an Article from **SCIENTIFIC AMERICAN**

APRIL, 1971 VOL. 224, NO. 4

Superconductivity at High Pressure

Experiments designed to measure the effects of compression on the superconducting properties of certain metals may lead to the creation of new, higher-temperature superconductors

by N. B. Brandt and N. I. Ginzburg

The discovery of superconductivity by Heike Kamerlingh Onnes 60 years ago gave birth to hopes that this phenomenon—the abrupt disappearance of all resistance to electric current in certain metals at very low temperature—might eventually be put to many practical uses involving the transmission of electricity. Unfortunately, although a great number of materials have been tried, superconductivity still is observed only at temperatures not very far from absolute zero, or zero degrees Kelvin. Twenty-four elements in the periodic table have been found to be superconductive, but the highest temperature at which any of them passes into that state is 9.3 degrees K.; this is the transition temperature for niobium. Alloys with a somewhat higher critical temperature have been synthesized, and the record-holder is an alloy of niobium with aluminum and germanium that becomes a superconductor at about 21 degrees K. So far efforts to produce materials with a still higher transition temperature by alloying superconductors with one another and doping them with impurities have not been successful. Another line of investigation has now been opened, however, by recent results achieved with the application of high pressure.

The high-pressure studies throw light on the theory of superconductivity as well as on the possibilities for the creation of new superconductors. The theory, proposed in 1957 by John Bardeen, Leon N. Cooper and J. Robert Schrieffer and now known as the BCS theory, has led to models that relate the experimentally measured parameters of metals in the superconducting state to their characteristics in the normal state. By observing how high pressure changes the parameters of the crystal lattice in the normal state and in the superconducting state, and comparing the measurements with the predictions of the theoretical formula, one can now test the validity of some theoretical models. The comparison of experimental results with theory also promises to clarify the mechanism by which a change in the lattice parameters brings about a change in a metal's superconducting properties. In addition, the measurement of the characteristics of a superconducting metal under high pressure gives us an insight into certain basic properties of the metal, such as the energy spectra of its electrons and its phonons (the quanta of the thermal vibrations of the crystal lattice). In some cases the relevant data under high pressure are considerably easier to obtain in the superconducting state than they are in the normal state of the metal.

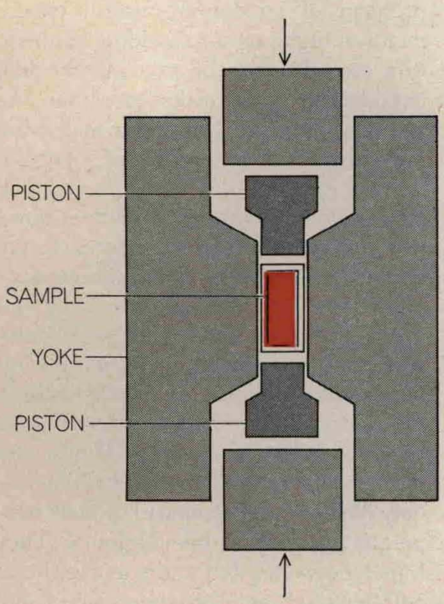
The experiments with high pressure give us hope that, just as the application of pressure made possible the production of artificial diamonds and other superhard substances, so it will become a useful means of synthesizing new superconductors, some of which will be superconducting at temperatures well above the present region and may possess unusual properties. It seems possible that some materials may be designed to be superconducting by a mechanism different from the one due to electron-phonon interaction that characterizes present superconductors.

It is already known that in the case of some transition metals (elements with an unfilled inner shell of electrons) and some of their alloys the critical temperature at which they become superconducting is raised when pressure is applied, whereas for superconductors in the nontransition category the application of pressure lowers the critical temperature. What is the mechanism that inhibits superconductivity in the latter case? Can high pressure alone completely suppress this property in nontransition metals? How does the application of pressure enable transition metals to become superconducting at elevated temperatures? What is the upper limit to the range of temperatures at which any substance could be superconductive? For several years we have been investigating these questions in our laboratory in the department of low-temperature physics at Moscow State University.

Kamerlingh Onnes and his co-workers G. Sizoo and W. J. de Haas at the University of Leiden attempted to investigate the behavior of superconductors under pressure as early as 1925. The problem of conducting useful experiments at high pressure and low temperature turned out to be exceedingly difficult, however. In order to obtain answers to interesting questions such as we have just listed, the sample of superconducting material must be examined over a range of temperatures sometimes down to a few hundredths of a degree K. under very high pressure, and the pressure must be reasonably uniform throughout the sample. Uniform application of pressure can be obtained only by using a liquid or some other highly plastic medium to transmit the pressure from a press to the sample. Kamerlingh Onnes and his associates used liquefied helium—the only element that remains liquid at temperatures as low as one degree K. They found, however, that under a pressure of 140 bars (about 138 times the atmospheric pressure at sea level) helium froze solid at 4.2 degrees K., and at lower temperatures it was converted to the solid state by even smaller pressures. Consequently studies of superconductors placed under very high pressure at ultralow temperatures were out of the question. Subsequent attempts to solve this problem with similar head-on attacks met with little success. It took 40 years and new ideas to develop an effective technique for the extensive investigation of superconductivity under high pressure.

The basis of the new approach was the stratagem of applying the pressure before the sample is cooled to the superconducting state instead of afterward. In the initial stage, usually at room temperature, water or some other substance that is liquid or highly plastic at ordinary temperatures can serve as the medium for transmitting pressure to the sample in a press; thus the pressure can be applied with a high degree of uniformity to the entire sample. The compression is then "frozen in" as the system is cooled to the temperature of the experiment. Assuming that the sample and the medium are both isotropic (that their properties do not change with direction), we can expect the pressure in the sample to remain homogeneous throughout, although the magnitude of the pressure may have been changed by the system's thermal contraction.

The first investigators to employ this idea in low-temperature studies were B. G. Lazarev and L. S. Kan of the Ukrainian Physical-Technical Institute. In 1944 they built a pressure-producing apparatus based on the fact that water increases in volume on freezing. With this device, called the "ice bomb" apparatus, they were able to produce pressures of about two kilobars in a chamber of constant volume at liquid-helium temperatures. In 1955 N. E. Alekseevskii and Y. P. Gaydukov applied the ice-bomb method to investigate the superconducting properties of cadmium under a pressure of about 1.6 kilobars at ultralow temperatures. By the end of the 1950's a number of investigators in various countries were using prepressurizing devices to explore the superconductivity of certain metals under pressures as high as 10 kilobars at liquid-helium temperatures and 1.6 kilobars at temperatures below one degree K.



CLASSIC PISTON METHOD of subjecting experimental samples to high pressures was devised originally by P. W. Bridgman of Harvard University. This basic design was adapted by the authors and their colleagues at Moscow State University in the construction of their experimental equipment.

We began our own studies at that time, with a resolve to obtain higher effective pressures and investigate superconductors over a wide range of temperatures. We set out to find a method of compression that would generate very high and homogeneous pressures and would operate automatically without the use of an external compressor.

We found that the simplest and most convenient form of device for this purpose was the classic piston method of P. W. Bridgman of Harvard University, who was the father of modern high-pressure studies of solids. In the Bridgman device the sample is placed within a rigid yoke and is compressed between two pistons [*see illustration at left*]. If we were to obtain a uniform distribution of pressure throughout our samples, we obviously had to overcome the distorting effect of the friction between the sample and the sides of the chamber. Bridgman had found that the coefficient of friction between metals there was about .1. From this we could calculate that in a cylindrical chamber with a radius of two millimeters the pressure within the sample at a distance of four millimeters from the piston would be 35 percent lower than the pressure at the piston's surface. We therefore had to find a lubricant that would sharply reduce the friction coefficient. We decided to try graphite. This was rubbed on thin cigarette paper until graphite particles filled all the pores in the paper, and the sheet was then wrapped tightly around the sample, forming a graphite layer only 50 microns thick between the sample and the walls of the pressure chamber.

The result was an astonishing reduction of the friction coefficient to the very low figure of .004, which meant that the difference between the pressure at the surface and the pressure at the four-millimeter depth in a sample in a chamber such as we have described would be only 2 percent! We had been lucky in our choice of a lubricating material. Other lubricants that we tested later (cadmium sulfide, silver chloride, Teflon and others) were not nearly so efficient, and it turned out that among the various forms of graphite we might have tried we had accidentally hit on the one with the best properties for our purpose. Had it not been for this fortunate choice, we might have attempted to proceed with our compression-chamber project in an entirely different way.

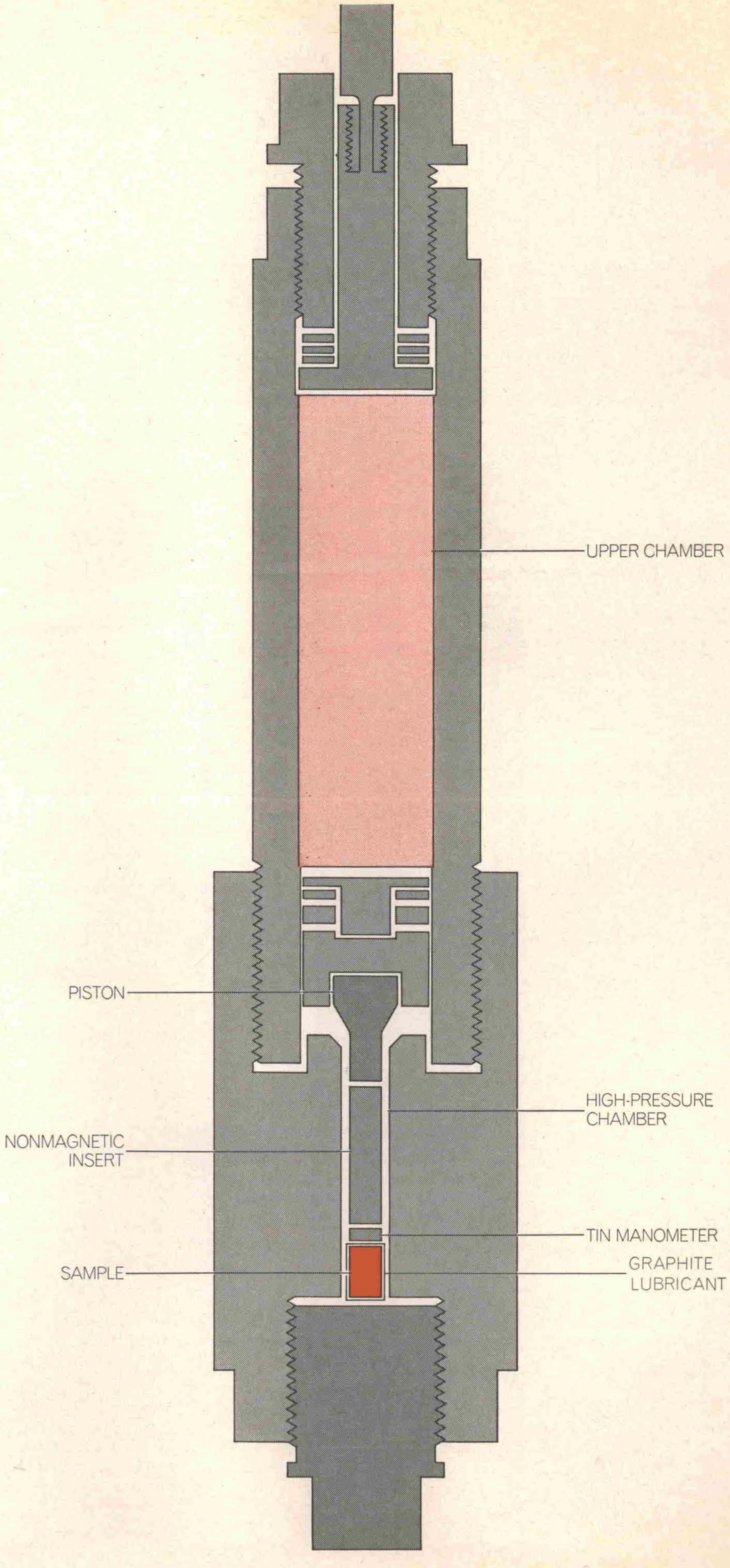
We went on to devise a pressure booster consisting of two chambers [*see illustration on opposite page*]. The upper chamber was filled with water or an aqueous solution of ethyl alcohol. As the apparatus was cooled the liquid froze, expanded and thrust against a piston at the bottom of the chamber with a pressure amounting to about two kilobars. The piston conveyed the pressure to the sample in a smaller chamber below. Because of the cross-sectional difference between the large chamber and the small one holding the sample, the pressure on the sample was increased by a multiplication factor depending on the ratio of the squares of the diameters of the two chambers. The optimum multiplication factor for our booster was about 17. We found that the maximum pressure on the sample was approximately 30 kilobars each time we froze the system. The pressure in the small chamber could be decreased by increasing the percentage of ethyl alcohol in the upper chamber.

In order to carry out measurements in the presence of a magnetic field, we used a nonmagnetic metal, heat-treated beryllium bronze, for the structure. For the piston we needed a stronger material, capable of withstanding a pressure of 30 kilobars or more; our choice was a hard alloy of tungsten carbide and 3 percent cobalt. This material is weakly ferromagnetic, so that we shielded the sample from its magnetic field by interposing a nonmagnetic bar between the piston and the sample.

For observation and measurement of events in the compression chamber and the sample a sensing system based on electrical inductance was devised. A thin disk of tin placed next to the sample served as a manometer for measuring the pressure in the chamber; the magnitude of the pressure was indicated by the amount of shift of the disk's transition temperature from the usual point of transition to superconductivity when tin is not under compression. This information and measures of changes in the sample itself were obtained by means of a system of coils arranged around the apparatus. The transitions of the sample and of the manometer into the superconducting state induced a current in the coils that could be recorded. Among other things, the system gave us a measure of the degree of homogeneity of the pressure within the sample. As the sample was scanned over a range of temperatures, a spread-out or smeared signal would mean that various regions in the sample were making the transition into the superconducting state at differing temperatures because they were under differing pressures; on the other hand, a sharp transition of the sample at or around a particular temperature would signify a high degree of pressure homogeneity. We found in our experiments that in fact the inhomogeneity generally did not amount to more than ±2 percent.

A modification of the device made it possible to carry out measurements of superconductivity at ultralow temperatures down to a few hundredths of a degree K. [*see illustration on next page*]. In this instrument we were able to cool samples by means of the adiabatic demagnetization of a paramagnetic salt (such as iron-ammonia alum) and study them under pressures of the order of 30 kilobars. Over a period of from eight to 10 hours the temperature rise in the pressure booster was so slight (from .06 to .6 degree K.) that measurements could be obtained at a practically constant temperature.

The excellent performance of the graphite lubricant prompted us to build another apparatus, designed to apply pressure to superconductors after they reached very low temperatures [*see top illustration on page* 87]. Based on a low-temperature press constructed in Alekseevskii's laboratory, this apparatus consists of two pistons, made of a hard alloy, that compress the sample in a narrow yoke of nonmagnetic material. The

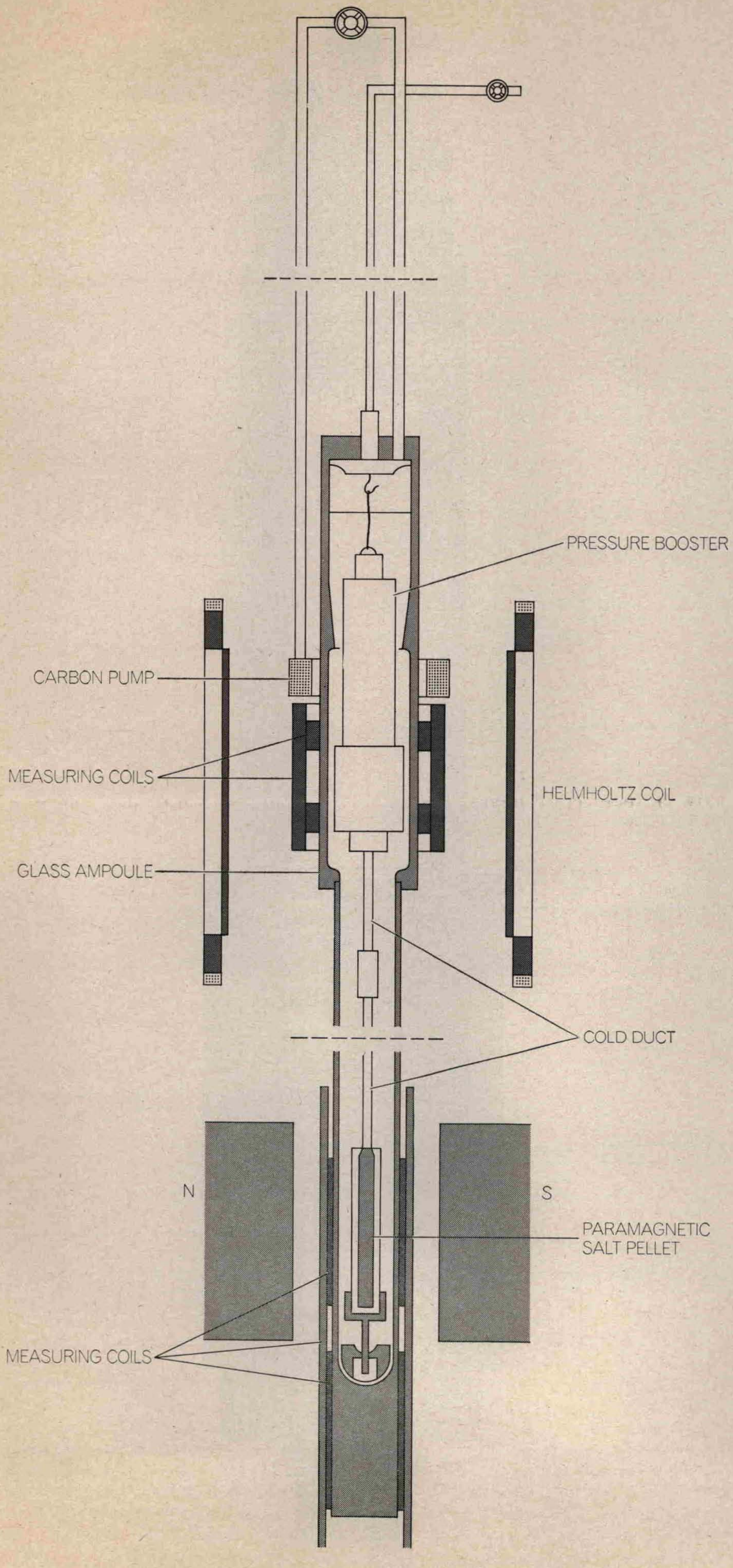


PRESSURE BOOSTER used by the authors in their early experiments on the effects of high pressure on superconductors consisted of two pressure chambers. The upper chamber was filled with water or an aqueous solution of ethyl alcohol. As the apparatus was cooled the liquid froze, expanded and thrust against a movable piston, which conveyed the pressure to the sample in the smaller chamber below. The pressure on the sample was increased by a multiplication factor depending on the ratio of the squares of the diameters of the two chambers.

pressure is controlled by turning a handle at the top, which produces a force that is concentrated by two successive worm gears and applied to driving a piston downward. The press can generate a pressure amounting to as much as three tons. This is not distributed in the sample as homogeneously as in the prepressurizing system, but it does enable an experimenter to vary the applied pressure (down to zero) on samples at very low temperatures. We were able to use pressures of up to 30 kilobars on samples at temperatures in the liquid-helium range.

Thus by 1962 we were equipped with appropriate instruments for probing the mysteries of superconductivity. In early experiments we found that high pressure could produce a considerable change in the transition temperature of cadmium, and this whetted our interest in the general question of the possible effects of pressure on superconductors. We soon found that high pressure could raise or lower the transition temperatures for a number of superconductive metals and their alloys. Among other things, two superconducting modifications of the element bismuth (Bi II and Bi III) were produced by compression of the metal's crystal structure.

In 1966 Jörg Wittig, a West German physicist, built an apparatus that more than tripled the pressure available for studying superconductors at low temperatures [*see illustrations on page 88*]. His principal innovation was the design of the pressure chamber. Its encircling wall is a ring made of pyrophyllite (an aluminum silicate), and the sample, in the form of a thin strip, is sandwiched between disks of the stony talc known as steatite. The behavior of the sample un-



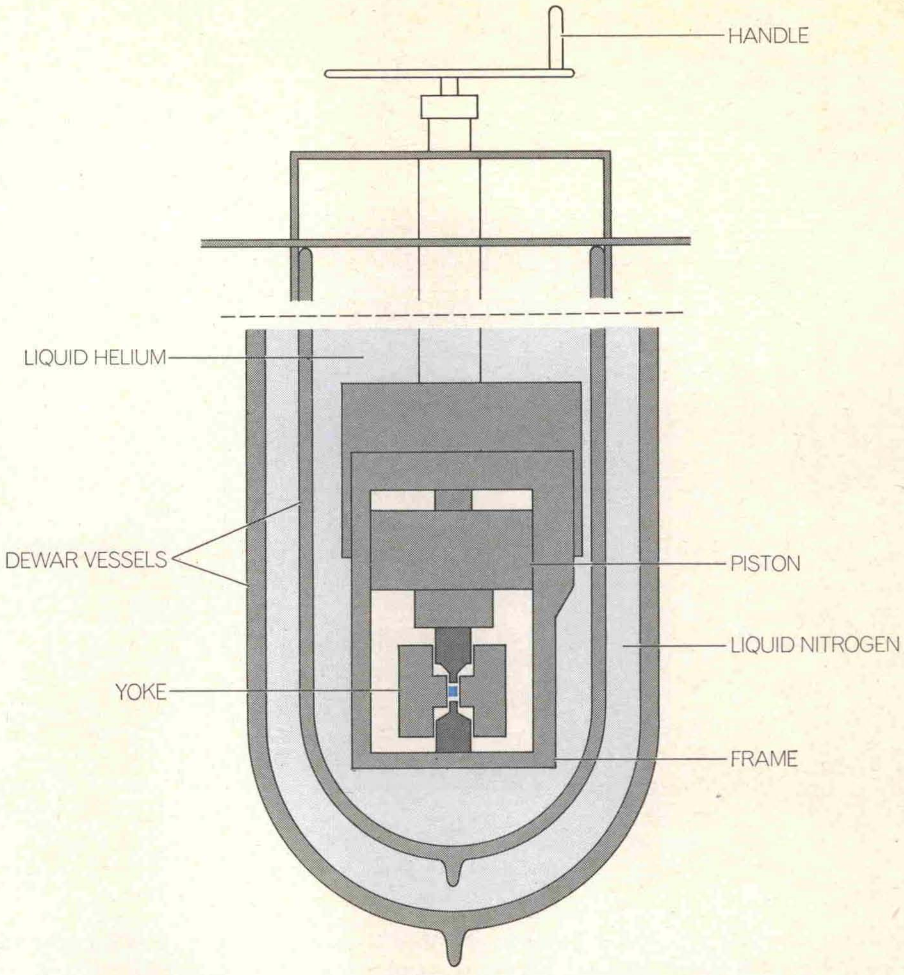
MODIFICATION of pressure booster made it possible to carry out measurements of superconductivity in compressed samples at ultralow temperatures. The pressure booster is connected by a long cold duct with a pellet of paramagnetic salt, which is suspended inside a glass ampoule that is evacuated with the aid of a carbon pump. Ultralow temperatures are achieved in the sample by means of the adiabatic demagnetization of the salt. The upper system of measuring coils detects the transitions of the sample from the normal state to the superconducting state and vice versa. The lower system of measuring coils measures the magnetic susceptibility of the salt in order to determine the temperature. The Helmholtz coils generate a strong magnetic field, which destroys the superconductivity of the sample.

der pressure is signaled by way of electrodes inserted in the chamber through slits. Pressure is applied by a hydraulic press capable of imposing a force of up to seven tons. The sample is compressed at room temperature and the entire system is then cooled in a cryostat. Wittig's apparatus was found to provide a means of studying materials under a pressure of about 160 kilobars at liquid-helium temperatures. Its use led immediately to the discovery of superconductivity in modifications of silicon, germanium, antimony, tellurium and selenium that are stable under high pressure.

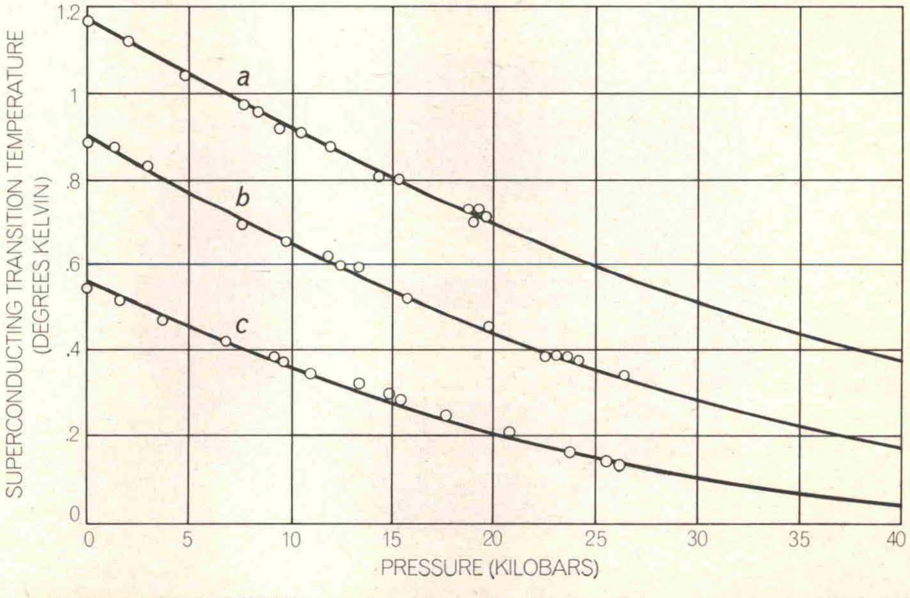
We felt that 160 kilobars was by no means the limit of what could be achieved, and we set out to find means of investigating superconductivity at higher pressures and at ultralow temperatures below one degree K. A graduate student in our department, I. V. Berman, joined us in the work we shall now describe.

Analyzing the Wittig apparatus, we concluded that the pressure in such a design could not be raised because of the uneven distribution of the pressure over the surfaces of the compressing anvils. The pressure was two and a half times greater at the center of the chamber than the mean pressure. As a result of the greater deformation of the anvils' center a concave meniscus was formed there, and this inevitably led to a breakup of the anvils or destruction of the electrodes by the slightly deformed peripheral ring [*see top illustration on page 90*]. We therefore set about redesigning the chamber to minimize the pressure "multiplication" coefficient at the center of the anvils and adopted more rigid materials for its construction.

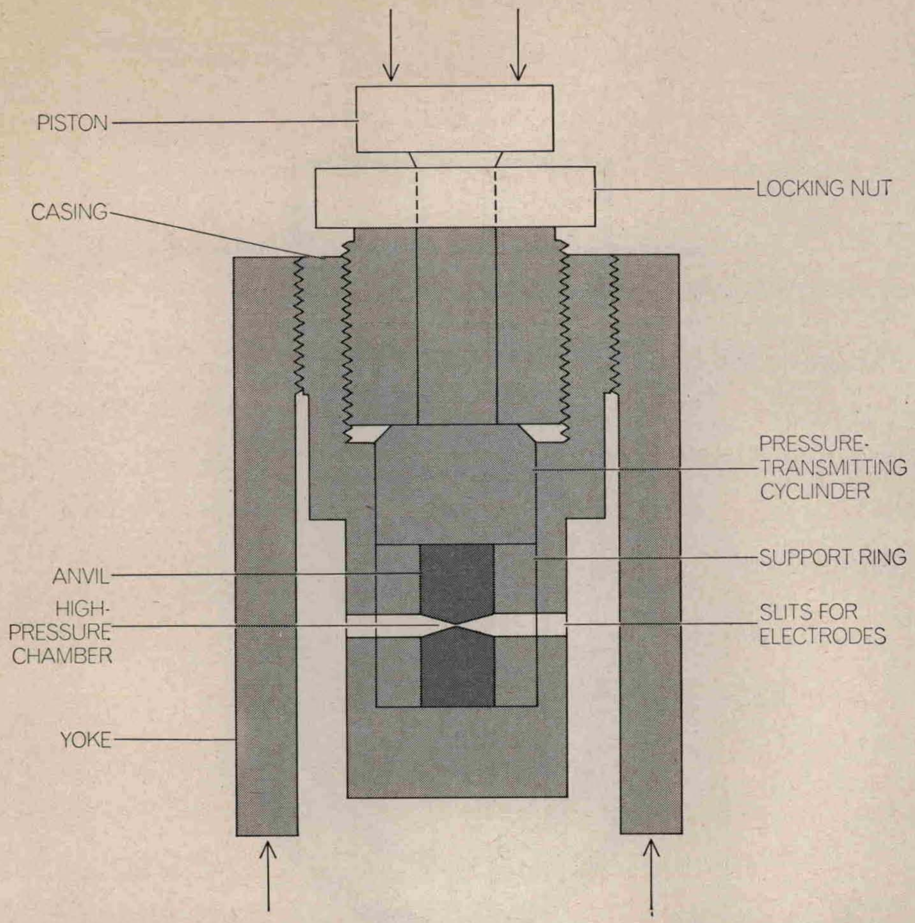
The chamber we eventually devised is smaller than Wittig's, having an inside diameter of half a millimeter, and it can withstand pressures much greater than 160 kilobars. It has two retaining rings instead of one; these are made of a mixture of ferric oxide and steatite that has been pressed into a rigid structure from finely divided powder. Thin disks of ferric oxide enclose the chamber at top and bottom; the sample is placed between two steatite washers also pressed out of powder; four thin strips of platinum serve as the electrodes, and the anvils that apply the pressure are made of a hard alloy [*see bottom illustration on page 90*]. To power the system we use a pressure booster of the ice-bomb type with which we started our high-pressure investigations, because it provides automatic controls and makes possible experiments at ultralow temperatures.



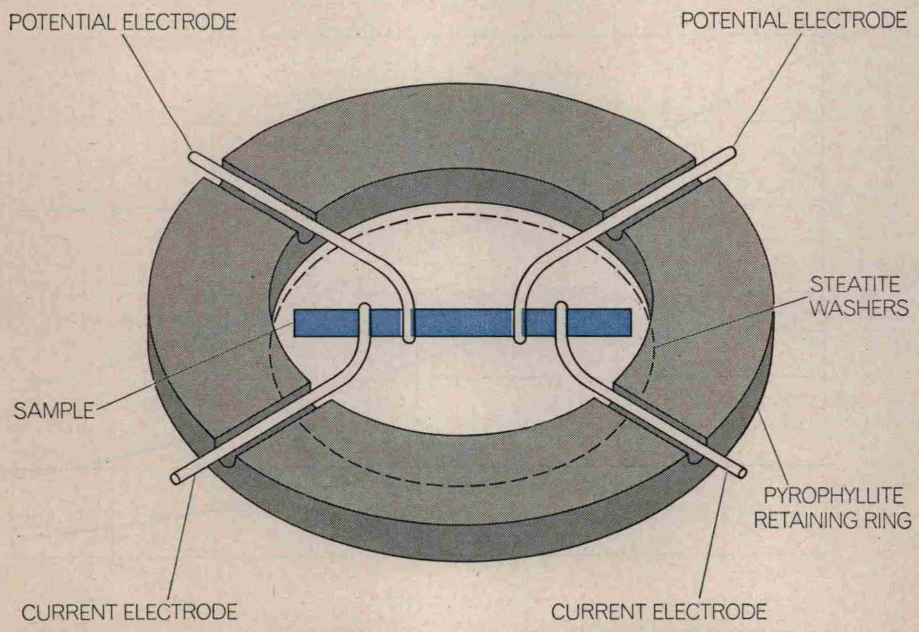
LOW-TEMPERATURE PRESS constructed by the authors in collaboration with N. E. Alekseevskii consists of a nonmagnetic yoke in which the superconducting sample, surrounded by a layer of graphite lubricant, is compressed between two pistons made of a hard alloy. The pressure is produced by the displacement of the top piston within a rigid frame by means of a reduction mechanism consisting of two worm gears. The pressure is controlled by means of a hand crank on top of the double-walled nitrogen-helium Dewar vessel.



INFLUENCE OF PRESSURE on the superconducting transition temperatures of three metals is indicated in this graph. Curve *a* summarizes the experimental data for aluminum, obtained by the Swiss investigators M. Levy and Jorgen L. Olsen in 1964; curves *b* and *c*, for cadmium and zinc respectively, were obtained by the authors in 1963 and 1966. These early findings stimulated later work on the effects of high pressure on superconductors.



IMPROVED APPARATUS invented by the West German physicist Jörg Wittig in 1966 made it possible to subject superconducting samples to pressures as high as 160 kilobars at liquid-helium temperatures. Pressure is applied to the sample at room temperature by means of an external hydraulic press capable of imposing a force of up to seven tons. After compression the pressure is maintained in the chamber by a locking nut and the entire system is then placed in a cryostat and cooled. This method of conserving the pressure with cooling was originally used by the British physicists P. F. Chester and J. O. Jones in 1953.



DESIGN OF PRESSURE CHAMBER was Wittig's main technical innovation. The sample, in the form of a thin strip, is encircled by a retaining ring of pyrophyllite (an aluminum silicate) and is sandwiched between disks of steatite. The sample's behavior under pressure is detected by electrodes inserted into the chamber through slits in the retaining ring.

Many difficulties had to be overcome to set up this facility, but when it was finally put in operation in 1968, it proved to be capable of applying controlled pressures of up to 300 kilobars and giving reliable information on characteristics of superconductors down to the region of hundredths of a degree K. In early tests of the apparatus we discovered several modifications of the nonmetallic elements phosphorus and arsenic that displayed superconductivity.

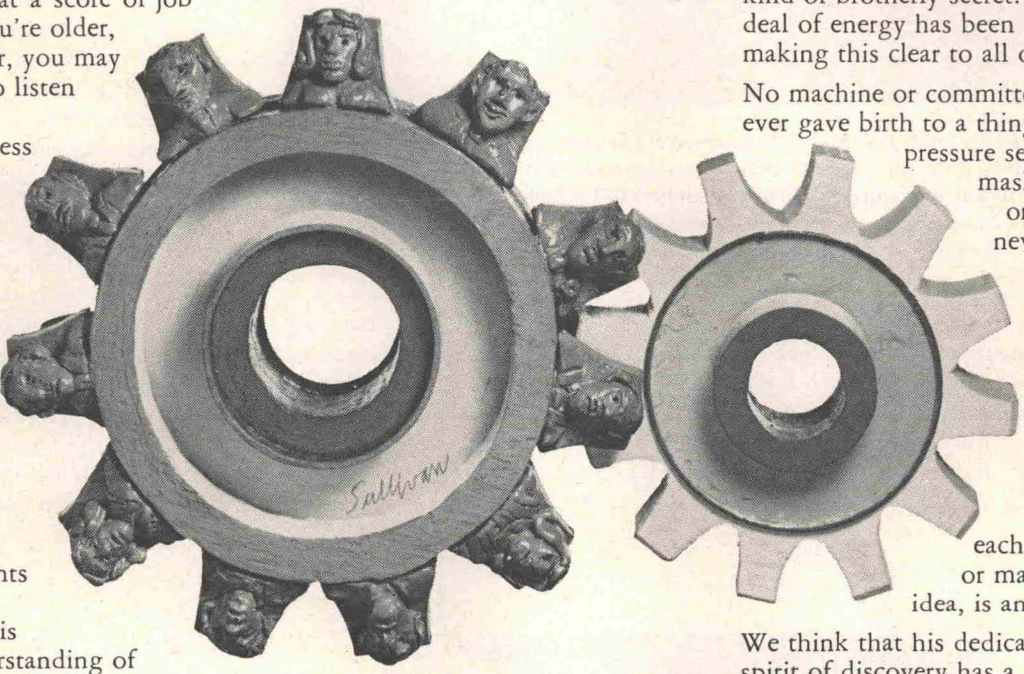
It is now possible to study some of the basic properties of superconductors at high pressures and to develop a hypothesis about the mechanisms involved in superconductivity.

One starts with the premise that the necessary condition for superconductivity is the overcoming of the Coulomb force of repulsion between electrons by a force of attraction. According to the BCS theory, this neutralizing force results from interactions of electrons and phonons that pair together electrons of opposite momentum and spin. The pairs are in energy states at the Fermi level, or Fermi surface: the energy level in a metal at the top of all the levels filled with electrons. In the model for metals that pictures the outer electrons as a gas of free particles, the Fermi surface is diagrammed as a sphere. The BCS theory holds that the density of electron states at the Fermi level, taken per unit volume, is a key factor in determining the critical temperature for the appearance of superconductivity.

Now, it turns out that the density of electron states at the Fermi surface is subject to change by pressure. The density's dependence on pressure can be calculated from measurements of the effects of pressure on the joint influence of temperature and a magnetic field on superconductivity. The superconducting state is destroyed above a certain critical magnetic-field strength just as it is above a critical temperature, and the two influences are related, so that, as the temperature is reduced, the field strength required to destroy superconductivity is increased. By measuring the effects of pressure on the critical temperature and critical magnetic field over a wide range of temperatures down to much below one degree K., we obtained data that made it possible to determine how pressure affects the density of electron states at the Fermi surface.

On the basis of the free-electron model one might expect that compression, by reducing the volume of the crystal of a metal, should slightly increase the den-

At some companies, the assembly line isn't the only place you find interchangeable parts.



Be wary of the organization whose executive lapses too quickly into the "we're-all-little-cogs-in-the-great-big-wheel, we're-all-just-members-of-the-team" brand of thinking.

You've met the guy. If you're young and unlucky, you may have confronted him at a score of job interviews. If you're older, wiser and luckier, you may only have had to listen to him at an infrequent business lunch (where at least he could do you no permanent damage).

At best, he is a bore talking to hear himself talk. More frightening is the possibility that he believes in what he says and represents accurately the shallowness of his company's understanding of the value of *individualism.*

What's wrong with a wheel full of little cogs?

Nothing, as long as you are talking about tractors, not people. But people are not stamped out of stainless-steel, neatly interchangeable with other pieces of stainless-steel.

People think. They grow. They make mistakes and learn. They have ideas. They offer opinions. They share knowledge. They enthuse. They lead. In short, they act like *individuals.*

Would the Minnesota Vikings knock "teamwork"?

Yes. If it meant to them a blind and desperate game of follow-the-leader, as it does to so many institutions.

We think that "teamwork", even narrowly defined, leaves room for exceptional contribution on the part of exceptional members of the team without diminishing the success of the whole. We'll bet that the Vikings agree with us.

There's a catch to it.

People need the right climate. They simply will not act like individuals unless you treat them like individuals. Mostly, they won't offer opinions unless you make it clear that you are seeking opinions. They certainly aren't going to risk the possibility of making mistakes unless they know that you believe a few mistakes on the way to greatness are inevitable.

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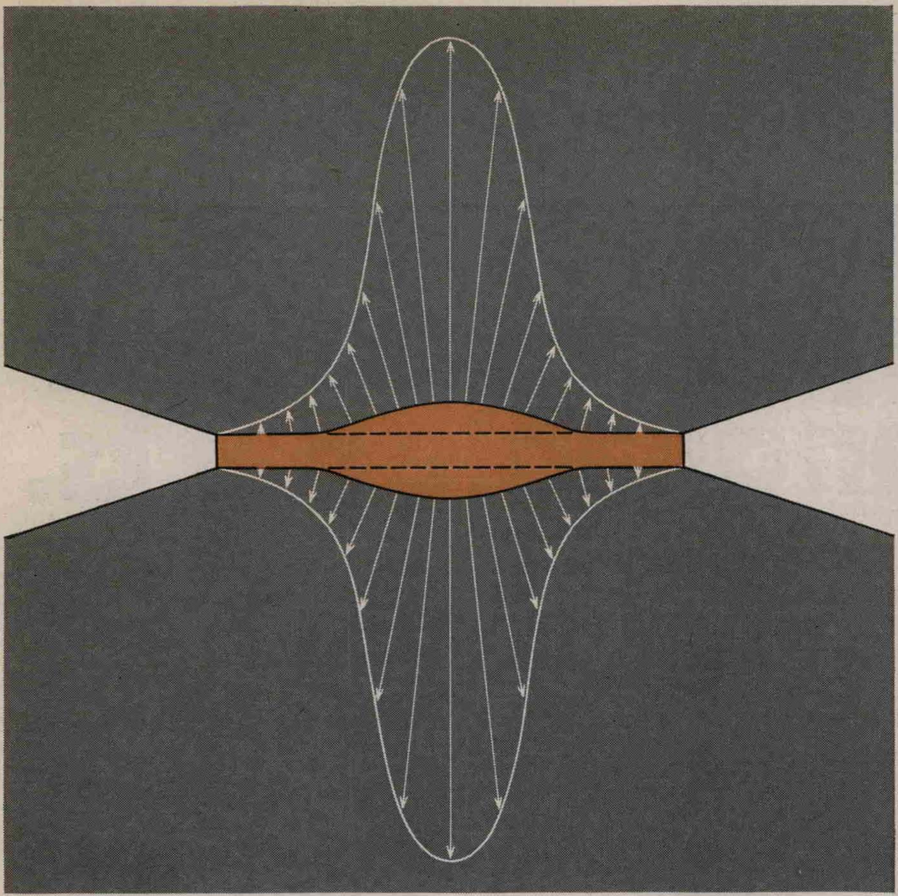
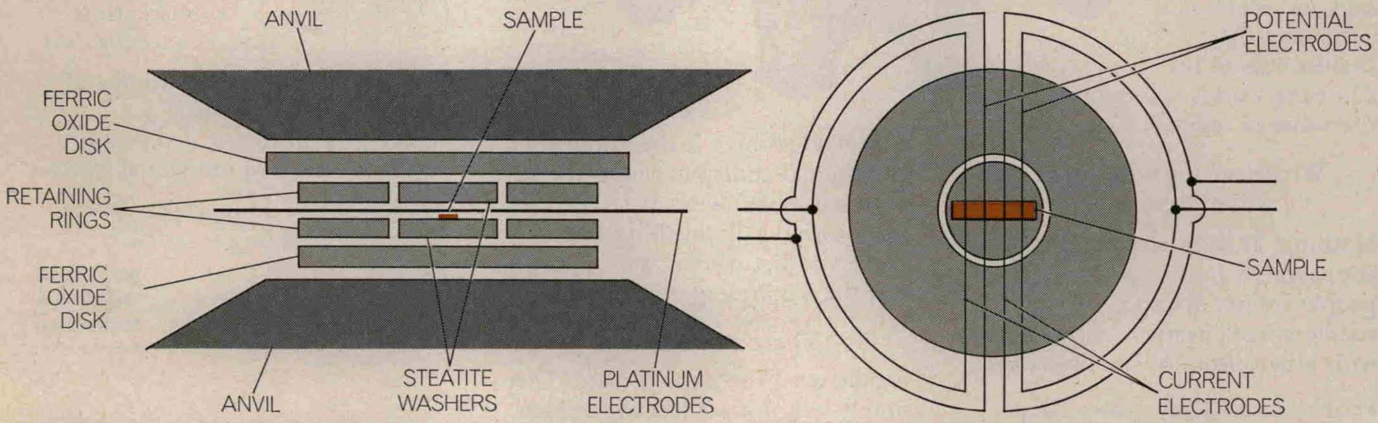


UNEVEN DISTRIBUTION OF PRESSURE *(arrows)* **over the surfaces of the compressing anvils in the Wittig press set an upper limit to the pressure that could be obtained with the device. As a result of the greater pressure at the anvil's center the metal there is deformed into the shape of a concave meniscus; this deformation leads to the breakup of the anvils or the destruction of the electrodes by the slightly deformed peripheral ring.**

sity of electron states. In actuality, however, measurements of the coefficient of thermal expansion of nontransition metals in the normal state had already indicated that the density of electron states decreases under pressure instead of increasing. Our measurements now not only confirmed this finding but also showed that the decrease was greater than had been thought. In examinations of cadmium, zinc, aluminum, tin and indium it was found that compression produced substantial decreases in the electron-state density at the Fermi surface, and the magnitude of these decreases provided a convincing explanation of the fact that in nontransition metals (those with filled electron shells) the critical temperature for superconductivity is lowered by pressure.

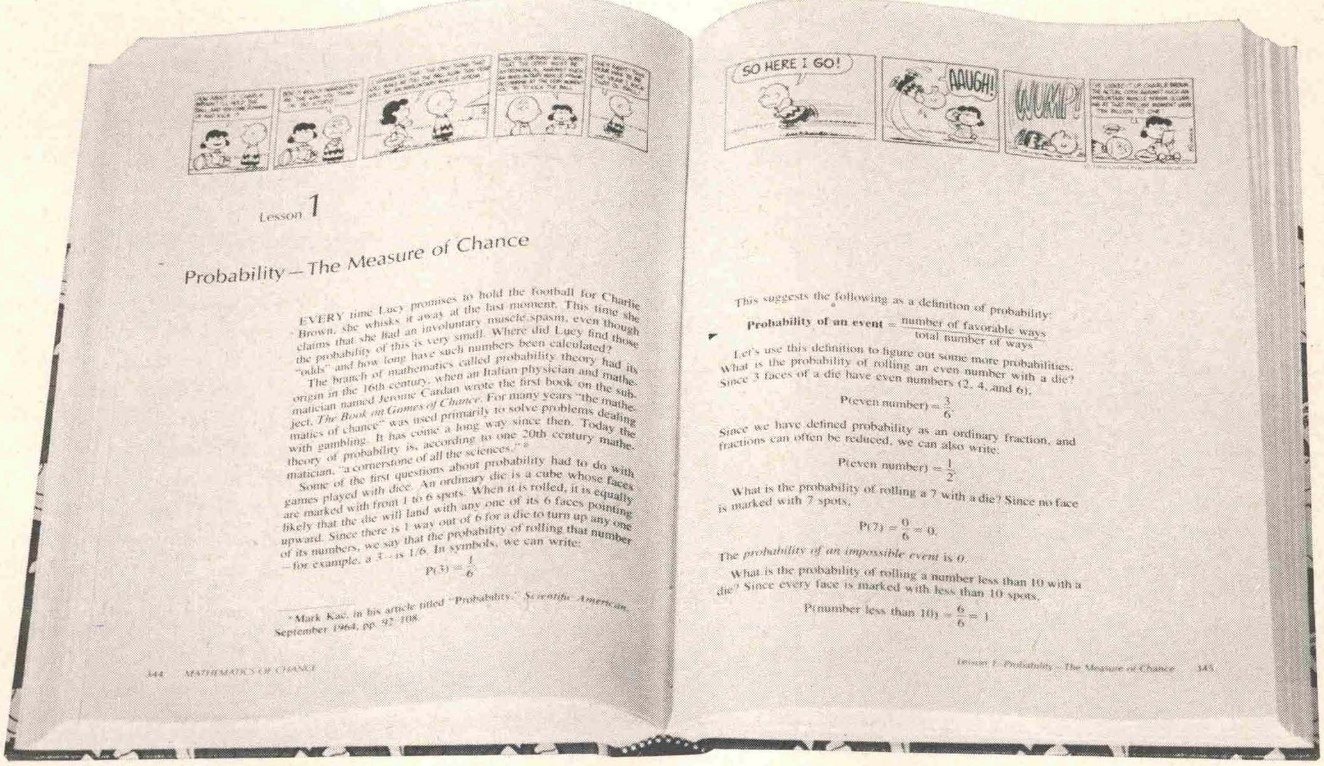
It now appears that we must modify the free-electron model of metals. In real metals the density of states at the Fermi surface evidently is considerably greater (experiments indicate one and a half to two and a half times greater) than the free-electron model would suggest. The basic reason is that the interaction of electrons with phonons, which can occur only near the Fermi surface, raises the effective mass and therefore the density of states of the electrons. In other words, a thin shell of "heavy" electrons, embodying a greater density of states than would be the case in a shell of free electrons, is formed at the Fermi surface of metals. The stronger the electron-phonon interaction is (in other words, the higher the critical temperature for superconductivity is), the greater is the increase of the density of states in the shell.

In this light we can deduce that compression brings about the observed decrease in the density of states at the Fermi surface in nontransition metals because it restricts the electron-phonon interactions that would raise the effective mass of the electrons. According to the modern theory of superconductivity, the pressure-induced increase of the Debye temperature, or characteristic temperature, in metals must lead to a reduction of electron-phonon interactions. One can therefore anticipate that pressure will always lower the critical temperature at which superconductivity is possible in metals whose electron shells are filled.



PRESSURE CHAMBER WAS REDESIGNED by one of the authors (Brandt) and I. V. Berman in order to obtain pressures higher than those that could be achieved with Wittig's original design. This chamber, which is much smaller than Wittig's, has an inside diameter of half a millimeter. Instead of one retaining ring it has two, made of a compressed mixture of ferric oxide and steatite powder. Disks of ferric oxide enclose the chamber at top and bottom, and two steatite washers encircle the sample. Four thin strips of platinum serve as the current and potential electrodes. The anvils that apply the pressure are made out of a hard alloy.

"I had been to school...and could say the multiplication table up to 6 x 7 = 35, and I don't reckon I could get any further than that if I was to live forever. I don't take stock in mathematics, anyway."—Mark Twain, *Huckleberry Finn*



Lesson 1

Probability – The Measure of Chance

EVERY time Lucy promises to hold the football for Charlie Brown, she whisks it away at the last moment. This time she claims that she had an involuntary muscle spasm, even though the probability of this is very small. Where did Lucy find those "odds" and how long have such numbers been calculated?

The branch of mathematics called probability theory had its origin in the 16th century, when an Italian physician and mathematician named Jerome Cardan wrote the first book on the subject, *The Book on Games of Chance*. For many years "the mathematics of chance" was used primarily to solve problems dealing with gambling. It has come a long way since then. Today the theory of probability is, according to one 20th century mathematician, "a cornerstone of all the sciences."*

Some of the first questions about probability had to do with games played with dice. An ordinary die is a cube whose faces are marked with from 1 to 6 spots. When it is rolled, it is equally likely that the die will land with any one of its 6 faces pointing upward. Since there is 1 way out of 6 for a die to turn up any one of its numbers, we say that the probability of rolling that number—for example, a 3—is 1/6. In symbols, we can write:

$$P(3) = \frac{1}{6}$$

*Mark Kac, in his article titled "Probability," *Scientific American*, September 1964, pp. 92–108.

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This suggests the following as a definition of probability:

$$\textbf{Probability of an event} = \frac{\text{number of favorable ways}}{\text{total number of ways}}$$

Let's use this definition to figure out some more probabilities. What is the probability of rolling an even number with a die? Since 3 faces of a die have even numbers (2, 4, and 6),

$$P(\text{even number}) = \frac{3}{6}$$

Since we have defined probability as an ordinary fraction, and fractions can often be reduced, we can also write:

$$P(\text{even number}) = \frac{1}{2}$$

What is the probability of rolling a 7 with a die? Since no face is marked with 7 spots,

$$P(7) = \frac{0}{6} = 0.$$

The *probability of an impossible event* is 0.

What is the probability of rolling a number less than 10 with a die? Since every face is marked with less than 10 spots,

$$P(\text{number less than } 10) = \frac{6}{6} = 1$$

Lesson 1 Probability – The Measure of Chance 345

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The situation in the transition metals (those with unfilled inner shells) is different. These metals owe their electrical conductivity to the fact that in the band structure of their electron energy levels narrow inner bands overlap the outer bands. The effective mass of an electron in a narrow band is always much larger than that of a free electron or of one in an outer band. Consequently the density of states at the Fermi surface depends predominantly on where that surface happens to lie; the density may be very large if the surface encompasses a narrow band. A shift of the Fermi surface under pressure may therefore effect a much larger change in its density of electron states than is produced by the inhibition of electron-phonon interactions caused by an increase of the Debye temperature. The shift may either increase or decrease the density of states in the Fermi surface. This means that in transition metals pressure may bring about either a rise or a fall in the critical temperature for superconductivity, the effect that was confirmed experimentally.

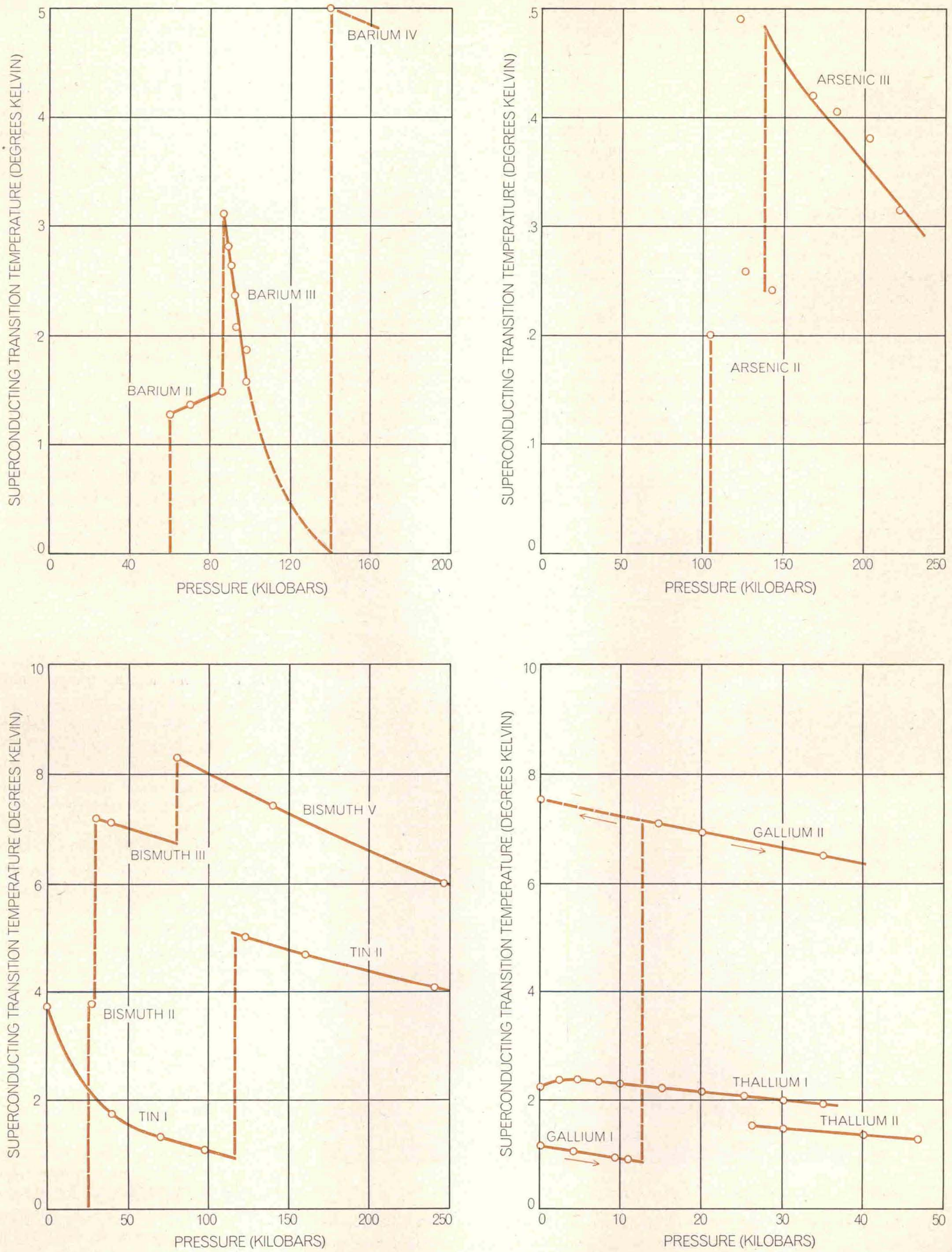
SAMPLE	PRESSURE (KILOBARS)	SUPERCONDUCTING TRANSITION TEMPERATURE (DEGREES KELVIN)
a		
GALLIUM I	0	1.07
GALLIUM II	35	6.4
LANTHANUM I	0	5.2
LANTHANUM II	23	8.1
THALLIUM I	0	2.39
THALLIUM II	35	1.45
TIN I	0	3.73
TIN II	113	5.3
b		
SILICON II	120	6.7
GERMANIUM II	115	5.35
BISMUTH II	25	3.91
BISMUTH III	27	7.1
BISMUTH V	80	8.3
ANTIMONY II	85	2.65
PHOSPHORUS II	160–200	5.8
PHOSPHORUS III	200	5.4
TELLURIUM II	45	3.3
SELENIUM II	130	6.8
ARSENIC II	100	.2
ARSENIC III	130	.5
BARIUM II	60	1.3
BARIUM III	96	3.1
BARIUM IV	140	5
CERIUM II	50	1.7
c		
INDIUM–ANTIMONY II	23	2.1
INDIUM–ANTIMONY III	30–150	3.3–5
INDIUM–ANTIMONY IV	30–150	4.1
GALLIUM–ANTIMONY II	70	4.2–6
BISMUTH–TIN	25	7.9
ALUMINUM–ANTIMONY	125	2.8

NEW SUPERCONDUCTORS created by the application of high pressure are listed in this table. They include new superconducting versions of elements that are already known to be superconducting (*a*), superconducting versions of elements that are not superconducting at atmospheric pressure (*b*) and new versions of known superconducting alloys (*c*).

Before going on to further experiments with high pressure, let us speculate for a moment on whether or not very high pressures could completely destroy the superconductivity of superconductors (at any temperature, however low). From the point of view of the BCS theory superconductivity will vanish only if and when the electron-phonon force of attraction between electrons is reduced to a point where it is canceled by the Coulomb force of repulsion. It was found that under pressure the critical temperature for superconductivity must decrease at an exponential rate and can reach zero at some critical pressure. Analyzing our data for cadmium and zinc and data for aluminum obtained by the Swiss workers M. Levy and Jorgen L. Olsen, we conclude that the possibility of superconductivity would be eliminated for cadmium at a pressure of about 120 kilobars, for zinc at 160 kilobars and for aluminum at 200 kilobars.

Efforts to produce new superconductors by means of pressure have been pursued along two lines: (1) the creation of new modifications of substances already known to be superconducting and (2) the transformation of substances that are not superconducting at ordinary (atmospheric) pressure into superconducting modifications. A considerable number of successes have been achieved in both directions, including the formation of superconducting versions of some nonmetals at ordinary pressures, and many other promising possibilities are being investigated [*see table at left*].

We have investigated in detail how the critical temperature for some of these superconductors varies with pressure [*see illustration on opposite page*]. The critical temperature for a particular element may decline under pressure and then be suddenly boosted. These abrupt changes obviously signal phase transitions that are produced by rearrangement of the electron and phonon spectra of the crystals under pressure. It is interesting to note that in most cases (modifi-



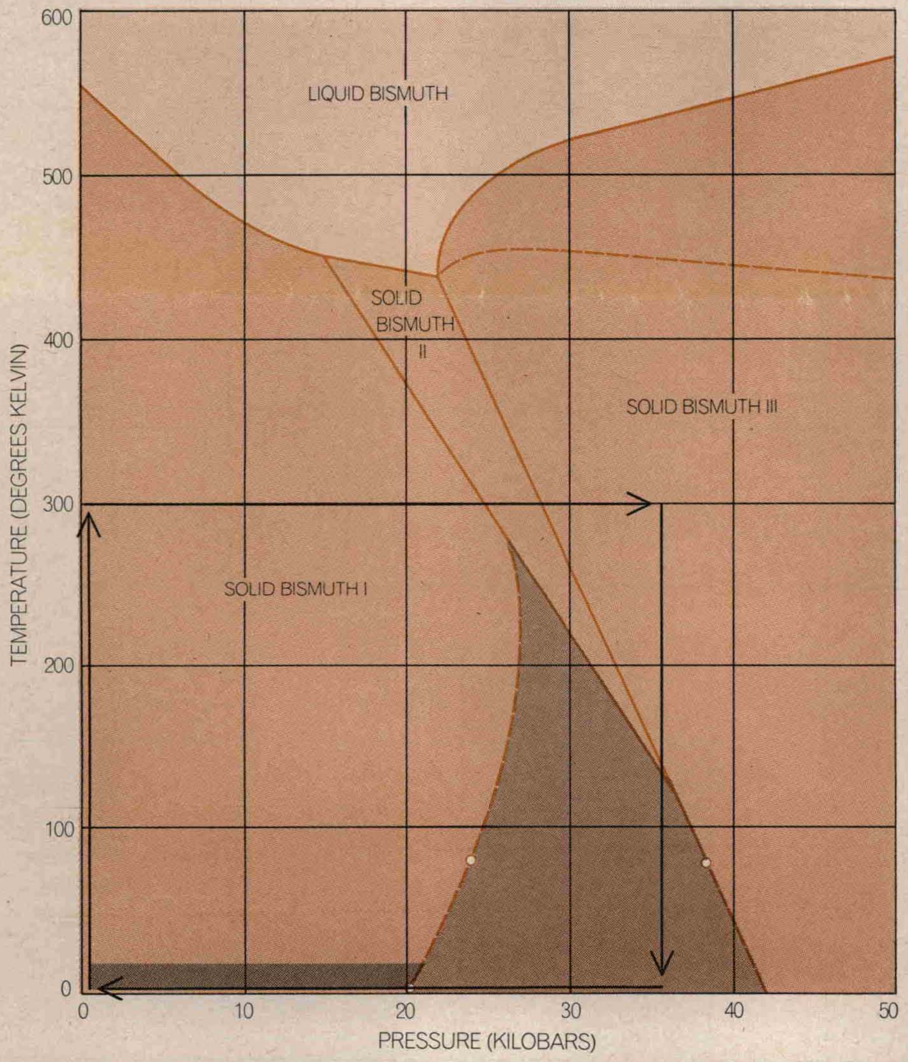
ABRUPT CHANGES in the superconducting transition temperatures of a number of metals were observed to take place at high pressures. In most cases (the modifications of barium, arsenic, bismuth, tin and gallium) the critical temperature of the new modification is raised; in other cases (the modification of thallium is the only example shown) the reverse is true. These variations in the critical temperature appear to correspond to rearrangements in the electronic structure of the crystals at the phase transitions.

cations of bismuth, arsenic, gallium, tin and barium) the phase transition raises the critical temperature, but sometimes (lanthanum and thallium) it lowers that temperature.

How stable are the modifications produced by pressure? In all cases the modified form of the substance returns to its original state when the pressure is reduced at room temperature or higher. Suppose, however, that one created the modification by high pressure at room temperature, cooled it to the temperature of liquid helium and then reduced the pressure to the ordinary atmospheric value. Would the modification survive in a state of metastability at the low temperature?

It was known that if a film of bismuth (which is not a superconductor in bulk) was formed by deposition on a substratum that was cooled down to the temperature of liquid helium, it became superconducting. The film had superconducting properties like those of the bismuth III modification produced by pressure, indicating that the film's crystalline structure was similar to that of bismuth III. Evidently the low-temperature condensation of the film had generated very strong stresses within it; when its temperature was raised to about 20 degrees K., it reverted to a nonsuperconducting modification (bismuth I), apparently by dissipation of the stresses.

This led us to tests of stability along the lines of the experiment suggested above. We compressed samples of bismuth at room temperature under pressures of up to about 30 kilobars, then cooled these bismuth III modifications to liquid-helium temperatures and proceeded to reduce the pressure gradually. Samples of bismuth III that were only slightly deformed changed abruptly into the nonsuperconducting modification bismuth I when the pressure fell to about 21 kilobars. In samples that had undergone plastic deformation creating internal stresses in part of the sample, that part retained the bismuth III modification in a metastable state down to atmospheric pressure. And strongly deformed samples remained in the bismuth III modification throughout the sample when the pressure was reduced to atmospheric, but of course at low temperature. The critical superconductivity temperature for these samples was 7.4 degrees K., three-tenths of a degree higher than for undeformed bismuth III at a pressure of 30 kilobars. From these interesting results we deduced that the internal stresses required to preserve bismuth III in a metastable state correspond to a pressure of 21 kilobars. These stresses disappear at a temperature of between 20 and 25 degrees K. and the superconducting bismuth III modification changes into bismuth I [*see illustration at left*].



PHASE DIAGRAM OF BISMUTH illustrates the effects of pressure and temperature on the phase transitions of a metal that is not superconducting in its usual crystalline state (bismuth I). The four black arrows indicate the sequence of operations carried out by the authors in their experimental study of the low-temperature region of the diagram. The light gray area is the hysteresis region. The dark gray area is the region in which a deformed superconducting modification of bismuth (bismuth III) exists in a metastable state.

It has been established by several workers that by similar treatment one can produce modifications of gallium, antimony and indium-antimony and bismuth-tin alloys that are metastable at low temperatures under atmospheric pressure. Most surprising is the possibility that one could create the metastable modification of antimony (Sb-II) at the temperature of liquid nitrogen (78 degrees K.). At room temperature this modification can be stable only at a pressure higher than 85 kilobars.

Presumably within five to 10 years it will become possible to study superconductivity under pressures of 500 kilobars or more. Expansion of the range of available pressures should lead to the discovery of new superconducting modifications of elements and compounds, and perhaps general rules governing the alteration of superconducting properties by very high pressures will emerge. High pressure may also be applied to the study of other phenomena (for example a tunnel effect in superconductors, investigation of which has already begun) that will yield new information on important matters such as the energy spectra of solids and electron-phonon interactions.

In the field of superconductivity the use of pressure may also open interesting new fields for exploration, such as the possibility of discovering varieties of physical structure, natural or synthetic, that can provide superconductivity by nonphonon mechanisms.