phys. stat. sol. (b) **235**, No. 2, 221–224 (2003) / **DOI** 10.1002/pssb.200301577

A personal view of the physics of high pressure studies of solids

Marvin L. Cohen*

Department of Physics, 366 LeConte Hall #7300, University of California, Berkeley, CA 94720, USA
Materials Sciences Division, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, CA 94720, USA

Received 5 August 2002, accepted 29 August 2002
Published online 4 February 2003

PACS 62.50.+p, 71.20.Nr

I will discuss some background and motivation for studies of high pressure properties of solids. My description will reflect my personal view as a theorist who feels strongly that condensed matter physics is a very important field of science and that high pressure studies have contributed greatly to this field.

Let me begin by discussing physics.

You are probably as tired as I am of hearing the statement, "Last century was the century of physics, and this century belongs to biology." First of all, nobody knows how science will develop in this century. As the baseball philosopher, Yogi Berra, said, "It's hard to predict – especially about the future."

I think it can be argued that physics has not lost its luster. New, exciting developments continue to emerge, and it's probably possible to argue that physics discoveries and developments in this century will be on the level of those of the last century. If I were to predict a change in science, I would suggest that in the future science will become more interdisciplinary. Nanoscience is a good example. Studies on this length scale have led to important collaborations between physicists, chemists, biologists, material scientists, computer scientists and engineers. These collaborations are generally not forced marriages by funding agencies which are sometimes prone to giving incentives for interdisciplinary work so that they can fund larger units. They exist because nanoscience collaborations are of mutual advantage.

I strongly believe physics is the "central science". If interdisciplinary research thrives, physics will provide instruments, concepts, and rigorous standards. I also think condensed matter physics (CMP) is the "central area" of physics. This view is not only based on length scales but on the scientific connectivity of our field. There are strong overlaps with atomic and molecular physics, plasma physics, biophysics, astrophsics, geophysics, and even particle physics. Think also of the connections between CMP and chemistry, computer science, engineering, and biology. And there are so many applications! Semiconductor physics is an extremely important part of CMP. Silicon alone is the backbone of the world's largest business.

One might ask, "Why is it that the front pages of newspapers worldwide feature science articles focused on astronomy and biology, but rarely CMP. Even string theory receives more attention in the media than CMP. When I'm asked this question, my answer is that "CMP is like fine wine – you have to develop a taste for it."

As you can probably tell, I believe that physics plays a central role in human intellectual thought and that CMP is a central part of physics. Now let me give you some arguments for why I feel that high pres-

* e-mail: mlcohen@uclink.berkeley.edu, Phone: +1 510 642 4753, Fax: +1 510 643 9473

 0370-1972/03/23502-0221 $ 17.50+.50/0

sure studies of solids are so important in this field. I will make the connection mainly through my own specialty, condensed matter theory – especially research related to explaining and predicting properties of semiconductors.

I'll start with two views from two "beautiful minds" of the last century, Einstein and Dirac. Essentially, Einstein said "the most incomprehensible thing about Nature is that it is comprehensible." And in 1929 after quantum theory had been developed, Dirac essentially said "quantum mechanics explains all of chemistry and most of physics, but the equations are too complicated to be soluble."

So, Einstein says it's doable, Nature is comprehensible, and Dirac says here's the tools, but it's hard. Dirac, in essence, posed a challenge. And I think to a large extent in condensed matter theory we have answered Dirac's challenge. We start with two input numbers characterizing the constituent atoms of a solid, and we can explain and predict the properties of the solids they form. We have electron density plots which tell you exactly where an electron "probably" is in a crystal. We compute electronic, optical, mechanical, vibrational, photoemissive, and even superconducting properties of solids. We predict new materials, and our methods apply to atoms, molecules, clusters of atoms, nanostructures, and macroscopic crystals. We even have ways of dealing with some forms of disorder and amorphous solids.

So, we theorists have developed a "standard model of solids" which explains and predicts many properties of a large class of solids from first principles with only a knowledge of the constituent atoms. In my opinion, the genesis of this ab initio approach was an empirical approach called the Empirical Pseudopotential Method or EPM developed in the 1960's and 1970's [2]. The EPM required experimental data as input. This data came mainly from optical studies [2] like those done by Manuel Cardona, Peter Yu, and others. And there were severe experimental tests of the theory. For example, can theory explain or predict what happens if you put a solid under pressure? Hydrostatic, non-directional pressure is relatively easy to simulate theoretically. We just change one parameter: the spacing between atoms. Experimentally it's not so easy. In fact, it's often easier to squeeze along just one direction. Although this is more difficult for theory, it is still possible to simulate.

So, what happens if you squeeze a solid isotropically or in effect decrease the separations of the atoms? A great deal happens! And it can be fascinating. For example, pressure can change semiconductor band gaps.

It can be argued that the semiconductor band gap is responsible for the economic success of Japan after World War II, and it is the underlying physical feature responsible for some of today's largest businesses. The size of the gap is important. It determines the possibility of applications such as semiconductor lasers, solar batteries, and transistors.

For the non-expert, let me state that the energy gap is a forbidden region of energy for electrons in a semiconductor or insulator. So, when light shines on a semiconductor and the light causes an electron to move to higher energy, this jump or transition in energy may be forbidden. For silicon, the gap is 1.2 electron volts. So, for example, if the photons comprising the incident light only have 0.5 electron volts of energy, the electrons can't absorb the energy. At least 1.2 electron volts is needed for the electron to "jump the gap". Using pressure, one can change the gap size and this completely changes the response of the semiconductor. Hence pressure can be used as an exquisite tool to study band gaps.

There is a joke about theoretical physicists. Actually there are many, but this one has to do with our wonderful open-mindedness and acceptance of new ideas. It goes like this: when one theorist explains his or her new theory, idea, or calculation to a second theorist, only two possible responses can result: (1) "it's wrong" or (2) "I thought of it before". I remember with pleasure when my responses were not (1) or (2) and a light went on giving me new understanding. One example was when Bob Laughlin, who had been a student of my student, John Joannopoulos and hence a grandson, told me of his theory of the quantum Hall effect. This theory later brought him a Nobel Prize. I recall the pleasure once I understood what he was saying. Another time was when I first heard of the proposal by Steven Groves and Bill Paul [3] that gray tin had no band gap–not just a small gap but an absolutely zero gap. Up to that time, gray tin had usually been called a semiconductor and sometimes a semimetal. Semiconductors and insulators have gaps, metals and semimetals don't – in fact, for semimetals and some metals, you can say they have "negative gaps". In my mind, all three-dimensional crystalline solids in the world could be classified in this way until I heard about Groves and Paul's paper on an absolutely zero gap model to

explain properties of gray tin. So here was an idea which was not wrong and I had never heard it proposed before. I was convinced it was not wrong once I got the point that it was symmetry which dictated an absolutely zero gap. And theorists always believe symmetry arguments.

Many of us tried to think of other applications of this model. I remember working on the analogy with relativistic theories of Dirac and dispersion curves for neutrinos because in those days we were told that neutrinos were massless – this has been challenged recently. In any case, for me the main stimulus of the zero gap gray tin model was intellectual. Nowadays we hear of hyped statements about discoveries of new states of matter. For me, a zero gap material can be viewed as a fourth electronic state of crystalline solids. So, there's insulators and semiconductors which can be grouped together, semimetals, metals, and zero gap solids.

There is another important aspect of band gaps that's a bit more difficult to explain to non-experts. When one refers to the band gap of a semiconductor, it usually means the minimum energy gap. However, there are higher energy gaps which refer to the separation in energy between an occupied electronic state and an empty energy state into which an electron can jump to if excited by light or other stimuli. And to make matters more complicated there are two types of jumps or transitions. "Direct transitions" where the electron does not change momentum and "indirect transitions" where it does.

If experimental data are obtained for the direct and indirect energy gaps, a model like the EPM can use this as input and produce a band structure which is a plot of the electron energy as a function of its momentum. The band structures are extremely useful for understanding materials. Bill Paul's pioneering experiments showed how these various energy gaps depended on pressure and provided the touchstone for many theoretical band structures. He developed general rules for how the gaps would respond to pressure for an important class of semiconductors. He later used pressure studies for superlattices, complex systems, amorphous semiconductors, and even nanocrystals to help understand these systems.

The influence of pressure experiments on pure and applied studies of semiconductors has been very significant. Since semiconductor gaps can be changed or "tuned" by pressure and temperature, it is possible to use this data and other theoretical input to design alloys of semiconductors with a specific band gap or other electronic features. This field, called "band gap engineering" is the basis for many applications using bulk semiconductors, surfaces, interfaces, and superlattices.

On the basic physics side, these experiments were crucial for the theory and allowed the empirical approaches like the EPM to develop into the modern ab initio approaches. A major motivation came from the semiconductor studies. First, it was established that when the EPM was used to compute optical spectra and other properties, these were compared with the wealth of experimental data produced by Manuel Cardona's group [2] and Bill Paul's pressure coefficients, there was incredible consistency. In effect, we could use experimental data to produce potentials for the valence electrons which described their interactions with the atoms in a crystal. The surprising thing was that an analysis of InSb and InAs, for example, allowed us to extract the In, Sb, and As potentials separately; and these potentials described the metal In and the semimetals As and Sb very well. So, Cardona could measure the optical properties of a semiconductor compound based on Al or In, and we could use that data to understand the electronic properties of the metals Al and In. Hence, the potentials are transferable and unique to each element. This approach had limited applicability, but conceptually it was a breakthrough.

Nowadays, we generate the potentials or so-called pseudopotentials from first principles using only the atomic number as input. The scheme is similar to one invented by Fermi in 1934 [4]. We can arrange atoms in any crystal structure we wish, on the computer, and calculate the total energy of this system using a scheme [5] we introduced in the 1980's. The pressure effects, compressibility, lattice constants, elastic constants, and lattice vibrational properties can then be obtained from first principles. At higher pressures, the structure changes and these changes can be computed.

A great success of the theory which involved pressure experiments was a study of silicon in 1984. The theory predicted that Si would transform from a semiconductor in the diamond structure into two types of hexagonal metals at high pressure. The calculations also predicted the structure, the separation of the atoms, the electronic structure, the vibrational structure, and how the electrons would interact with the lattice vibrations. The most dramatic prediction was that these metals would be superconducting.

People were skeptical, but fortunately, Gerard Martinez decided to try the experiment and he and his colleagues in Grenoble found superconductivity. This was followed by Peter Yu's beautiful diamond anvil experiments in Berkeley which mapped out the dependence of the superconducting transition temperature on pressure. As a result, the theory received a great deal of respect. Superconductors are difficult to predict, yet here was a case where not only was the superconducting temperature predicted, the material itself and its properties were predicted from first principles. Because of this, I often state that silicon is the best understood superconductor.

So, once again high pressure studies helped promote theory, and the current "standard model" of solids [5] used worldwide for calculating electronic, structural, optical, mechanical, superconducting, and other properties owes its popularity in part to experimentalists like Bill Paul, Manuel Cardona, Gerard Martinez and Peter Yu.

Speaking more generally, there are conceptions or approaches which govern how well we do scientific research. A good, successful social example is the high degree of collaboration between experiment and theory in semiconductor physics. Another more physical example is the use of a probe like pressure to sort out properties of materials. Bill Paul's success is an excellent example of the advantages of experimental-theoretical joint efforts, and his pioneering experimental approaches have carried over into other areas of research. For example, when Paul Chu found that the superconducting oxides were sensitive to pressure, he inserted different size atoms to compress and expand this lattice. This approach of "chemical" pressure sometimes leads to new materials with desirable properties as demonstrated with semiconductor alloys and "band gap engineering". For Chu and Wu, the result was the discovery of YBCO, the first liquid nitrogen superconductor.

So, I hope I have given you some food for thought about what we do, about Bill Paul's influence, and about the importance of collaborations. Recent studies and reports from the United States National Academy of Sciences suggest that particle physicists working on the very small should collaborate with astrophysicists working on the largest objects, including the universe. Particle astrophysics is in fact beginning to thrive. As I mentioned earlier, condensed matter physicists are working dimensionally in the middle, and we don't need encouragement to collaborate. Collaborations with other fields of physics and other fields of science are normal, natural, and are increasing.

I'm also happy that we have healthy collaborations between experiment and theory in CMP. However, I want to note that we theorists in CMP know our place – it's an experimentally dominated field and we are parasites. Benjamin Franklin said, "Something done is better than something said". I always felt that he was mocking theorists with that statement.

I often repeat the statement that "all decisions in physics are made by experiment" and point to experimental discoveries like magnetism, superconductivity, and other phenomena. However, I secretly feel that theoretical progress has been so rapid and so successful that one of us may discover a new state of matter or some new phenomena using a new concept or by varying parameters of interaction on a computer. But until we surprise you and one of "our people" proves that she is right, I would like to offer a toast to all experimentalists and at this time, especially to Bill Paul.

Acknowledgements This work was supported by National Science Foundation Grant No. DMR00-87088 and by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

[1] P. A. M. Dirac, Proc. R. Soc. (Lond.) A **123**, 714 (1929).
[2] M. L. Cohen and J. R. Chelikowsky, Electronic Structure and Optical Properties of Semiconductors, edited by M. Cardona, P. Fulde, K. von Klitzing, and H.-J. Queisser (Springer Verlag, Berlin, 1988).
[3] S. Groves and W. Paul, Phys. Rev. Lett. **11**, 194 (1963).
[4] E. Fermi, Nuovo Cimento **11**, 157 (1934).
[5] M. L. Cohen, Phys. Scr. **T1**, 5 (1982).
[6] K. J. Chang, M. M. Dacorogna, M. L. Cohen, J. M. Mignot, G. Chouteau, and G. Martinez, Phys. Rev. Lett. **54**, 2375 (1985).