search & discovery

Soviet and US groups seek hydrogen's metallic phase

A group of Russian experimenters has recently reported (*ZhETF Pis. Red.* **5**, 286, 1972) that they may have produced metallic hydrogen at a pressure of 2.8 megabars; at the transition the density changed from 1.08 to 1.3 g/cm^3. Last year a Livermore group reported on an apparently similar experiment in which they observed a pressure—volume point centered at 2 megabars and 1 cm^3/g. Some people have predicted that metallic hydrogen might be metastable, and others that it would be a room-temperature superconductor.

The Russian experimenters, F. V. Grivorev, S. B. Kormer, O. L. Mikhailova, A. P. Tolochko and V. D. Urlin, work at an unknown Soviet institute, which some believe is defense-related. Although their paper does not give too much experimental detail, it does say that they measured the density of hydrogen by gamma radiography during isentropic compression by a cylindrical charge of high explosive. The explosive accelerates a shell that compresses gaseous hydrogen to high densities and pressures. To measure the diameter of the cavity containing the compressed hydrogen as the shell converges to the axis, Grivorev and his collaborators use a gamma-radiography device with a short exposure time; from the diameter of the cavity they determined the density of the hydrogen. They then varied the initial pressure of the gas and the parameters of the charge to determine the compressibility of hydrogen over densities between 0.45 and 1.95 g/cm^3; values of pressure ranged from 0.4 megabars to 8 megabars.

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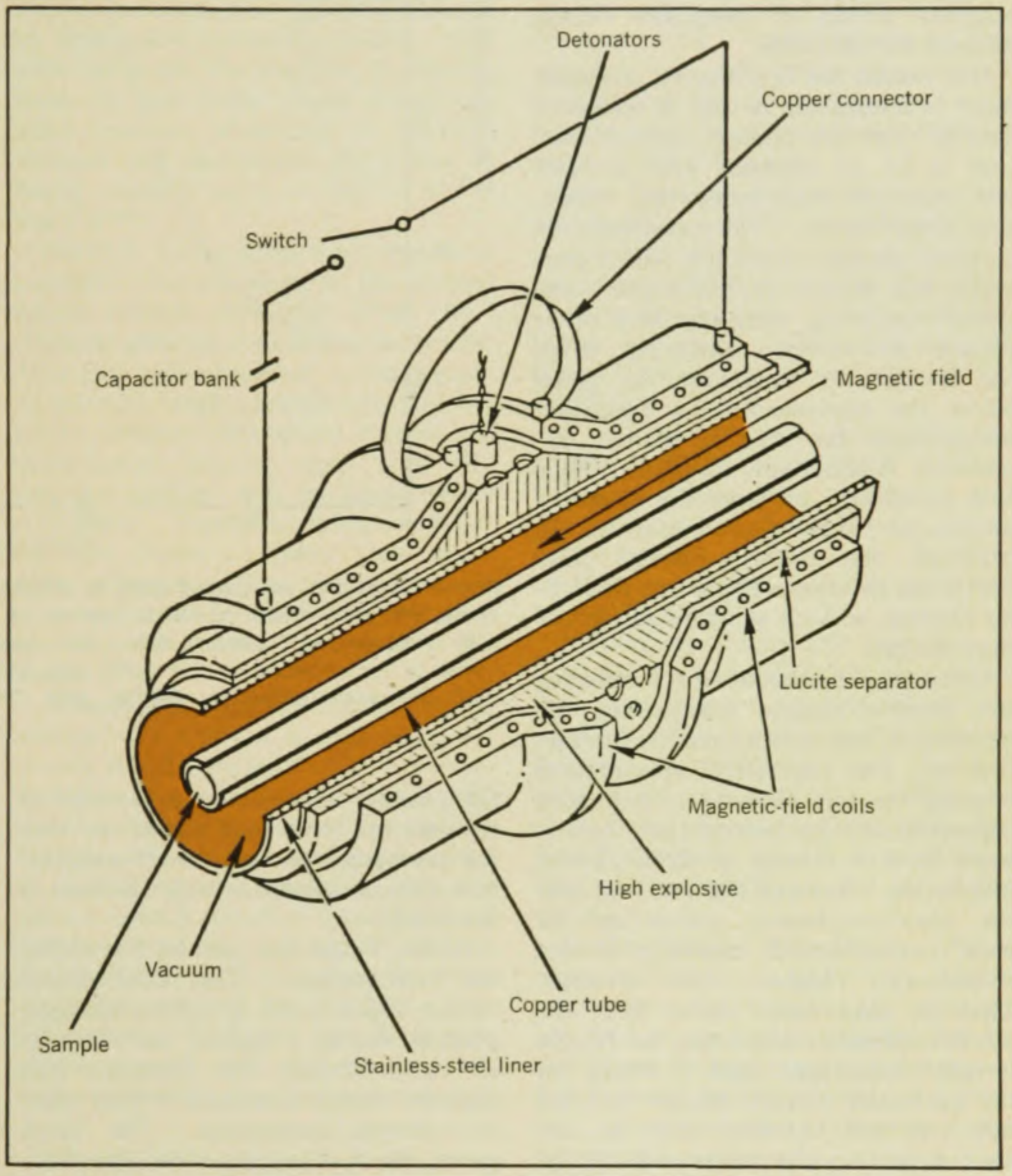


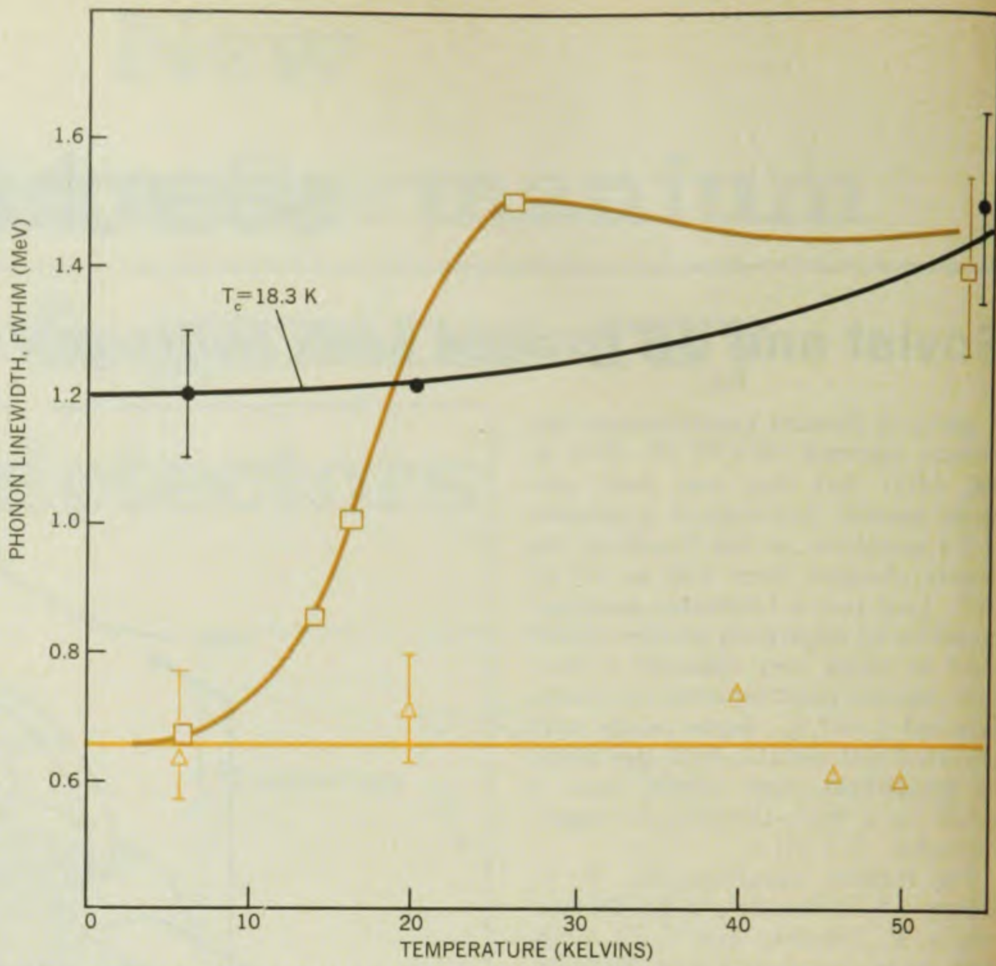
Schematic of Livermore magnetic-compression device. The high explosive is detonated and implodes the stainless-steel liner shortly after a 60-kG magnetic field is applied; the field serves to transfer momentum from the outer cylinder to the inner cylinder. The magnetic-field intensity increases, and a pressure is generated on the hydrogen sample.

Phonon linewidths measured by neutron scattering

Two Brookhaven experimenters, John D. Axe and Gen Shirane, have used inelastic neutron scattering to detect the influence of the superconducting energy gap upon phonon lifetimes in Nb_3Sn. Speaking at the January meeting of the American Physical Society in New York, Axe said their results yield estimates of the superconducting energy gap and the size and anisotropy of the electron-phonon coupling. Axe and Shirane feel that their method of using inelastic neutron scattering will be useful in studying low-lying electron excitations in superconductors.

Many people believe that by increasing the electron-phonon interaction one can achieve better superconductivity properties—higher transition temperatures, higher critical fields and so on. At the same time, however, there is concern that by turning up the electron-phonon interaction the lattice may become unstable under these additional kinds of forces, as has been pointed out by Bernd Matthias (University of California, La Jolla). One way to increase the effectiveness of the electron-phonon interaction is by reducing the average phonon energy. The whole structural class of A15 or β-W compounds, of which Nb_3Sn is a member, tend to have a particular group of phonons, {110} transverse modes with unusually low energies, Axe told us. Some people have speculated that this group of soft phonons leads to enhanced superconductivity. (Soft phonons are those whose frequency is anomalously low.) Nb_3Sn is an extremely important material for superconducting magnets; the material has a transition temperature of 18.3 K; magnets wound of composite ribbon produce 150-kG fields.

One reason the Brookhaven measurement is interesting is that it measures specific electron-phonon interactions, that is for all phonons with energies less than the superconducting transition temperature. The experimenters measure phonon linewidth, which generally has several contributions: impurity scattering, collisions with other phonons and electron scattering. With the Brookhaven technique, by going below the superconducting transition temperature the electron-phonon interaction is selectively nullified. Thus it is possible to measure the electron-phonon part of the phonon lifetime. In principle the electron-phonon linewidth can be measured for any particular phonon, so long as its energy is less than the gap.



Phonon linewidth vs. temperature in Nb_3Sn. Light-colored curve is for a {100} transverse phonon. Black curve is typical of the linewidth of {110} transverse phonons with frequencies greater than the superconducting energy gap. Dark-colored curve is for phonons in the same soft {110} transverse branch but with energy less than the superconducting energy gap; this curve shows dramatic increase at T_C.

Given the technique for measuring the electron-phonon interaction, the question is how anisotropic the interaction is. The theoretical speculations relating the soft phonons to enhanced superconductivity assume that there is some kind of average electron-phonon interaction. Axe and Shirane find that the electron-phonon interaction for these particular soft modes is in fact considerably higher than average. That is, they have shown that the electron-phonon interaction in Nb_3Sn is quite anisotropic and is strong for the particular phonon modes that are soft and will therefore play an enhanced part in the superconductivity, Axe said.

In the experiment a monochromatic beam of neutrons from the Brookhaven High Flux Beam Reactor struck a sample. With a monochromator the scattered neutrons are sorted by energy and then a detector counts them. By scanning the energy of the scattered neutrons as a function of scattering angle, the energy and momentum that the scattered neutron imparts to the sample are deduced. A peak in the spectrum means one is observing a phonon in the solid. Axe and Shirane were limited to studying transverse phonons rather than longitudinal phonons because their triple-axis crystal neutron spectrometer could only focus transverse phonons. They measured the phonon linewidth as a function of temperature and found that at very low temperatures, very small temperature changes caused a large increase in linewidth.

In the figure the phonon linewidths are summarized. The light-colored curve, which is for a {100} transverse phonon, shows a narrow linewidth at all temperatures; this behavior, Axe explains shows a normal (weak) electron-phonon interaction. The black curve, which is typical of the linewidth of {110} transverse phonons with frequencies greater than the superconducting energy gap, is much higher. This shows that the electron-phonon interaction is strong and anisotropic. It does not matter whether the material is superconducting or normal—there are still electron-phonon collisions at any temperature and the curve increases monotonically with temperature. The dark-colored curve, which is for phonons in the same soft {110} transverse branch but with energy less than the superconducting energy gap, shows a dramatic increase around the critical temperature. Then the linewidth decreases to some minimum value at low temperature, which shows the basic effect of turning off the electron-phonon interaction. These phonons do not have sufficient energy to excite quasiparticles up from the ground state.

One difficulty with the experiment was that no one has been able to grow large single crystals of Nb_3Sn. The experimenters used a crystal grown by J. J. Hanak and S S. Berman of RCA, which Axe says is the largest available in the scientific community. But it is only 0.05 cm^3, and for inelastic neutron scattering it is desirable to have at least 1 cm^3 volume. To maximize the energy resolution, the experimenters had to tighten up the collimation. At the same time they had to ensure sufficient signal.

Axe feels their technique will be valuable for studying other superconductors, but only those that are strong coupled, such as niobium. These superconductors have high transition temperatures. The Brookhaven experimenters find their results agree qualitatively with a calculation by V. M. Bobetic (then at the University of Illinois), but because he assumed a weak-coupled superconductor, they have not tried to make a quantitative comparison.

Although the superconducting energy

gap has been measured by other spectroscopic techniques, these methods suffer from surface problems, Axe told us. Both tunneling and infrared spectroscopy measure the energy gap at the metal surface, which may differ from the bulk value, Axe said. He feels that although the Brookhaven measurements are not terribly precise, they are clearly bulk measurements. —GBL

Neutrons probe protein structure

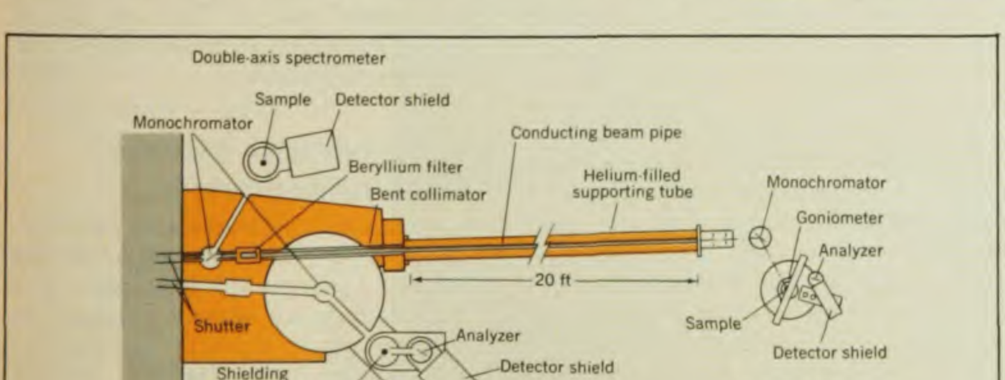
Although x-ray diffraction has for years been valuable in revealing the structure of biological molecules, some kinds of information have remained beyond the reach of x rays. More recently, neutron diffraction has been applied in biophysics,[1] and some experimenters at Brookhaven National Laboratory have successfully used neutrons to map such large complexes as sciatic nerve membrane (myelin)[2] as well as for the location of individual hydrogen positions on smaller, more ordered molecules such as the protein myoglobin.[3] Most of the work has been done at the Brookhaven High Flux Reactor with equipment built by Benno Schoenborn of the BNL biology department.

A major drawback for x rays in biological-structure studies is their inability to locate hydrogen atoms. Hydrogen, which plays a significant role in enzyme action, has a very low x-ray scattering factor. (X-ray form factors increase with atomic number.) Neutron-diffraction studies of hydrogen, on the other hand, exploit the dependence of scattering on nuclear size and on nuclear spin. Because hydrogen and its isotope deuterium have scattering factors that differ in sign as well as in magnitude, isotopic substitution can show clearly where the hydrogen atoms are. Similarly, nitrogen (atomic number $Z = 7$, number of nucleons $A = 14$) is distinguishable from carbon ($Z = 6$, $A = 12$) and from oxygen ($Z = 8$, $A = 16$).

Unlike x rays, the neutrons cause no significant radiation damage, so that a single crystal can be used repeatedly—an important advantage, particularly for large, hard-to-grow crystals. The use of one crystal throughout an experiment also eliminates problems caused by differences between crystals. And with neutrons, the problem of phasing (how do you know which diffraction order you are observing) is resolved through the anomalous dispersion of heavy isotopes such as Gd^{157}, Sm^{149} and Cd^{113}.

Neutron fluxes from even the most powerful sources, such as the Brookhaven reactor, are only about 10^{-5} times as great as available x-ray fluxes. This major disadvantage is compensated for with larger crystals (possible because neutron absorption factors are considerably smaller than x-ray absorption factors) and by longer exposure times. Neutrons, being nonionizing, are harder to detect than are x rays. They must be converted to ionizing radiation by reactions with such nuclei as boron and He^3 and then detected.

Myoglobin. Schoenborn has nearly completed a study of myoglobin, a relatively simple protein that can be crystallized. He is aiming at atomic resolution and regards this work as a prototype experiment to assess the feasibility of studying other proteins. He uses the myoglobin structure found by John Kendrew and his colleagues[4] (nonhydrogen atoms only) as a basis for phase determination and has located a majority of the hydrogen and deuterium atoms present, as well as over 100 water molecules clearly associated with polar surface groups on the myoglobin.



Neutron diffraction in biology. Beam from the Brookhaven High Flux Reactor separates into components for the double-axis and beam-pipe spectrometers. A germanium monochromator selects shorter-wavelength neutrons for relatively high-resolution work, such as the myoglobin studies. The beryllium filter and beam pipe provide neutrons with wavelength greater than 4 Å for molecular-arrangement studies of large complexes.

The myoglobin experiments were done with a single large crystal (4 mm × 3 mm × 2 mm) that had been soaked in deuterated mother liquor; here D_2O replaced much of the H_2O, reducing the incoherent scattering by hydrogen, which is of course present in both spin-up and spin-down states. A germanium-crystal monochromator selected 1.6-Å neutrons from the high-flux beam, and the resulting neutron flux at the sample is about 10^7 per cm^2 per sec. He measured about 10 000 reflections, with a counting time of five minutes per reflection; the average background was about 100 counts per minute and the strongest signal count about 22 000 per minute.

From the data, hydrogen (or deuterium) bonding between the CO (carbonyl and NH (amide) groups of the various amino acids forming the myoglobin can be determined. These hydrogen bonds are largely responsible for the three-dimensional (helical) order of the myoglobin.

A total of 106 water molecules were located, 8 on the "main chain" amides, 30 on the "main-chain" carbonyls and the remainder on side chains. Different myoglobin molecules were found to be linked by nine water bridges and ten salt bridges.

Schoenborn points out that the results should be treated with caution in this first attempt at detailed protein analysis. Errors are probably present because of inaccurate phase determinations or other effects. Once an anomalous phased neutron map has been completed, he will have a better idea of the validity of the myoglobin results.

Large protein complexes. For a neutron-diffraction study of rabbit sciatic nerve membrane, the spacings involved are rather large (about 200 Å), and Donald Caspar (now at Brandeis), Schoenborn, Anthony Nunes and Donald Kirschner used relatively long-wavelength neutrons to achieve high resolution. The aim here is to determine molecular, rather than atomic, arrangement, with resolution about 10 Å.

Soaking the membranes in a D_2O solution substituted deuterium for part of the exchangeable hydrogen. The beam pipe and a beryllium filter remove all but lower-energy ($\lambda > 4$ Å) neutrons. By comparing the neutron and x-ray results, the chemical identity of some x-ray Fourier peaks were determined.

Donald Engelman and Peter Moore (both at Yale), who also do their experiments with the BNL apparatus, have suggested[5] a novel way to determine the gross (quaternary) structure of the protein complexes known as ribosomes;