MECHANISM OF SHEAR-INDUCED METALLIZATION *)

JOHN J. GILMAN

Department of Materials Science and Engineering,
University of California at Los Angeles, Los Angeles, California, 90024, USA

Received 14 July 1995

It is well-known that volumetric compression converts insulators into metals (the Herzfeld-Mott transition). Not so well-known is the fact that finite shear strains have a similar effect. For example, uniaxial compression of Si and Ge causes them to become metallic. A simple band-structure model for this is presented in this paper. Shear induced metallization has several important consequences, including: mechanically induced phase transformations, other mechanochemistry; the hardnesses of semiconductors and carbides; and ultra-fast reactions at detonation fronts.

1 Introduction

It has been a great pleasure for me to have been asked to contribute to this volume in honor of Frank Kroupa. My only direct contact with him occurred when I was at the University of Illinois. In his adventurous way, he had bought a "bargain" bus ticket (for $99, I think) that was good for unlimited mileage in the USA, and he stopped off in Urbana for a short visit as he made his way across the country. I was impressed with his exceptional intelligence and friendly demeanor. I can only hope that he enjoyed the visit as much as I did.

I want to describe a new phenomenon in the chemistry and physics of solids that I discovered a few years ago. Namely, metallization induced by shear; particularly by the bending of covalent bonds. By metallization I mean closure of the energy gap between bonding and the anti-bonding levels in molecules and solids. In physics this is called the valence-conduction band gap, while chemists call it the LUMO-HOMO gap (LUMO means lowest unoccupied molecular orbital, and HOMO means highest occupied molecular orbital). When the gap closes, the normally localized bonding electrons can access the delocalized anti-bonding states so they become "free" to move from one place to another in a molecule, or a solid.

It should be no surprise that metallization has profound effects on behavior. It greatly facilitates chemical reactions; especially athermal ones. Needless to say, it changes transport properties dramatically. It determines dislocation motion in covalent solids. It enables ultra-fast reactions to occur at detonation fronts. It changes optical properties.

Metallization caused by isotropically increasing the density of an array of atoms has been known for a long time. The effect was originally proposed by Herzfeld in 1927, and was rediscovered by Mott in 1949. It has become known as the Mott transition. As the density of a non-conducting solid is increased (or the concentration of dopant atoms in a semiconductor) the wave-functions of the valence electrons

---

*) Dedicated to Dr. František Kroupa in honour of his 70th birthday.

eventually overlap enough for the electrons to become delocalized, and therefore conductive. In other words, the valence-conduction band-gap closes.

What was not recognized until recently is that shear deformation can also close the gap; and in some cases (at least) strains of smaller magnitude are needed. Perhaps this effect was overlooked because it is difficult to decouple shear strains and dilatations in continua. However, at the level of discrete atoms and/or molecules it is quite apparent whether bond lengths are changing at constant bond angles, or bond angles are changing at constant bond lengths. This requires microscopic information provided by crystallography, it cannot be deduced from macroscopic thermodynamic properties.

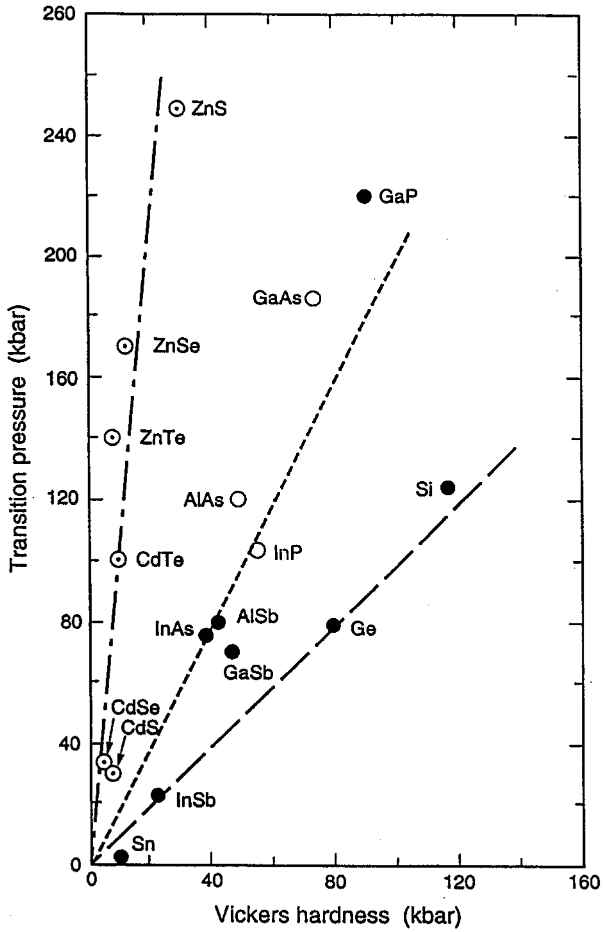

Fig. 1. Correlation between observed critical transformation pressures and Vickers hardness numbers for a variety of tetrahedrally bonded crystals. The initial structures are diamond and zincblende. The final structures are of the β-tin and rocksalt types. Initially the crystals are semiconductors; finally they are metals.

Trefilov and Mil'man [1] had pointed out in 1964 that the indentation hardnesses of Si and Ge at low temperatures (temperatures below their Debye temperatures) seemed to be determined by their transformations from the diamond to the β-tin structure. The most simple evidence is that the hardness numbers are numerically equal to the critical transformation pressures (approximately). Since the β-tin phases are metallic, other evidence is provided by measuring the electrical conductivity under an insulating indenter as it presses into a specimen.

I became interested in whether this phenomenon is general, so I collected hardness data together with critical transformation pressures. Figure 1 shows the results. Good correlations exist between the measured values for some 15 substances. There are three sets. The line of large dashes for homopolar crystals has slope of one reflecting equality of the two kinds of pressure. The line of short dashes has a slope of two, and the data for the III-V compounds follow it. The line of both long and short dashes which is followed by the II-VI compounds has slope of ten. Thus, the greater the ionicity of the bonding, the more the transformation pressure exceeds the hardness number.

Topologically there is no difference between the β-tin and diamoond structures. As pointed out by Musgrave and Pople [2], if the diamond structure is compressed about 50% along its four-fold axis, it becomes the tetragonal β-tin structure (Figure 2). Conversely, if the β-tin structure is stretched along its tetragonal axis by a factor of about two, it becomes the diamond structure. Eight cases from Figure 1 transform from the diamond to the β-tin structure under pressure and become metallic as a result.

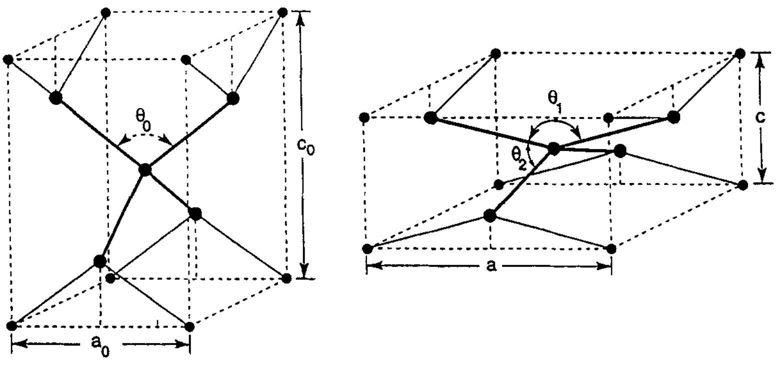

Fig. 2. Transformation from the cubic diamond structure to the tetragonal β-tin structure by compression along the four-fold axis of the diamond structure.

The lack of topological change in the eight cases of interest made me wonder whether the volume changes (about 20%) result from changes in bond lengths, or bond angles, or both. Study of the crystallographic data for the structures before, and after, the transformations showed that the bond lengths changed very little (average = +4.4%), but the bond angles changes markedly (one increases 37%, while the other decreases 14%) [3].

Some texts say that the coordination number in β-tin is six but this is not true because there is a difference of 5.6% between the separations of the nearest neighbor atoms and the next nearest neighbors. Thus, since the bond lengths increase slightly, the atomic overlaps decrease, so they cannot account for the metallization.

It might be argued that the metallization is due to the increase in the average electron density resulting from the volume decrease when the diamond structure transforms tothe β-tin structure. This would not account for the fact that the coordination number remains four after the transformation, suggesting that the valence band remains just filled with electron pairs. Therefore, it is argued here that closure of the minimum gap between the bonding and the anti-bonding levels is the effect that results in metallization. And, this closure is caused by the shear strains (bond bending) associated with the transformation.

2 Shear-induced energy-gap closure

Numerical calculations based on band theory have shown, in the case of diamond, that hydrostatic compression cyuses the energy gap to increase, but compression plus shear causes it to decrease [4,5]. See Figure 3 which is based on a figure given in Reference [4]. Note that the effect of shear plus hydrostatic strain is of much greater magnitude than that of hydrostatic compression. Unfortunately, there are neither measurements nor calculations for pure shear strains. Also the quantitative aspects of Figure 3 are in some doubt because the indicated metallization pressure for the [001] compression is about 290 GPa, but experiments indicate that the gap has not yet closed at 440 GPa [6].

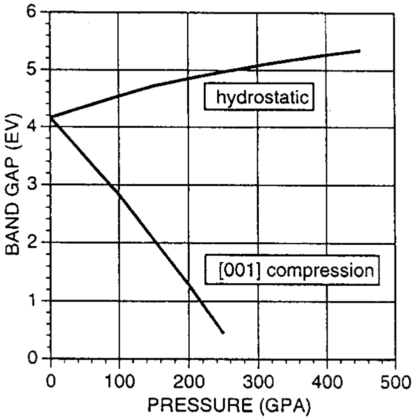

Fig. 3. Calculated band gaps for diamond as a function of applied pressure for the case of zero shear strain (hydrostatic); and for compression along the four fold axis of diamong (combined shear and hydrostatic strains)

My purpose here is to present a simple model that gives some insight to the effect of shear on electronic structure. It is intended to suggest that the effect is general.

It is not intended to yield numbers that can be compared with measurements. The essential feature of the model is that hydrodynamic compression shortens all three principal axes, while shear shortens one axis, and lengthens another one; leaving the third principal axis unchanged. Figure 4 illustrates the idea, assuming: a square two-dimensional lattice; and the nearly free-electron approximation (the argument is similar for the tight-binding (LCAO) approximation).

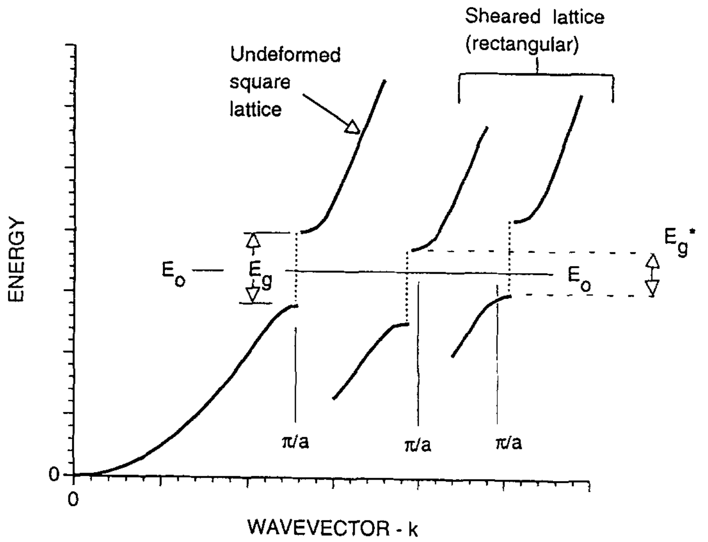

Fig. 4. Schematic diagram of energy vs. wavevector for the states of nearly-free-electrons in a square atomic lattice of spacing a. The undeformed square lattice is shown on the left. Simple shear converts it into a rectangle with axes $= a \pm \delta$ where δ is small but finite. To a first approximation this does not change the gap, but it shifts it on the energy scale thereby decreasing the minimum gap.

A schematic energy vs. wave number sketch is shown in Figure 4. The lattice spacing of the square array is a, so the wave vector at the zone boundary is $2\pi/a$, and the energy of the electronic states is $E = \hbar^2 k^2/2m$, where $2\pi\hbar$ is Planck's constant, m is electron effective mass, and $2\pi k$ is the electron wavelength, λ. On the left, the energy states are shown with an energy gap at $k = \pi/a$. At the mid-point of the gap, the energy level is $E_0 = (h/a)^2/8m$. The gap is given by $E_g = 2|V|$, where V is the periodic potential energy with period, a. The same E vs.k dependence occurs in the two directions perpendicular to the sides of the square lattice. Since a shear deformation is inherently two-dimensional, there is no need for a simple model to be three-dimensional.

Suppose that a hydrostatic strain is applied to the square lattice. Then, in both directions, the atomic spacings, a, will decrease and the E vs. k plot will shift as shown on the far right in Figure 4. The lattice spacings will become $a(1-\epsilon)$, where ϵ is the strain. To a first approximation, E_g will remain the same, but the position of the gap relative to E_0 will increase. The value of k at the zone boundary will become $\pi/a(1-\epsilon)$. Since the shifts of the band-gap mid-points will be the same in the two orthogonal directions of the square lattice, the minimum band gap will be unchanged (first approximation). This is consistent with the relatively small change shown in Figure 3 for diamond.

The case of an applied shear strain is very different. Shear will cause one axis to increase, and the other to decrease. Therefore, the zone boundaries will become: $k = \pi/a(1 \pm \epsilon)$, and the band-gap mid-points shift in opposite directions. Thus the minimum gap becomes, E_g^* as indicated in Figure 4. Note that the effect is relatively large because of the parabolic dependence of E on k. When the strain becomes large enough to close the gap, the bonding electrons can delocalize into the anti-bonding states. In other words the activation energy for the reaction, or transformation, becomes zero, and it can proceed athermally. In intermediate cases, the electronic process may be assisted by phonons.

A similar mechanism is expected to operate on the LUMO-HOMO gaps in symmetric molecules when shear deformation is applied to them.

The strain needed to close the gap can be estimated from inspection of Figure 4. It is approximately $2mE_g a^2/h^2$. Then, if m is electron mass, $E_g = 2\,\mathrm{eV}$, $a = 2.5\,\text{Å}$, and $h = 6.6 \times 10^{-34}\,\mathrm{J\,s}$, the critical strain is about 8%. This is the right order of magnitude within a factor of 2–3.

3 Some consequences

Observations of shear-induced metallization, together with the simple rationale of the phenomenon presented above indicate that shear strains can effect reactivity in solids profoundly. It seems to me that this has not been appreciated in the past. One reason is the historical emphasis on gases and liquids in the study of chemical reactions. A corollary of this has been the emphasis on pressure as a state variable in thermodynamics. Another reason is the focus in mechanical engineering on tensile stresses, and uniaxial strains, both of which entangle shear and dilatation. Studies in which these two modes of deformation are clearly separated are rare.

If one takes the viewpoint that crystals are giant molecules, then the chemists' view that chemical stability is determined by the magnitude of the LUMO-HOMO gap applies (the reader is reminded that metals have little intrinsic stability; they are all passivated by surface films). Thus shear strains induce instability by closing the gaps. It seems likely that they play a key role in the whole field of what has becoome known as mechanochemistry. That is, athermal chemical reactions that can proceed at low temperatures. Low temperatures are those below the Debye temperature in solids; and below the temperaturees needed to excite appropriate vibrational modes in molecules. Also, it has been suggested that shear is the key to understanding ultrafast reactions such as those at supersonic detonation fronts [7]. By closing the electronic gaps, shear gives direct access of the bonding electrons to the antibonding states so they become delocalized, and can rearrange at electronic frequencies, instead of being limited to atomic vibrational frequencies.

Shear strains are also the key to the embedded atomic scale reactions that determine dislocation mobilities in covalent crystals [8], and reactions that occur at the tips of cracks.

Although the details are unknown, bond-bending with the resultant reduction in chemical stability is important in friction, wear, cutting processes, and related phenomena.

Finally, a multitude of biochemical processes are strongly affected by shear strains. A simple demonstration of this can be had by closing an eye and pressing againt it with a forefinger.Through shear strains this induces electronic processes that are manifested by an illusion of light flashes. Shear-induced chemistry is also important in muscular contraction, and many other biochemical phenomena.

References

[1] Trefilov V.I. and Mil'man Yu.V.: Soviet Physics – Doklady *8* (1964) 1240.

[2] Musgrave M.P.J. and Pople J.A.: J. Chem. Phys. Solids *23* (1962) 321.

[3] Gilman J.J.: Philos. Mag. B *67* (1993) 207.

[4] Surh M.P., Louie S.G., and Cohen M.L.: Phys. Rev. B *45* (1992) 8239.

[5] Van Camp P.E., Van Doren V.E., and Devreese J.T.: Solid State Commun. *84* (1992) 731.

[6] Ruoff A.L., H Luo, and Vohra Y.K.: J. Appl. Phys. *69* (1991) 6413.

[7] Gilman J.J.: Chemical Reactions at Detonation Fronts in Solids (to be published in Philos. Mag., 1995).

[8] Gilman J.J.: Science *261* (1993) 1436.