

PREFACE

X-Ray Diffraction at Extreme Conditions



The past decade has seen a revolution in our ability to study matter at extreme conditions: transient experiments have been conducted up to the 100 Megabar ($10 \text{ TPa} = 10^8$ atmospheres) range of pressure, and samples can now be examined under sustained, equilibrium conditions of about 5 Megabar and 6000 K in pressure and temperature. Indeed, the diamond-anvil cell makes it possible to study the structures and properties of materials at "multi-Megabar" pressures on a regular, if not absolutely routine, basis.

Why are such extreme pressures of interest? There are at least two answers to this question. First, on a fundamental level, the energy density achieved upon compression to Megabar pressures is of the order of eV, comparable to atomic binding energies. Therefore, pressure can be used to probe the bonds in condensed matter electronic states, interatomic potentials and the nature of bonding can be changed entirely. For example, the archetypal ionic solid, an alkali halide, can be transformed to a semiconductor and even to a metal simply by compression. Second, ultrahigh pressures are used in a variety of applied studies, from creating new materials to simulating the conditions of deep planetary interiors.

The major technical breakthrough in ultrahigh-pressure research has come from the development of the diamond cell over the past few decades. With this instrument, one compresses a tiny sample ($\sim 10 \mu\text{g}$ or less) between the points of two gem-quality diamonds; by using a gasket between the diamond points (e.g., metal foil) it is possible to contain a fluid as a pressure medium around the sample. Diamond makes an ideal anvil for achieving high pressures, not only because it is the hardest material known but also because it is an excellent window for observing the sample *in situ*. Except for two-phonon absorptions at about 0.2 to 0.5 eV and interband electronic transitions from 5.5 eV to about 10 keV, the diamonds are transparent to electromagnetic radiation extending from the far infrared to X-ray and γ -ray energies. And finally, there is the advantage that the high-pressure diamond-window (or diamond-anvil) cell is very small, typically weighing no more than a few kilograms even for the highest-pressure models. Therefore, a sample can be examined by many techniques while at pressure, being transported from a spectrometer in one laboratory to an X-ray source in another, for example.

Powder X-ray diffraction remains the primary technique for obtaining structural information at ultrahigh pressures. Due to the presence of the diamond anvils and the small sample volume, down to the femtoliter range, both electron and neutron diffraction are virtually ruled out. Also, because no pressure-transmitting medium is known that remains fluid above 0.14 Megabar (14 GPa) at room temperature, it is almost impossible to retain a sample as a single crystal into the Megabar range. Nevertheless, with high-intensity X-ray sources becoming routinely used, whether a rotating-anode generator in the laboratory or a synchrotron beam line at a major facility, the range of structural problems that can now be investigated at extreme pressures is truly spectacular.

The pressures that can now be achieved make it possible to examine crystals, liquids and glasses to very high compressions. Recent examples include the compression of alkali halides to less than 50 percent of their initial volumes and hydrogen to 21 percent of its initial volume (it is impressive that X-ray diffraction could be observed through 5 mm of diamond, conventional anvil thicknesses, whereas the sample of H₂ was less than 0.01 mm thick). Through such studies, there is increasing evidence that the pressure-volume relation of a wide variety of solids and liquids can be accurately described by a single functional form. Such a universal form to the equation of state of condensed matter implies a regularity in the bonding forces that is currently not well understood, except to say that it is ultimately based on the Pauli exclusion principle.

Other directions being pursued include the use of Rietveld methods for examining crystalline samples and the determinations of radial distribution functions in amorphous materials under pressure. Indeed there is good evidence from spectroscopic and theoretical studies that melts and glasses can undergo major structural transformations with pressure: analogous to the familiar polymorphic transformations induced by pressure or temperature in crystalline matter, and similarly accompanied by large changes in physical properties.

Finally, there is the fascinating observation that many crystalline materials become amorphous when subjected to high pressures. The crystal → glass transition takes place when the sample is at sufficiently low temperatures that it cannot transform to its equilibrium high-pressure crystal structure; that is, when the crystalline material is brought to extremely metastable conditions under pressure. Unusual glasses can be formed in this way as there is no melting involved, in fact no heating of the sample whatsoever. Perhaps stranger yet, is the observation that upon decompression some of these pressure-induced glasses transform back into the initial crystalline phase. The crystalline order reappears spontaneously out of the amorphous phase.

These few examples illustrate the rapid advances being made in ultrahigh-pressure research. As all materials are condensed at these pressures, atomic packing structure (whether crystalline or amorphous) is one of the single most important properties that needs to be characterized.



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