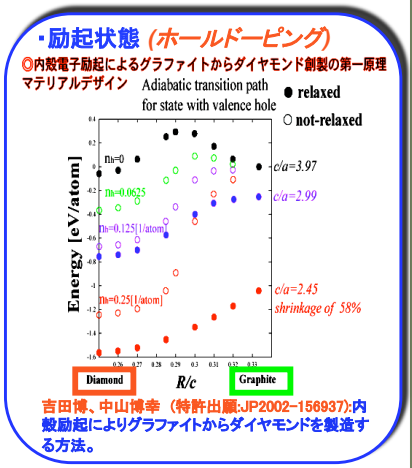


Fig. 7. Lowering of the energy barrier between graphite and diamond by electronic excitation

Use of electronic excitation could bring about unusual reactions which otherwise impossible in thermal equilibrium conditions. An interesting application of this method is conversion of graphite to diamond without help of high pressure. Figure 7 shows this possibility to lower the barrier height between graphite and diamond by electronic excitation.

H. Nakayama, et al., J. Phys. Condens. Matter, **15** (2003) R1077.



National academic projects which we are participating

Grant-in-Aid for Scientific Research in Priority Areas "*Development of New Quantum Simulators and Quantum Design*" of MEXT, Japan, (Head: H. Akai, Osaka Univ.) 2005-2009.

carried out the editorial office of the project. There are a couple of news letters. → http://ann.phys.sci.osaka-u.ac.jp/-tokutei/news.html

Grant-in-Aid for Scientific Research in Priority Areas "*Areas of New Materials Science Using Regulated Nano Spaces -Ubiquitous strategy*" of MEXT, Japan, (Head: K. Tanigaki, Tohoku Univ.) 2007-2011, "Superconductivity research icosahedron-based semiconductor boron"

http://www-nano.phys.sci.osaka-u.ac.jp/nanospace/