

EXCURSIONS INTO HIGH PRESSURE PHYSICS*

S. RAMASESHAN†

I. INTRODUCTION

Two decades ago little or no work was being done in high pressure science in India. The subject appeared to me replete with possibilities for new discoveries in condensed matter physics and in chemistry as also for applications in the preparation of alloys and for forming them into precise shapes. Consequently, a decision was taken in 1967 to set up a high pressure laboratory for fundamental and applied research at NAL, Bangalore. Experts were invited to help us (particularly Dr A. Jayaraman from the United States who was previously in RRI); physicists and metallurgists were gathered to work in this new and exciting field at this centre. The high pressure equipment, and the associated measuring instruments (including those for metallurgical processing) were designed and fabricated. Mention may be made of the following items of equipment—a piston cylinder device (50 kb, 1000°C), a Bridgman anvil (150 kb, 1500°C), a cubic press (70 kb, 1800°C) and a diamond anvil cell (500 kb, 400°C). Now, after twenty years, it is gratifying to note that this science has spread far and wide, and there are many excellent laboratories dotted all over the country (e.g. Bangalore—NAL, RRI, IISc; Bombay—BARC; Delhi—NPL and University; Hyderabad—NGRI, DMRL; etc).

In this brief discourse I shall recall some of the experimental excursions I made along with my students and collaborators into this field—an experience which proved to be very satisfying.

2. THE EFFECT OF PRESSURE ON THE OPTICAL DISPERSION FREQUENCY

My interest in pressure as a variable was

aroused by the first problem suggested to me by Prof. C. V. Raman in 1943 which was to make precise measurements of the Faraday rotation in diamond. Since most diamond plates exhibit birefringence caused by accidental (?) strain, a method had to be devised for eliminating the effect of birefringence and to extract the true magneto-optic rotation. In this process one also ended up with a technique for measuring birefringence accurately¹.

It is well-known that when an isotropic solid is uniaxially stressed, it exhibits birefringence. Does this photoelastic birefringence arise because the transition probability of the dispersion electron is altered (as was thought at the time) or does it actually change the frequency of the absorption line? Accurate measurement of the dispersion of the stress birefringence with wavelength (using the technique mentioned above) could easily settle the issue as the two effects could give very different dispersions. Measurements in fused silica and glasses² and later in the alkali halides conclusively established that the effect was almost entirely due to the frequency of the absorption line changing. *Uniaxial stress splits the absorption line into two; one component absorbs light polarised parallel to the direction of stress and the other that polarised perpendicular to it*³.

3. STRESS INDUCED OPTICAL ACTIVITY

Optical activity or the rotation of the plane of polarisation was first discovered in single crystals of quartz. Even isotropic atoms or molecules when arranged spatially in a specific manner (say chirally) can cause optical activity. If, however, the molecules themselves are optically active, the crystalline and the molecular optical rotations in a given direction have to be combined in a proper manner to get the net rotation in that direction. How does stress affect optical activity? The gyration tensor and the stress tensor are related

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† Raman Research Institute, Bangalore 560 080, India.

by the "piezo rotatory tensor" which turns out to be an axial tensor of the 4th rank⁴ (a tensor not till then described in crystal physics) and these piezo rotatory coefficients ultimately determine the changes in rotation caused by pressure in various directions.

One also obtained the exciting result that pressure can actually induce optical activity in certain optically inactive crystals⁴. This was to me not an unexpected result since all that pressure really does is to remove the mirror symmetry (in the non-centro symmetric groups). Of the 32 point groups, 21 are non-centro symmetric. Of these, only 15 are optically active. Stress can induce optical activity in the remaining six.

4. PRESSURE INDUCED LIQUID CRYSTALS

Molecules are known to condense to form *liquid crystals* (a state of matter discovered by Lehman) if fairly strong intermolecular forces are present. Molecules could have orientational order, could arrange themselves to form a liquid in two dimensions while it is in effect a solid in the third, or as in the case of the recently discovered discotics⁵ it could form a solid in two dimensions while it remains a liquid in the third. Surface tension and viscosity of these liquid crystals become direction dependent tensorial properties and even melting seems to be direction dependent! How would pressure affect the liquid crystalline state? I noticed from the early publications that, of the many organic molecules belonging to various homologous series, the higher members were often liquid crystalline while the lower ones were not. With pressure, molecules must surely come closer, effectively increasing the intermolecular attraction. It would, therefore, be natural to expect some of the lower homologues to become liquid crystalline when pressure is applied. In liquid crystals pressure could be used to study many thermodynamically significant phenomena like tricritical points, etc. Experiments were conducted at NAL in collaboration with the RRI liquid crystals group, and it was found that pressure did indeed induce liquid crystallinity in the lower homo-

logues⁶. It was gratifying that my simplistic conjecture proved so fruitful and many new pressure induced transitions were soon observed opening up a new avenue of scientific activity.

5. CHARGE TRANSFER COMPLEXES

Hassel's pioneering work showed that when certain liquids were mixed in definite molecular proportions, Charge Transfer (CT) complexes were formed. A change in colour is the earliest indication that such a CT complex is formed. When the atom with high electronegativity in a molecule attracts electrons from an atom in the other, the van der Waals distance decreases and the covalent bond involving the electronegative atom lengthens. Hassel showed the existence of these effects by crystallising these liquids at low temperatures and determining their crystal structures. It occurred to us that these liquids could as well be solidified under pressure in a diamond anvil cell, single crystals grown, and the structure determined. Most of the conclusions of Hassel on his CT complexes were verified, but one could also go much farther. When the electronegativities are not so high, the mixture shows no colour change. However, colour develops as the pressure increases and becomes deeper and deeper with further increase of pressure. As the liquid is compressed, the molecules come closer and the propensity to form complexes increases. Again, single crystals could be grown and the structures confirmed the formation of CT complexes⁷.

Under the microscope in a diamond cell, two liquids immiscible at atmospheric pressures, can be seen mixing at higher pressures. Single crystals of these mixed substances can be grown sometimes and their structures determined. This gives us one more possible technique by which two molecules can be made to crystallise in a single lattice.

This method of growing mixed crystals at high pressures may be another aid to the synthetic organic chemist who uses photo synthetic techniques⁸ to effect reaction between two molecules fixed in a specific geometry in a crystal (also used by the Israeli chemists even to get asymmetric

synthesis). When diamonds transparent to the ultraviolet are used for the anvils, mixed crystals can be grown, their structure determined, photo-synthesis effected between the molecules and the structure of the new substance determined, all in the same anvil set up!

6. CRITICAL POINT PHENOMENON IN SOLIDS

Samarium sulphide is a semiconductor – black in colour and having a NaCl structure. At about 6.5 kb it becomes a metal with the resistance decreasing by five orders of magnitude, the volume decreasing by 15% and a colour change to a metallic solid. In spite of all these drastic changes, it retains its NaCl structure. Much work on this transformation was done by my colleagues at NAL along with Dr A. Jayaraman who was visiting us. Since this transformation is isostructural with no change in symmetry, it occurred to us that it must also show the critical point phenomenon. The critical point for this semiconductor metal isostructural transformation was discovered to be at 825°C and 10.5 kb, the second solid at that time to show this effect⁹.

7. COEFFICIENT OF VISCOSITY

A study of the variation of the viscosity of a liquid with pressure can contribute greatly to the understanding of the liquid state. With pressure, viscosity increases by many orders of magnitude and so its measurement poses many problems. One possibility is to measure the velocity of the shear waves (which according to Raman¹⁰ could exist in these high viscosity liquids) using Brillouin scattering. The other would be to use the well-known Stokes falling sphere method in a diamond cell. By replacing the weak gravitational field by a strong magnetic field and by making the tiny sphere (of radius 5 microns) with a special magnetic material, the range of viscosity measurements can be increased by 10⁸. The diamond cell, however, has to be made of non-magnetic materials which limits the pressure to only 20 to 25 k bars.

8. FRICTION

Another important mechanical property is friction and there are very few measurements of the coefficient of friction at high pressures. A simple but elegant modification of “the angle of friction” method has been devised for the measurement of this coefficient at high pressures in a diamond cell. One surprising result we obtained in preliminary studies was that in some minerals and rock samples the coefficient of friction dropped suddenly, by two or more orders of magnitude, at a particular value of pressure (specific to the sample). One possible explanation is that at these pressures the bound water in the material gets released and lubricates the surfaces of contact, reducing greatly the coefficient of friction. This is a good example of how such simple laboratory studies can prove of immense value in the understanding of the mechanics of many geophysical phenomena such as large rock movements, plate tectonics, etc.

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