Moons of Jupiter: Io Seems to Play an Important Role

Jupiter and its Galilean moons were observed from the ground long before the space program began, and few people expected startling discoveries from terrestrial telescopes. But a recent observation of the innermost Galilean moon has motivated a theory that seems to correlate many older observations from the earth as well as some of the new discoveries by Pioneer 10. Last year Bob Brown, at Harvard University, Cambridge, Massachusetts, discovered evidence of sodium on the moon Io. The initial observation was so straightforward that it could have been done 50 years ago. Furthermore, the existence of atomic sodium on a planetesimal seemed so unlikely that few people believed the initial observation until it was confirmed by high-resolution studies at the Smithsonian Astrophysical Observatory, Mount Hopkins, Arizona, by Brown and Fred Chaffee. A new model for sodium emission that was prepared just before Pioneer 10 reached Jupiter predicted several of Pioneer's discoveries, most notably the existence of an ionosphere on Io.

The innermost of the four large Galilean moons of Jupiter, Io has a 42-hour orbit around Jupiter and a mass comparable to that of the earth's moon, and for some time ammonia ice has been suspected on Io. To explain the observations of sodium emission, Michael McElroy, Yuk Ling Yung, and Bob Brown at Harvard propose that the surface of Io is covered with a layer of ammonia ice containing traces of sodium, and perhaps potassium and calcium. Even at the low surface temperature of Io, some ammonia would evaporate. Ultraviolet sunlight would then dissociate the ammonia to produce molecular nitrogen, which could excite sodium atoms to produce the emissions that have been observed. (Nitrogen would do this most efficiently if it were excited to a metastable state, perhaps by a mechanism similar to the auroral process on the earth.) The dissociation of ammonia would also produce atomic hydrogen, which is so light it would escape from the gravitational attraction of Io.

McElroy and his associates predict that there should be an extensive cloud of hydrogen, nitrogen, and sodium around Jupiter in the vicinity of Io's orbit. Pioneer 10 was not designed to find nitrogen or sodium, but a torus of hydrogen with a diameter of about the diameter of Io's orbit has been observed (page 317, this issue). The sodium emission model also requires hydrogen in the atmosphere of Io, as possibly detected by Pioneer 10, and the existence of an ionosphere formed by photoionization of sodium. The discovery of an ionosphere for Io was, of course, one of the most definitive early results from Pioneer (page 323).

Two other phenomena associated with Io can be incorporated within the sodium emission model. After Io emerges from Jupiter's shadow, it is unusually bright for about 15 minutes and then gets dimmer. Several people have suggested that ammonia from the atmosphere falls as snow onto Io while it is on the night side of Jupiter, then the brilliant snow evaporates as Io emerges into sunlight.

Another striking observation known for several years is that the bursts of radio noise from Jupiter are strongly correlated with the position of Io in its orbit. To explain this, Peter Goldreich of California Institute of Technology, Pasadena, and D. Lynden-Bell University of Cambridge, England, proposed that if Io had a conducting ionosphere, it could generate a large voltage as it cut through the magnetic field lines of Jupiter. The voltage could drive a plasma process, perhaps like the aurora, which would produce the observed radio noise. The sodium emission model provides the needed ionosphere, of course. In return, the generator model provides a method of exciting nitrogen and also heating the atmosphere to high temperatures needed for sodium to escape. No evidence for a torus of sodium around Jupiter has been found, but Lawrence Trafton at the University of Texas, Austin, and associates have made Earth-based observations that suggest a cloud of sodium emission around Io extending to about 20 times the diameter of the moon.

Other possible implications of the new model, to be published in the *Astrophysical Journal (Letters)*, are that the gases from Io could be the source of trapped radiation belts, and that high-temperature neutral gases could move out far beyond Io's orbit, become ionized, and perhaps cause the stretching of the magnetic field that is observed.

The new observations suggest that Io affects the environment of Jupiter in many ways. Jupiter is unique, but the moons of Jupiter, and perhaps Saturn and Neptune, may be much more significant than their sizes alone suggest.—WILLIAM D. METZ

Superconductivity: Surpassing the Hydrogen Barrier

Progress in making superconducting metals with higher and higher superconducting transition temperatures (T_c) has been a slow and intermittent process, with increases in T_c coming in intervals of several years. Thus it was with a great deal of excitement and some sense of relief that the community of researchers in superconductivity received the news last September that John R. Gavaler (*1*) of the Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, had, by means of a new sputtering process, produced a niobium-germanium compound (Nb_3Ge) that was superconducting up to 22.3°K. (Gavaler has now produced material with T_c's up to 22.9°K). Shortly thereafter, Louis R. Testardi, J. H. Wernick, and W. A. Royer (*2*) of the Bell Laboratories, Murray Hill, New Jersey, reproduced Gavaler's results and made niobium-germanium with a T_c of 23.2°K (in one sample).

There is a strong motivation to raise the T_c of superconducting materials to at least the boiling point of hydrogen (20.4°K), but the higher the better. Until now, the highest T_c obtained was only slightly higher than this (very nearly 21°K), in an alloy of niobium, aluminum, and germanium, and that was achieved in 1967 by B. T. Matthias of the University of California at San Diego, La Jolla, in collaboration with several other scientists at the Bell Laboratories. Thus all superconductors have required the use of liquid helium (which boils at 4.2°K under 1 atmosphere pressure) as a refrigerant. Although relatively abundant in the United States at present, helium is scarce on a world-wide basis and may become hard to find anywhere, if projected rates of its consumption materialize (*Science*, 11 January, p. 59). In addition, liquid helium is expensive to make, and, as compared to other cryogens, it has a lower efficiency and a higher operating cost in practical engineering applications.

Niobium-germanium with a T_c near 22° to 23°K represents the first superconductor that, in principle, could be made into a device that would operate with liquid hydrogen as a coolant. Moreover, the surpassing of the "hydrogen barrier" significantly enhances the probability, according to some observers, that other, even higher temperature, superconducting materials may be found. And, although in the past many techniques have been used with varying degrees of success to produce high temperature superconductors, it appears that the new sputtering technique used to produce niobium-germanium may open the way to synthesis of a number of new superconducting materials. If so, the sputtering technique itself may ultimately prove to be more significant than the making of the niobium-germanium compound.

In the sputtering process, a target material with a composition close to that of the material to be produced and an appropriate substrate (which may be as simple as a glass slide) are placed inside a vacuum system in an ionized gas produced by an electric field. The field also accelerates the gas ions toward the target, whose atoms are knocked loose by the bombarding ions. The target atoms then move toward the substrate, where they are deposited in the form of a thin film with a typical thickness between 10 angstroms to 1 micrometer. Normally sputtering is carried out with gas pressures below 8×10^{-2} torr and with voltages of several thousand volts. The high T_c niobium-germanium superconductors, however, are best produced at much higher pressures and lower voltages. Gavaler, for example, reported using 0.3 torr and 750 volts in his experiments at Westinghouse, although the researchers at the Bell Laboratories indicated that they found some latitude in choosing the precise pressure and voltage.

The temperature of the substrate is also a critical parameter. In the past,

How to Make a Superconducting Wire

The discovery of a new high-temperature superconductor such as niobium-germanium (see story above) immediately raises the question of how suitable the new material may be for commercial application in electromagnets and electrical machinery, and, perhaps someday, in power transmission lines and levitated, high-speed ground transportation. Whatever the application, the superconductor must be shaped into a wire, ribbon, or tape, and fabrication of some superconductors has proved difficult. Moreover, the superconducting material must have a high enough transition temperature that practical refrigeration methods are available; a high enough upper critical magnetic field that it remains superconducting in high magnetic fields; and a high enough critical current density that it remains superconducting while carrying high electrical currents. Progress in practical superconducting materials has been divided between two materials: niobium-titanium alloys, which have good mechanical properties and hence are easily fabricated and handled but have less than optimum superconducting properties, and a niobium-tin compound (Nb_3Sn), which is very brittle and difficult to handle but has quite good superconducting properties.

In about 75 to 80 percent of today's superconducting devices, the superconducting wires are composites of niobium-titanium and copper. Such composites are made by inserting small (0.3-centimeter diameter) rods of niobium-titanium into copper tubes and stacking these tubes into a billet. The billet is extruded into a rod with a diameter of about 2.5 cm and is then drawn into wires of appropriate size. Composites as small as 0.02 cm in diameter are produced routinely in this way. After the final drawing step, the wire is twisted to reduce electrical power losses when carrying alternating current and to improve the magnetic stability of the wire. Finally, the wire is either coated with an insulating layer and used directly, or it is braided together with other wires to make cables for larger applications.

Despite its widespread use at the present time, niobium-titanium is limited for some applications by its superconducting properties. The transition temperature of niobium-titanium is about 9°K, which is almost uncomfortably close to the temperature of the refrigerant, liquid helium (4.2°K). Another limitation of niobium-titanium is that its superconducting properties are destroyed by magnetic fields above about 10 teslas, so that its use in high field magnets is precluded.

Niobium-tin (Nb_3Sn) with a transition temperature of about 18°K and a critical field of 21 teslas is the material manufacturers use for commercial applications involving high magnetic fields. Unfortunately, it is brittle, breaks easily, and is difficult to handle. Moreover, because of its poor thermal conductivity, there are problems in maintaining a stable superconducting state.

To circumvent these difficulties, niobium-tin superconductors are made in the form of a tape or ribbon composed of several layers of different materials. One method begins with a niobium ribbon (elemental niobium is ductile) into which tin is diffused to make a niobium-tin surface layer. Copper or aluminum is sandwiched around the ribbon for improved thermal conductivity. The resulting superconducting tape may be 0.1 millimeter thick and a few millimeters wide. Later stainless steel layers are added for mechanical strength.

Despite its good superconducting properties, niobium-tin in the form of a tape or ribbon is still not adequate for some applications, and the problem of the poor thermal conductivity of the superconductor is not completely solved by the copper or aluminum layers in the tape. A multifilamentary structure similar to that used in superconductors prepared by sputtering have been deposited onto substrates maintained at low temperatures—that is, room temperature or lower. Subsequently, these materials could be annealed at higher temperatures in order to optimize their superconducting properties. The production of niobium-germanium represents a major success of a new approach to sputtering superconductors begun in the last few years, in which the substrate is maintained at quite high temperatures. Gavaler at Westinghouse reported using substrates kept between 700° and 950°C, and the Bell Laboratories group found optimum results with substrates kept between 650° and 750°C. Depositing niobium-germanium onto substrates outside this temperature range resulted in a much lower T_c.

Although it is agreed that a combination of high substrate temperature, low voltage, and high gas pressure is required to make niobium-germanium with a high T_c, precisely what it is about these conditions that makes sputtering so effective is still a matter of conjecture. Some scientists, including Gavaler, believe that the key to achieving the high T_c in niobium-germanium is the composition. In the niobium-germanium system, the intermetallic compound with the nominal composition Nb_3Ge actually exists over a composition range of several percent. Thus, for example, the first Nb_3Ge phase made (by Matthias and co-workers at Bell Laboratories in 1963) actually had a composition closer to $Nb_{3.3}Ge$ and had a T_c of only 6°K. Later work at Bell Laboratories and by J. J. Hanak, J. I. Gittleman, and co-workers at the RCA Laboratories, Princeton, New Jersey, increased the T_c to about 17°K and moved the composition closer to that of Nb_3Ge.

Assuming this relationship between composition and T_c to continue, one could conclude that the high T_c niobium-germanium is nearly stoichiometric (has the exact composition Nb_3Ge). Gavaler cites at least two pieces of evidence to suggest that this is so. First, by extrapolating the lattice parameters (obtained from x-ray diffraction measurements) of niobium-germanium superconductors known to be nonstoichiometric, it is possible to estimate the lattice parameter of stoichiometric Nb_3Ge. The lattice parameters of Gavaler's high transition temperature samples coincide with the expected value. Second, though somewhat less persuasive, Gavaler's original sputtering target was a composite made up of a niobium sheet which halfway covered

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the niobium-tin alloy superconductors can overcome these difficulties, while at the same time carrying nearly as high electrical current densities (10^5 to 10^6 amperes per square centimeter) as the tape. They are also easier to handle.

Such a multifilamentary niobium-tin superconducting wire has already been made, and several companies are developing it for commercial application. Because of the poor ductility of niobium-tin, it cannot be drawn into a wire, but this problem can be overcome if the drawing step precedes the formation of the niobium-tin. For example, pure niobium rods may be inserted into a copper-tin alloy. After this assembly is extruded and drawn, the niobium-tin is formed by heating the wire to about 700°C, so that the tin is leached from the copper and forms a niobium-tin layer around the niobium cores. But because the copper-tin alloy work hardens—as it deforms during the drawing, it becomes progressively more difficult to deform it further—the assembly must be annealed frequently as the cross-sectional area is reduced. Scientists at Brookhaven National Laboratory, Upton, New York, have shown that this difficulty may be overcome if a pure copper matrix, rather than copper-tin, is used. Niobium-tin superconductor is produced by diffusing tin from outside the wire through the copper to the niobium only after the wire is formed.

While the multifilamentary niobium-tin superconductor looks very promising for the next generation of commercial superconductors, a ductile niobium-tin structure would be still better. One development (*Science*, 6 April, p. 57) is the production of a ductile, superconducting wire made up of discontinuous, whisker-like filaments of niobium-tin embedded in a copper matrix.

These wires, developed at the California Institute of Technology, Pasadena, by C. C. Tsuei who is now at IBM's Thomas J. Watson Research Center, Yorktown Heights, New York, are made by heating the constituents (for example, 10 percent niobium, 1.5 percent tin, and 88.5 percent copper) sufficiently to produce a molten alloy, and then rapidly cooling the molten material (at about 100°C per second). This treatment results in a copper-tin alloy containing niobium precipitates which is cold-rolled and drawn into a wire. The wires are heated to about 650°C to cause the formation of niobium-tin superconductor. The cold-rolling and drawing causes the niobium precipitates to become elongated into whisker-like filaments with irregular cross sections. It is not yet known whether these filaments overlap or if they are just very close.

The wires are superconducting, although some samples do exhibit a small residual resistivity, 10^{-10} to 10^{-12} ohm-centimeters. Tsuei has also reported that after his wires are bent around a 2.5-cm mandrel, there is no deterioration of the superconductivity—an indication that the superconductor acts as if it were ductile even though the brittle niobium-tin phase has been formed.

A number of problems remain, however. For example, it has not yet been demonstrated that Tsuei's process can be scaled up to produce commercial quantities of ductile superconducting wires. Moreover, because of the relatively small amount of superconductor in the wire, its current-carrying capacity is relatively low (about 1 percent of that of niobium-tin tapes), and some observers have suggested that in order to carry a higher current, the amount of niobium-tin in the wire may have to be so large that the ductility of the wire will be lost. Finally, some uncertainty exists about the origin of the superconducting current after the wire has been deformed by bending. Thus, while the advent of truly ductile niobium-tin superconductors would be a significant breakthrough, more research needs to be done to show that Tsuei's ductile wires will be practical.—A.L.R.

Additional Reading

1. *Proceedings of the 1972 Applied Superconductivity Conference* (New York, IEEE, Inc., 1972).

a germanium slice. As a result, the composition of the deposited superconductor varied according to its position underneath the target, from nearly pure niobium on one side of the substrate to nearly pure germanium on the other. The T_c similarly varied from that characteristic of niobium (9.2°K), through the record 22.3°K, to 0°K for pure germanium (which is not a superconductor). The problem is that, while the T_c is clearly composition dependent, it is not easy to tell how sensitive to composition it is.

Gavaler also speculated about the role of the sputtering process in achieving a stoichiometric composition. He suggested that the high gas pressure and low voltage in the sputtering system could have two effects, both related to the observation that under these conditions the sputtered species would undergo many collisions before reaching the substrate. First, the sputtered atoms would have time to thoroughly mix and hence deposit with the preferred Nb_3Ge composition. Second, the resultant low energy of the incoming atoms combined with the high substrate temperature would permit a high surface mobility that could further enhance the composition or structure of the superconductor. The critical role of the substrate temperature similarly has two aspects. At substrate temperatures above those at which high T_c niobium-germanium superconductors can be produced, the stoichiometric Nb_3Ge composition may not be the thermodynamic equilibrium phase, whereas at substrate temperatures below this range, the reduced surface mobility of the sputtered atoms may not permit the achievement of the desired composition or structure.

Most superconductivity researchers, including Gavaler and the Bell Laboratories scientists, agree that the superconductors with the highest T_c's crystallize in a complex cubic structure known as the A-15 structure (also called the beta-tungsten structure) with the nominal composition A_3B. For example, the commercially used niobium-tin (Nb_3Sn) superconductor, the niobium-aluminum-germanium alloy [$Nb_3(Al,Ge)$] which previously held the T_c record, and niobium-germanium all have the A-15 structure. Moreover, these high temperature superconductors often have an associated structural instability that appears to be intimately related to their superconducting properties. For example, when niobium-tin is cooled to below 45°K it can undergo a transformation in which the cubic structure is distorted into a tetragonal one. The relation between an unstable lattice and a high T_c, though not understood in detail, is understood in general terms. The instability is related to the details of the lattice vibration spectrum of the superconductor, and, of course, it is the interaction between the free electrons and the lattice vibrations of the superconductor that gives rise to the superconductivity.

Testardi related that the group at the Bell Laboratories began looking for new superconducting materials a few years ago with these ideas as a guide. The ideal high temperature superconductor ought to have an unstable lattice, yet not be so unstable as to precipitate a transformation to a stable structure with a lower T_c (that is, it should be metastable). The place to begin looking for these materials should be in alloy systems whose structures are similar to those of the high T_c materials. A way to produce the desired metastable structure might be by sputtering the material onto a substrate heated to a temperature very close to that of a structural transformation in the solid state. Such transformations at elevated temperatures are common in transition metal alloy systems. Hopefully, cooling to room temperature would "freeze-in" the metastable structure obtained, and cooling to cryogenic temperatures would not induce any further transformations.

Niobium-Germanium Repeated

A successful test of the proposed scheme for producing metastable structures was made in 1971 by the Bell workers when they sputtered molybdenum-rhenium alloys at a temperature corresponding to a solid state phase tranformation, and thereby obtained enhanced T_c's (*3*). Later, when the details of Gavaler's success with niobium-germanium were received, they duplicated his results in a short time, and also managed to attain a T_c of 23.2°K in one sample.

Testardi is not yet convinced that a nearly stoichiometric composition is what causes sputtered niobium-germanium to have a high T_c. For one thing, he notes, high T_c material can be produced using sputtering targets with a variation in germanium composition of up to 20 percent (although he admits that no one yet knows the relation between target composition and the composition of the sputtered film). He also pointed out that, in alloys in the molybdenum-rhenium system prepared by sputtering onto heated substrates, the structure (as indicated by x-ray measurements) of the films having a higher T_c was definitely different from the structure of films having a lower T_c. Although the structural differences were small, the implication is that these differences and the instabilities they reflect were decisive in determining the T_c's obtained. Similar studies on niobium-germanium have not been completed. Moreover, the details of the niobium-germanium phase diagram are not known. This lack of knowledge precludes an unequivocal assertion that there is a phase transition in the temperature range 700° to 900°C, so that a direct analogy between molybdenum-rhenium and niobium-germanium is not yet possible.

Commercially usable superconductors (see box), in addition to having a high T_c, must also remain superconducting in large magnetic fields (often over 10 teslas) and while carrying large currents (10^5 amperes per square centimeter). Gavaler has had some of his niobium-germanium material measured at the National Magnet Laboratory, Cambridge, Massachusetts. Preliminary measurements have indicated performance comparable to commercially used niobium-tin superconductors when tested at 4.2°K (10^5 amp/cm^2 in a field of 21 teslas). At 20.4°K, the performance has dropped off considerably (much less than 10^4 amp/cm^2 in high magnetic fields), as might be expected at a temperature only a little below the transition temperature.

Gavaler noted that in the present thin film form, niobium-germanium superconductors are usable only for thin film devices, such as Josephson junction devices (*4*). To be useful in large-scale commercial applications, such as high field magnets, electric motors, and power transmission lines, a large development effort would be required. Niobium-germanium may not, in any case, be the ultimate superconductor, and the prospect of other materials to come, with the use of the techniques and ideas on which the research leading to high T_c niobium-germanium was based, may be the most important contribution this material has to make.

—Arthur L. Robinson

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