RICC Usage Report for Fiscal Year 2009

Project Title:

High pressure structures of solid methane (CH4)

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The significant advantage of the hydrogen rich materials in pursuing the high temperature superconductor is in its high Debye temperature due to the lightest atomic mass. Based on this principle, N. W. Aschroft [1] has proposed that the hydrogen rich materials of methane, silane, germane, and stannane could be the high temperature superconductors under high pressure when they are metallic. Indeed, the previously theoretical calculations on silane [2] and stannane [3] have revealed very high superconducting transition temperatures (Tc) of 55 K at 125 GPa and 80 K at 120 GPa, respectively. However, in order to correctly understand the superconductivity for these materials, the right crystal structures are considered as essential. Pickard and Needs [4] using the random sampling method had predicted the crystal structures of silane under pressure. We [5] had predicted germane has very high Tc of 64 K at 220 GPa, which had received great supports from RSCC system in the fiscal year 2008. Up to now, the crystal structures of methane and stannane under pressure are still open. With the current project, we plan to systematically explore the crystal structures of the two hydrides based on the newly invented evolutionary algorithm [6] in the crystal structure prediction and then to perform extensive electron-phonon coupling calculation using the predicted structures within the linear response theory in guiding the experimentally superconducting explorations.

Reference

[1] N. W. Aschroft, Phys. Rev. Lett. 92, 187002 (2004).

[2] J. S. Tse, Y. Yao, Phys. Rev. Lett. 98, 117004 (2007).

[3] Y. Yao, J. S. Tse, Y. Ma and K. Tanaka, Euro. Phys. Lett. 78, 37003 (2007).

[4] C. J. Pickard and R. J. Needs, Phys. Rev. Lett., 97 045504 (2006).

[5] G. Gao, A. R. Oganov, A. Bergara, M. Martinez Canales, T. Cui, T. Iitaka, Y. M. Ma, and G. T. Zou, Phys. Rev. Lett. 101, 107002 (2008)

[6] A. R. Oganov and C. W. Glass, J. Chem. Phys. 124, 244704 (2006); C. W. Glass, A. R. Oganov, and N. Hansen, Comput. Phys. Commun. 175, 713 (2006); A. R. Oganov, C. W. Glass, and S. Ono, Earth Planet. Sci. Lett. 241, 95 (2006).

We run crystal structure predictions, structure optimization, and enthalpy calculations using VASP code in RICC machine. After the enthalpy calculations for the selected structures, we then performed the phonon and electron-phonon coupling calculation using the PWSCF code in RICC system.

With the use of RICC machines, we have obtained many scientific results. **For stannane (SnH4)**, we propose the existence of two unique high-pressure metallic phases having space groups Ama2 and P63⁄mmc, which both contain hexagonal layers of Sn atoms and semimolecular (perhydride) H2 units. In the Ama2 phase, Sn atoms form a simple hexagonal packing, where the trigonal prismatic holes are filled with semimolecular H2 units (H-H distance 0.79 Å, which is longer than the 0.74 Å in the isolated H2

molecule). The H2 units are aligned either along the pseudohexagonal axis, or perpendicular to it, and these two orientations alternate (Fig. 1A). The P63⁄mmc phase here is based on the much denser hexagonal close packing of the Sn atoms (c⁄a 1.84 at 200 GPa, relatively close to the ideal value of 1.63). In this structure, the ordered H atoms are clearly split into two categories. One sort forms semimolecular H2 units (the magenta atoms in Fig. 1B) occupying hexagonal channels of the hexagonal close packing structure, whereas the other sort of H atoms occupies positions just below and above Sn atoms, forming chains Sn-H…H-Sn-H…H-Sn-H running along the c axis (Fig. 1B). Enthalpy calculations (Fig. 2) reveal that the Ama2 and P63⁄mmc structures are stable at 96–180 GPa and above 180 GPa, respectively, while below 96 GPa SnH4 is unstable with respect to elemental decomposition (Sn+H2). The application of the Allen-Dynes modified McMillan equation reveals high superconducting temperatures of 15–22 K for the Ama2 phase at 120 GPa and 52–62 K for the P63⁄mmc phase at 200 GPa. The larger Tc in the P63⁄mmc structure is mainly attributed to the stronger λ of 0.87 and the larger ωlog of 1,135 K. The larger N(Ef) and higher intermediate frequencies in the phonon spectrum of the P63⁄mmc structure are probably responsible for the stronger λ. The current study will inevitably stimulate the future high-pressure experiments on the structural and conductivity measurements. These results have been published in Proceedings of the National Academy of Sciences **107**, 1317, (2010).

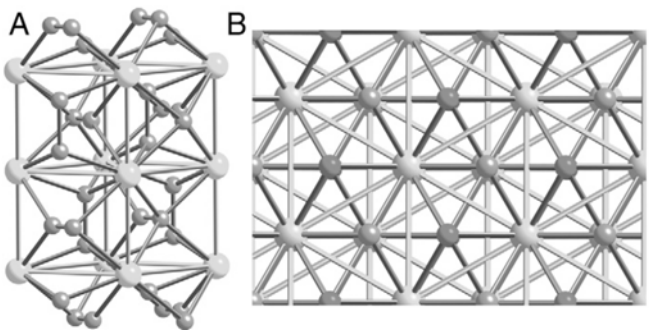

Figure 1. Ama2 (A) and P63⁄mmc (B) structures.

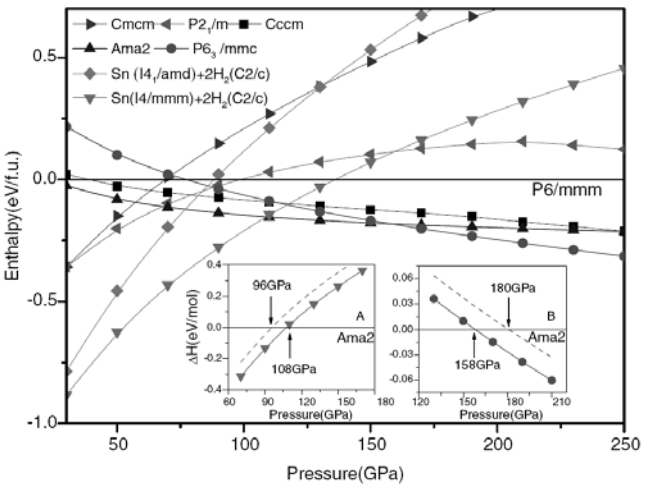

Fig.2 Enthalpy curves for the predicted structures. Ama2 and P63⁄mmc structures are stable at 96–180 GPa and above 180 GPa, respectively, while below 96 GPa SnH4 is unstable with respect to elemental decomposition (Sn+H2).

For methane (CH4), its zero-temperature phase diagram under pressure has been systematically investigated, as shown in Fig. 3. At low pressure, methane keeps its molecular form and adopts P212121 symmetry below 78 GPa. In the range of 78-105 GPa, two novel structures with space groups Pnma and Cmcm are found to be the most promising candidates. Under higher pressure, methane becomes unstable and dissociates into the mixtures of C2H6, and C4H10 with hydrogen below 305 GPa, above which a mixture of diamond and hydrogen is stable. Our results also show that methane remains insulating up to very high pressures, which might be helpful to resolve the long-standing debate on the possibility of this compound as a superconductor within the reach of current high pressure techniques.

Since diamond, a decomposition product of methane, is denser than hydrogen and hydrocarbons, there should be gravitational precipitation of diamond inside giant planets Neptune and possibly Uranus. However, C_2H_6 and C_4H_{10} do not precipitate. They may partly leak into the atmosphere. The complex

transformation products, such as C_2H_6, C_4H_{10}, diamond and hydrogen, have to be realistically taken into account in the models of internal evolution and energetic of these planets. These results have been submitted to Physical Review Letters.

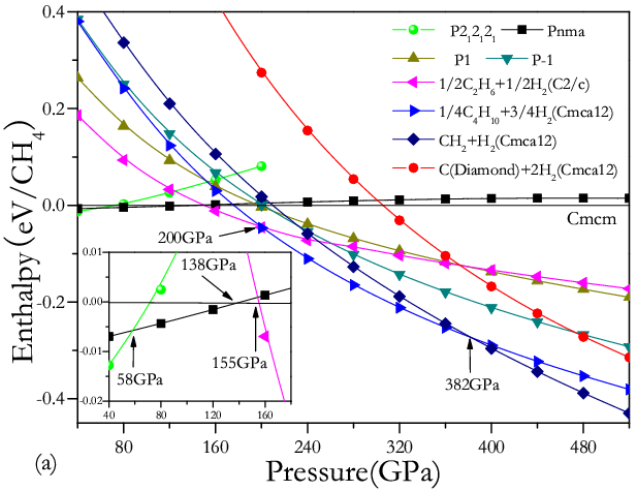

Fig. 3. Enthalpy curves (relative to our predicted *Cmcm* phase) for CH_4 as a function of pressure

For this year, we have nearly finished all the computing time as a quick user account. We plan to extend the use of RICC system as a quick user since we have several new topics.

Fiscal Year 2009 List of Publications Resulting from the Use of RICC

[Publication]

1. Guoying Gao, Artem R. Oganov, Peifang Li, Zhenwei Li, Hui Wang, Tian Cui, **Yanming Ma**, Aitor Bergara, Andriy O. Lyakhov, **Toshiaki Iitaka**, and Guangtian Zou "High-pressure crystal structures and superconductivity of Stannane (SnH4)" **Proceedings of the National Academy of Sciences 107**, **1317, (2010).**