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62. I have been very fortunate in having the collaboration of many able students and colleagues. The work of Dr. C. G. Kurland, Dr. David Schlessinger, and Dr. Robert Risebrough established many of the ideas reported here. Equally significant have been experiments by Drs. Kimiko Asano, Michael Cannon, Walter Gilbert, François Gros, Françoise Gros, Johns Hopkins, Masayasu Normura, Pierre François Spahr, Alfred Tissières, and Jean-Pierre Waller. The visit of François Gros in the spring of 1960 was crucial in focusing attention on messenger RNA. Most importantly, I wish to mention my long collaboration with Alfred Tissières. Since 1960 I have had the good fortune, also, to work closely with Walter Gilbert.

The Physics of High-Field Superconductors

New materials, used in lossless magnets at low temperatures, challenge scientific understanding.

Charles P. Bean and Roland W. Schmitt

The electrical resistance of all metals decreases as the temperature of measurement falls. In 1911, H. Kammelingh Onnes of the University of Leiden, in attempting to find the limits of this behavior, discovered that some metals become perfect electrical conductors abruptly at very low temperatures. The discovery created an important problem for theoretical physics—Why does this "superconductivity" occur?—and simultaneously permitted visions of exciting practical results. One of these visions was the production of intense magnetic fields with no electrical losses. Now, more than 50 years after its discovery, the scientific and practical advances in superconductivity are reaching new heights.

One of the stories that contribute to the broader narrative of superconductivity is that of high-field superconductors—materials which, in contrast with most superconductors, remain perfect conductors in very high magnetic fields. The story of these materials is a small but representative illustration of the sporadic, disorderly advance of superconductivity, a field in which 45 years separated discovery from the development of a satisfactory fundamental theory. High-field superconductors were a dream of the moment of discovery, but a dream destroyed by a disappointing surprise.

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The Early Story

In September 1913, 2 years after his discovery of superconductivity, Onnes reported to a meeting in Chicago (*1*) on the progress of his laboratory in this new field. Mercury, tin, and lead had each been found to be superconductive, and a current density of 100,000 amperes per square centimeter had been sent through lead without developing resistance. This current density is 200 times that permitted in normal house wiring. Onnes's discovery lent substance to the dream of creating 100,000-oersted magnetic fields, 200,000 times the intensity of the earth's field and three or four times the intensity of the field of powerful iron electromagnets. The extravagant amount of power needed to achieve a field of this intensity in any other way had destroyed earlier hopes, but now Onnes could say (*1*); "The problem which seems hopeless, in this way enters a quite new phase when a superconductive wire can be used."

Onnes had one reservation: "there remains of course the possibility that a resistance is developed in the superconductor by the magnetic field." But, if this were the case, Onnes reasoned, the resistance should go up proportionally to the intensity of the field or its square, as the resistance of normal metals does. Therefore, even at 100,000 oersteds the superconductor would have an infinitesimal resistivity. Onnes began the experiment but spent several months preparing a 10,000-oersted field (*2*), not troubling to use one of 2000 oersteds, already available, because he was certain of being unable to detect resistance at the lower intensity. With surprise, Onnes found that resistance returned abruptly in just a few hundred oersteds, and his hope for a superconducting coil vanished. Only the excitement of the scientific discovery relieved his disappointment.

Now, 50 years later, physicists again hope to build 10^6-oersted superconducting solenoids because materials have at last been found that have no resistance in a field of this intensity. The break came in 1961 when scientists at Bell Telephone Laboratories announced that the intermetallic compound Nb_3Sn was still superconducting and able to carry a large current in an 88,000-oersted field (*3*). During the intervening 2 years scientists have developed other high-field superconductors and have found the principles that underlie the superconductivity of materials in high fields. But as the principles have become more firmly established, the realization has grown that certain results obtained in the years 1930 to 1935 anticipated contemporary theory and experiment.

In the years that followed Onne's surprising result other scientists examined metals, alloys, and compounds but always found that superconductivity existed only in weak fields. But in 1928, W. T. de Haas, E. van Aubel, and J. Voogd, at Leiden, began investigating alloys and compounds (*4*), and in 1930 de Haas and Voogd found one series of alloys, Pb-Bi, that remained superconducting in high fields (*5*)—some alloys in fields up to 20,000 oersteds. Immediately the thought of a superconducting solenoid reoccurred, and they remarked (*5*), "we should be able to generate magnetic fields of 14,000 Gauss at the boiling point of helium without development of heat and at 2°K even fields of 19,000 Gauss."

But no coil was built. In 1933 Mendelssohn of Oxford revived the idea and proposed a method of energizing a coil while avoiding the conduction of heat down the leads to it, a problem he thought was the "chief remaining difficulty" (*6*). Finally, in 1935 a short report on experiments made by Keesom at Leiden appeared (*7*), and again the hope of obtaining high-field coils was dashed. The difficulty this time was stated to be the low limiting current carried by the Pb-Bi alloys of de Haas and Voogd. The current-carrying capacity is a critical factor in making a high-field coil; if the capacity is low, the amount of wire needed to produce a high field is prohibitive. The wire must also be able to carry the large superconducting currents in a transverse field, since the innermost windings of a solenoid are in its full field. Keesom was discouraged because the current density he observed in zero field ($\approx 3 \times 10^4$ amp/cm^2) was less than that of a lead wire of the same diameter. Recent measurements on similar alloys show that he could have produced a field of 4000 or 5000 oersteds had he persevered. Furthermore, by using thermal and mechanical treatments to increase the limiting current density he could have made a coil to go beyond 10,000 oersteds (*8, 9*).

Even though physicists were unable to produce a high-field coil in the 1930's, they attacked the problem of why some materials present no resistance in high fields. This fundamental problem, like that involved in constructing a high-field solenoid, again came to the fore with the discovery by Bell Laboratories scientists in 1961. Subsequent work has shown that there are two conditions each of which is sufficient to cause a critical field to be abnormally high: (i) the material has a filamentary structure —interconnected threads of superconducting material embedded in a matrix of different material; or (ii) the material, though homogeneous, spontaneously breaks up in a magnetic field into a mixed state of tiny normal and superconducting regions. How these two conditions arise and contribute to the properties of high-field superconductors is discussed later in this article.

Here again, contemporary work was anticipated, for in 1935 these conditions were suggested as the cause of the superconducting behavior of alloys. C. J. Gorter (*10*), K. Mendelssohn (*11*), and H. London (*12*) had each arrived at a substantial part of today's thought about high-field superconductors. Mendelssohn pointed out that the special properties of impure metals and alloys would occur if the critical field were high in some parts of the alloy while of about the same value as in pure metals in the main part of the alloy. He remarked (*11*) that "such a model would act like a fine supraconducting sponge the meshes of which are formed by annular regions of high threshold value . . . ," and (*13*) that "the skeleton of the sponge would be very fine. . . ." As we shall see, the only step in contemporary theory that goes beyond Mendelssohn's conception is a quantitative mathematical theory of these "filamentary" materials. Both Gorter and London recognized the importance of tiny dimensions. London showed that a homogeneous superconductor should break up into thin superconducting and normal regions in a magnetic field, but he did not know why alloys do this and why pure metals do not. Gorter, too, though knowing that a mixture of thin superconducting and normally conducting regions had the correct properties, could say why the behavior of alloys and pure metals differed only by using ad hoc assumptions.

Meanwhile, in Russia L. W. Shubnikow and his associates were studying the superconductivity of lead alloys—$PbTl_2$ and Pb-Bi—and found properties (*14*) now known to be characteristic of materials that enter a mixed state in a magnetic field. But it was two decades before a satisfactory understanding of this behavior began to evolve; appropriately, it came largely through a chain of theoretical work done in Russia (*15–17*).

It is a slight step from the understanding of the 1930's to modern theory, but progress faltered and turned to other paths. A small further advance of theory or experiment might have been enough to give complete knowledge of high-field behavior or lead to the finding of other alloys, better than Pb-Bi. But this advance was not made; physics paused for a quarter of a century before the chase was resumed.

Materials and Coils

The first magnet to be made of a superconductor was a little iron-core electromagnet with niobium windings that G. B. Yntema (*18*) reported in 1955. More significantly, he found that hard-drawn niobium wire would carry a current density of 70,000 amp/cm^2 in a field of 5000 oersteds. This work, published only as the abstract of a talk, caused no particular stir, as the field was one easily reached with iron electromagnets. Five years later, S. H. Autler (*19*) at the Lincoln Laboratory of the Massachusetts Institute of Technology made an extensive study of solenoids and electromagnets wound from niobium. Again the fields were low. He made a solenoid that reached 4300 oersteds and demonstrated that it had zero resistance by inserting a superconducting shunt while current flowed through the coil. The current continued flowing even when the battery was disconnected, and in one case it remained completely steady for 8 hours. He noted, however, that niobium might not be the ideal substance for high-field coils and said that B. T. Matthias of Bell Telephone Laboratories had recommended the compound Nb_3Sn, a compound that Matthias and his co-workers (*20*) had discovered 5 years earlier. This compound is characterized by a high transition temperature, 18°K.

The work of Autler stimulated work at the Bell Telephone Laboratories on high field superconductors. In the Bell Laboratories program a number of materials were considered for investigation. Matthias suggested the ductile alloys of molybdenum and rhenium, whose superconductivity had been discovered by Hulm (*21*). Using these alloys, Kunzler and his co-workers produced lengths of wire sufficient to wind solenoids, and fields of intensity up to 15,500 oersteds were attained (*22*). In a study of the magnetic properties of niobium-tin, Bozorth showed (*23*) that part of the sample remained superconducting in fields up to 70,000 oersteds. These magnetic properties arise from large superconducting currents that are induced to flow by application of the magnetic field. Subsequent theory (*24*) has shown how to calculate these currents. For instance, it is estimated that about 30,000 amp/cm^2 flow when a field of 30,000 oersteds is applied. Then came the direct observation by J. E. Kunzler and his colleagues that niobium-tin could carry very large currents in high fields (*3*). The compound Nb_3Sn is brittle. To make wires of it they took the important step of packing a niobium tube with a mixture of niobium powder and tin powder. The tube was then formed into a long length of fine wire which was still ductile because its core was still the mixture of powders. The wire was then bent into its final shape before being heated to nearly 1000°C so that the niobium and tin powders would react and form the brittle compound. One straight section of wire showed a current density within the reacted core of more than 100,000 amp/cm^2 in a field of 88,000 oersteds.

These discoveries prompted much additional work; one item of great interest was the ultimate critical field of Nb_3Sn. Several groups made measurements in pulsed magnetic fields (*25, 26*) (currents that will destroy a copper solenoid if they are continuous will not do so if they are applied for only a fraction of a second). In Fig. 1 are shown the measurements made by Hart and his co-workers (*26*) in our laboratory. They indicate, as Kunzler had expected (*27*), a critical field of approximately 200,000 oersteds.

A search for ductile alloys was also begun. Matthias again suggested a system (*27*)—namely, a niobium-zirconium alloy that he had discovered 8 years earlier (*28*). Its relatively high critical temperature, about 11°K, made it a good candidate. His suggestion proved to be a good one, and Kunzler reported the results (*29*) in April 1961. Some data (*30*) are given in Fig. 1. They show that the upper critical field is independent of the state of deformation of the wire, while the critical current density is controlled by deformation. Two other laboratories also studied this system, Atomics International (*31*) and Westinghouse (*32*). Both of these laboratories constructed coils of $Nb_{.75}Zr_{.25}$ alloy (*32, 33*). Autler of Massachusetts Institute of Technology also reported a Nb-Zr solenoid (*34*). With each of these materials fields somewhat higher than 50,000 oersteds were attained in small solenoids. One magnet of Nb-Zr produced a field of 68,000 oersteds (*35*) at 4.2°K. One Nb_3Sn magnet has been operated at fields near 70,000 oersteds (*9*).

Many other materials have interesting high-field properties; among them are V_3Si and the niobium-titanium system. One of the most interesting is V_3Ga, which is similar in structure and properties to Nb_3Sn, and with which an even higher critical field may be attained (*27*).

While this activity to discover, measure, and use high-field superconductors moved rapidly ahead, equally vigorous efforts were being made to understand why the materials behaved as they did. Such understanding begins with some of the things we know about the simplest type of superconductors.

Ideal Superconductors

Superconductors such as lead, tin, and mercury are called "ideal" superconductors. They have elemental properties that scientists attempt to explain by means of the quantum theory. Each is a perfect conductor of electricity below a transition temperature T_C, but each loses this property at a critical value of the magnetic field, H_C.

For more than 20 years these were thought to be the principal electrical properties of superconductors, but in 1933 Meissner and Ochsenfeld (*36*) discovered another property: superconductors expel magnetic flux. The magnetic induction B is zero.

These remarkable facts were used by F. London and H. London (*37*) as the cornerstone for an electrodynamic theory of superconductors. According to their theory the Meissner effect, the property of flux expulsion, depended on the establishment of lossless supercurrents in a thin surface layer of the superconductor. These currents flow in a direction such that the inside of the superconductor is shielded from impressed magnetic fields, and therefore they produce the state of zero induction within the sample. But the impressed magnetic field can penetrate into the thin surface layer where the lossless currents flow. The London theory implies that both the field intensity and the current density decrease exponentially toward the inside of a sample according to the relation $H = H_0 \exp(-x/\lambda_L)$, where H_0 is the applied field and λ_L is what is called the London penetration depth. Figure 2*a* illustrates the field and current distribution near a surface.

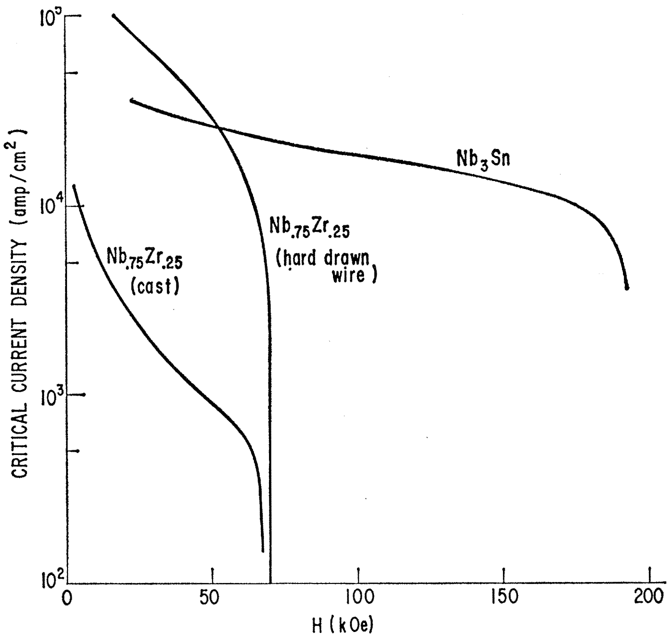
According to the theory, the value of λ_L is determined by n, m, and e—the number density, mass, and charge of electrons in the superconductor; the value is around 100 angstroms. The occurrence of this London penetration has been thoroughly confirmed by experiment (*38*), but the value for penetration depth is usually several times higher than the predicted value (*39*). Furthermore, the value is affected by the magnetic field and by the normal-state resistivity of the material, whereas, according to the London theory, neither of these factors would be expected to alter λ_L. Therefore, modifications of the theory have become necessary, and some of these modifications play a key role in the theory of high-field superconductors. They are discussed later in this article. Meanwhile, the distance λ can be regarded as an empirical parameter (*40*) for specifying the depth of penetration of fields and currents into superconductors.

To expel flux from within a superconductor takes energy; if a uniform magnetic field H_0 is distorted through being pushed out of a region of space, the energy of the field increases by $H_0^2/8\pi$ per unit volume of space vacated. An ideal superconductor can keep fields up to H_C, the critical field, out of the space it occupies, but at higher fields it reverts to the normally conducting state. Therefore, the Gibbs free energy of the superconducting state in zero field is lower than that of the normal state by $H_C^2/8\pi$ per unit volume, and in an applied field H_0 the total difference in Gibbs energy density is

$$\Delta g \equiv g_s - g_n = (H_0^2 - H_C^2)/8\pi \quad (1)$$

where g_s and g_n are the Gibbs free energy densities of the superconducting and normal phases, respectively. This relation is shown in Fig. 3*a*.

The term $-H_C^2/8\pi$ represents the condensation energy of the superconducting state—the energy that can be drawn upon to set up the surface currents that expel flux. It represents the fact that below T_C the electrons in a superconductor rearrange themselves into a configuration of lower energy than that of the normal state. The rearrangement produces a small region of forbidden energies—an energy gap—near the Fermi energy of a supercon-



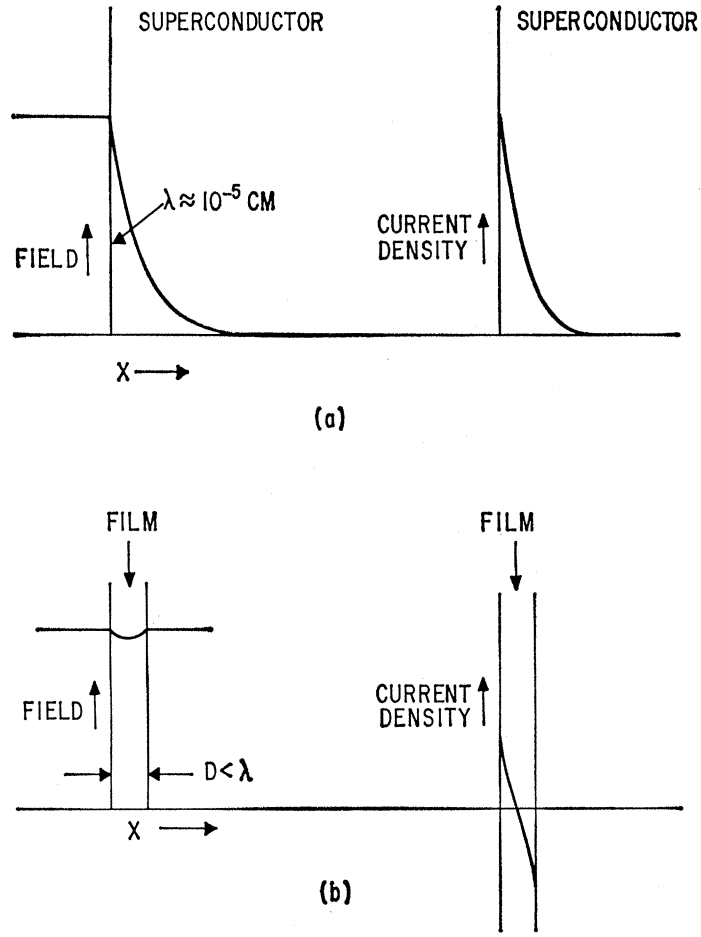
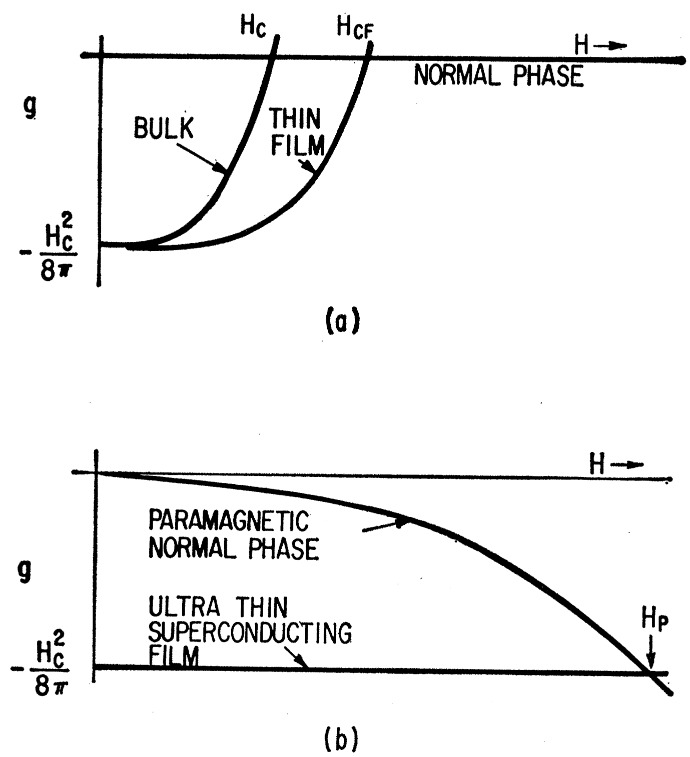


Fig. 1 (above). Measurements on superconducting niobium alloys. The maximum lossless current density is plotted against the magnetic field applied transverse to the direction of current flow. The Nb-Zr data are from Kunzler (*30*); the Nb_3Sn data are from Hart *et al.* (*26*), who used a pulsed magnetic field. The current density for the reacted core of Nb_3Sn is four times higher than for the total wire area. Fig. 2 (right). Field penetration and lossless currents at the surfaces of superconductors. (*a*) Field profile and related current density profile for a thick specimen. (*b*) The same quantities for a thin film. The current density, which is proportional to the slope of field, is less than in the thick specimen.



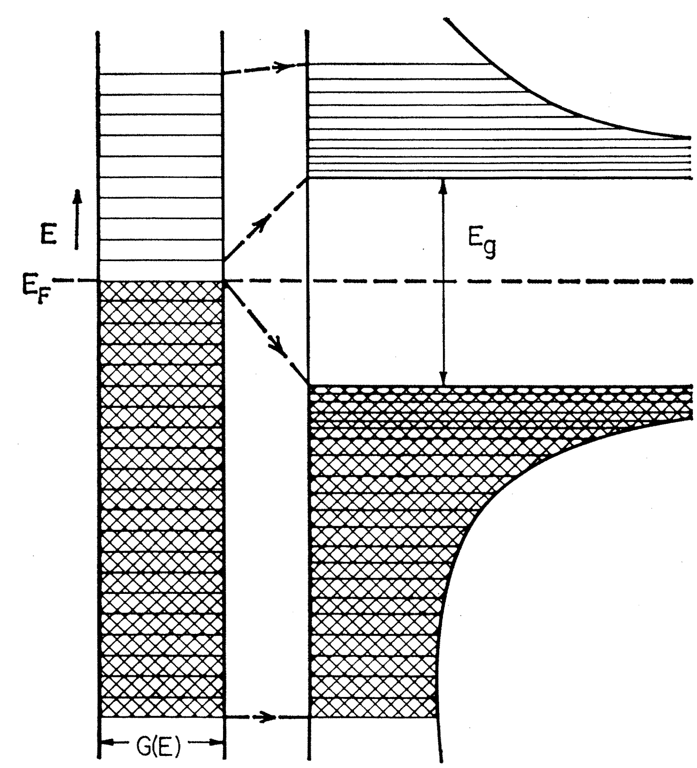


Fig. 3 (left). Thermodynamic reasoning applied to superconductors. The Gibbs free energy is plotted against a magnetic field applied parallel to the surfaces of superconductors. (*a*) Origin of the high critical field of films. (*b*) The paramagnetic limit; all magnetic susceptibilities common to the normal and superconducting phases have been neglected, and only the extra Pauli paramagnetism of the normal state is considered. Fig. 4 (right). The energy gap in superconductors. At left are shown the energy levels of a normal metal. The metal has a uniform number, $G(E)$, of energy states per unit interval of energy, and at $T = 0$ these states are occupied only up to the Fermi energy, E_F. On becoming superconducting a gap E_g opens, pushing the occupied states down, the unoccupied ones up. The energy of the system is lowered.

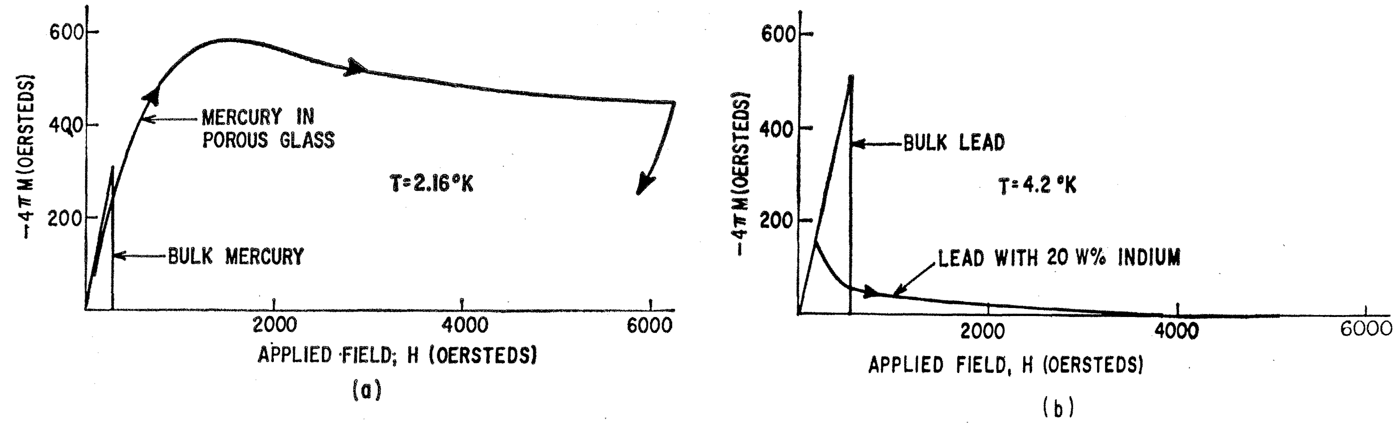


Fig. 5. Magnetization of the two prototypes of high-field superconductors. (*a*) Magnetization of bulk mercury and of mercury transformed into a filamentary superconductor through being pressed into the 40-angstrom holes of porous Vycor glass (*48*). (*b*) Magnetization of bulk lead and of lead alloyed with indium (*50*). The alloy is a mixed-state superconductor with a reversible magnetization, in contrast to the mercury in Vycor.

ducting metal. (The Fermi energy is the highest energy level occupied by the conduction electrons of a metal at $T = 0$).

During the transformation to superconductivity, as the gap opens, the electronic states below the Fermi energy are pushed down in energy; those above are pushed up. The total energy decreases, and the condensation energy exists because the states that are pushed down in energy are more fully occupied by electrons than those that are pushed up.

The decrease at $T = 0$ (see Fig. 4) is given by the equation

$$\Delta g_{cond} = -[E_g\, G(E)/2]\,[E_g/4] \quad (2)$$

where $G(E)$ is the density of electron states—the number of states per unit energy range—at the Fermi energy in the normal metal (*41*). The first bracket of Eq. 2 represents the number of electrons pushed down, the second bracket represents the average reduction in energy of each, all interactions having been taken into account (*42*). According to the very successful quantum theory of superconductivity advanced by Bardeen, Cooper, and Schrieffer (*42*), the energy gap E_g approaches 3.5 kT_c (k is Boltzmann's constant) as T approaches 0. Therefore, the condensation energy at $T = 0$ can be written in either of the two forms

$$\Delta g_{cond} = -[(3.5\; kT_c)^2 G(E)]/8$$
$$\Delta g_{cond} = -H_{c0}^2/8\pi \quad (3)$$

where H_{c0} is the critical field at $T = 0$. This relation shows that ideal superconductors with high critical fields will be those of high density of electron states, $G(E)$, and high transition temperature. None has been found with a critical field above about 1500 oersteds; for high-field properties we must turn to superconductors that are not "ideal."

Penetration and Dimensions

Because of the slight penetration of magnetic fields the properties of samples of tiny dimension are not the same as the properties of ideal superconductors. A film of thickness less than the penetration depth cannot completely shield the interior of the sample from the magnetic field; the distribution of field intensity and induced current density is shown in Fig. 2*b*. The energy of flux exclusion is less than it would be if flux exclusion were complete, and therefore the applied field must be much higher than H_c before the condensation energy of the superconducting state is overcome and the film transforms to the normal state (see Fig. 3*a*). This is the fundamental property that permits high-field superconductors to exist, and it comes into play when fine dimensions of a superconducting phase allow the magnetic field to enter a significant fraction of the volume occupied by that phase.

According to Ampere's law the current density parallel to the surface of a film is proportional to the normal derivative of the field; hence the surface current density in a thin film is less than that at the face of a bulk sample in the same external field. Figure 2*b* illustrates this point. Only in a field higher than H_c, when the film transforms to the normal state, does the current density reach the critical current density, J_c, that defines the limits of the superconducting state (*38*). The London theory and thermodynamic arguments (see Fig. 3*a*) suggest that, for very thin films, the critical field of the film is given approximately by

$$H_{cF} \approx H_c\,(\lambda/D) \quad (4)$$

where D is the thickness of the film.

We mentioned earlier that λ is affected by the electrical resistivity. It is also affected (that is, increased) by scattering of electrons at the surfaces of thin specimens. The penetration depth in Eq. 4 is consequently a function of film thickness, and the critical field is higher than one would otherwise expect from application of Eq. 4 (*39, 43*).

The effect of film thickness on λ also results in modification of the critical current density in films as compared with the critical current density in the bulk. As we implied, in the London theory the critical current densities in a film and in the bulk are equal; they are given by $J_c = 10\, H_c/4\pi\lambda$ amp/cm^2 if H_c is in oersteds and λ is in centimeters (this may be seen by applying Ampere's law to the configuration of Fig. 2*a*). For the usual superconductor, J_c is on the order of 10^8 amp/cm^2, if one uses the value of λ for bulk specimens. But because λ becomes greater in thin films, the critical current density goes down; it is estimated to be only a few million amp/cm^2 for films of lead a few hundred angstroms thick (*43*).

Equation 4 implies that the critical field for superconductivity could be made higher without limit if at least one dimension of the superconductor were made smaller and smaller. However, in calculating the difference in free energy between the normal and the superconducting states it has been assumed that the normal phase is not magnetized in a field—that its susceptibility is zero (*44, 45*). This assumption implies that the number of conduction electrons with spin parallel to the field remains equal to the number with spin antiparallel. But in the normal metal, energy is lowered if a few electrons with antiparallel spin turn over into alignment with the field—that is, the energy is lowered by the Pauli paramagnetism. The amount by which the free energy density of the normal phase is lowered is given by the equation

$$\Delta g_n = -\chi_P H_0^2/2 \qquad (5)$$

where χ_P is the Pauli paramagnetic susceptibility. According to a basic postulate of the quantum theory of superconductivity (*42*), the spins of the conduction electrons in superconductors are strongly paired; hence, at $T = 0$ no Pauli paramagnetism is to be expected. Consequently, as shown in Fig. 3*b*, an infinitely thin superconducting film would have a free energy independent of field. The point of intersection is reached when the energy density of Eq. 5 is equal to $-H_C^2/8\pi$, the condensation energy of the superconducting phase. The field when this occurs, called the paramagnetic limit H_P, is then given by

$$H_P = H_C/\sqrt{4\pi\chi_P} \qquad (6)$$

The Pauli paramagnetism is proportional to the density of states at the Fermi level. Using this fact and Eq. 3, we get at $T = 0$ the interesting result

$$H_P = KT_C \qquad (7)$$

The constant K is calculated by Clogston (*44*) to be 18,400 oersteds per degree Kelvin. If this theory is correct, the problem of getting high-field superconducting materials with even higher critical fields becomes the same as the problem of finding materials that have higher transition temperatures. Niobium tin, with the highest known critical temperature (18°K), would have a paramagnetic limit of about 330,000 oersteds.

There is evidence from nuclear magnetic resonance (*46*) that the assumption of rigid spin pairing must be relaxed because the superconducting phase still has Pauli paramagnetism, though less than that of the normal state. Clogston and his co-workers (*44*) have gathered evidence indicating that, even so, in several intermetallic compounds the paramagnetic limit should not exceed a value 30 percent above that calculated on the basis of the simple theory.

Models and Model Materials

Because superconductors of very small dimensions remain superconducting in very high fields, large samples that are composed of these minute components should also remain so. There are two ways of converting an ideal superconductor into a material that meets one of the two conditions of high-field superconductivity: (i) to break it up by physical processes into a filamentary structure, or (ii) to add impurities or alloying elements to the homogeneous superconductor in order to promote spontaneous dissociation into the mixed state (*47*) in a field. Both of these processes have been used to transform ideal superconductors into the prototype of high-field superconductors.

Figure 5*a* shows the magnetization of a large sample of pure mercury and of a sample of mercury pushed under pressure into unfired Vycor glass, a silica glass interlaced with a network of interconnected pores only 40 angstroms or so in diameter. Mercury, on being broken up into filaments, is converted from an ideal superconductor into the prototype of a filamentary, high-field superconductor (*48*). Figure 5*b* shows the magnetization of a large sample of pure lead and of a similar sample of lead-indium alloy. Lead with other metals added is converted from an ideal superconductor into the prototype of a

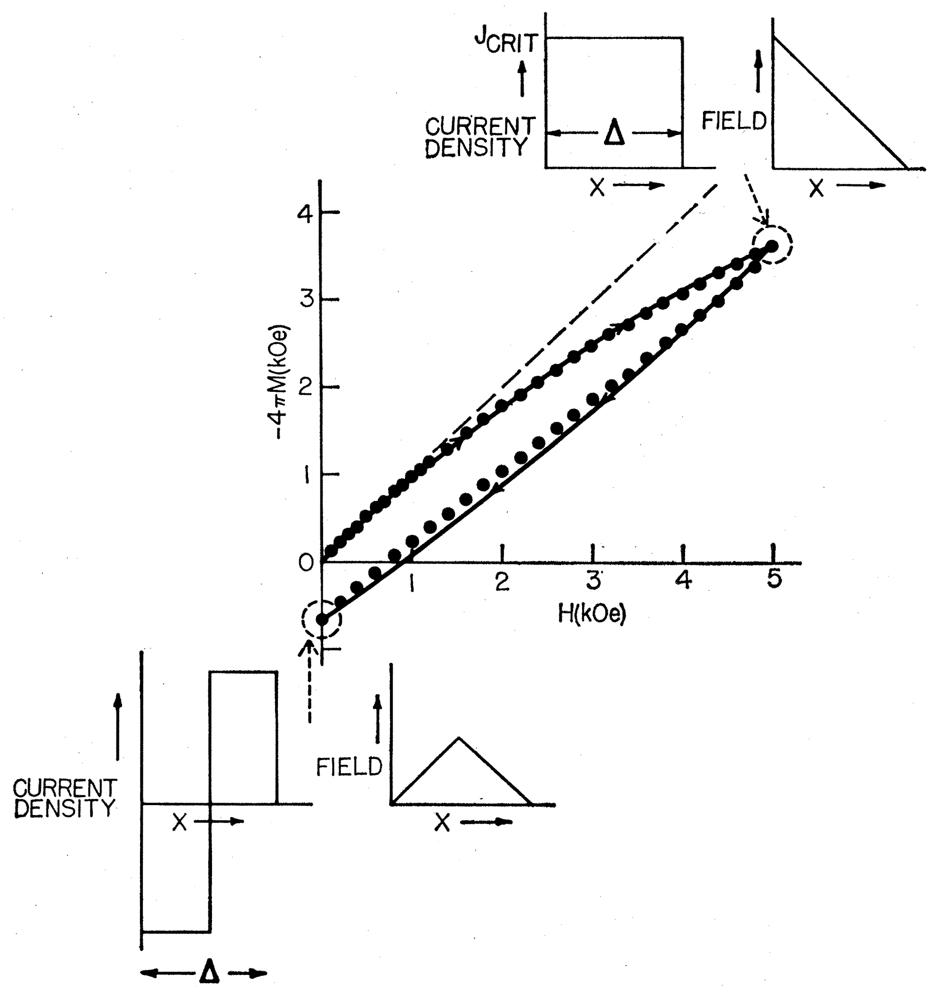


Fig. 6. Magnetization and demagnetization curves of V_3Ga. (Dashed line) The result expected if flux were completely excluded. (Solid line) The theoretical expectation, based upon the model implied by the sketches. The critical current density is taken to be 66,000 amp/cm² and assumed to be independent of field. (Solid points) Experimental data (*51*).

mixed-state, high-field superconductor (*49, 50*).

Let us consider the filamentary material first. A simple model of these materials is a set of concentric, cylindrical superconducting films, less than the penetration depth in thickness, with insulating material between the cylinders and with the magnetic field applied parallel to the length of the cylinders. The model resembles the important features of filamentary materials in that it consists of very thin regions of superconductivity that are connected so as to permit circulating supercurrents around the direction of the field. When the field is applied, these supercurrents are induced in the shells. At a relatively low value of the field the current density in the outermost film reaches the critical value J_C, and thereafter, until the film finally transforms to the normally conducting state at the high field H_{CF}, the film carries the critical current density. When a film is carrying this current density, increases in field soak undiminished right through it and deeper films are brought, one after another, into the same "critical condition."

We can represent this state of affairs on a macroscopic scale where the individual films are indiscernible; this representation should yield a model which is not too closely tied to the structure of concentric cylindrical shells and which is therefore appropriate for any highly interconnected filamentary structure. The representation is as follows. As the impressed field increases it induces a current of macroscopic critical density, J_{CRIT}, to flow, first near the surface, then deeper and deeper in the sample. For each value of the impressed field there is a depth from the surface, Δ, in which J_{CRIT} is flowing and beyond which the current is zero. The value of J_{CRIT} is fixed by the product of J_C for the individual films or filaments and the density of their distribution in the sample. Decreasing the impressed field induces J_{CRIT} to flow in the opposite direction at the outer surface, and reducing the external field to zero leaves the sample with currents flowing in this counterdirection in its outer parts and flowing in the original direction farther in. Therefore the magnetization processes are not reversible in filamentary materials.

With these physical assumptions about the behavior of induced supercurrents, one can work out the distribution of fields within the sample by using Maxwell's equations. The current and field distribution for the first application of a field are shown in Fig. 6. The magnetic induction B is, by definition, the volume average of the local field in the sample, and it is calculated from the field distribution. The magnetization, $4\pi M$, is calculated from the usual relationship, $B = H + 4\pi M$. Figure 6 shows part of a hysteresis loop, calculated with one adjustable parameter (J_{CRIT}), as compared with experimental data (*51*).

In this calculation the critical current density has been assumed to be independent of field. This assumption is not valid for all materials and conditions (*52*), but the analysis may easily be extended to include this variation.

A filamentary material could be made up of interconnected networks of line defects, such as dislocations (*53*), or of precipitates or composition fluctuations in alloys and compounds. In this case the filaments might be imbedded in another superconductor, and the foregoing theory would have to be modified slightly.

One of the principal predictions of this theory is that the magnetization of samples is size-dependent, decreasing as the size of the sample decreases. The magnetization of several common high-field superconductors follows this prediction. An example is V_3Ga; the hysteresis loop of Fig. 6 is actually one for a synthetic filamentary material. From the value for J_{CRIT} needed to fit the data and an estimate of the J_C that filaments of V_3Ga might have, one would conclude that only a fraction of 1 percent of the sample consisted of connected filaments. However, specific-heat measurements (*54*) in high fields show that a large fraction of the material remains superconducting in high fields. This result is what would be expected of a mixed-state superconductor, and we must next consider these materials.

In 1935, H. London recognized (*12*) that, on the basis of the London theory and thermodynamic arguments alone, even an ideal superconductor such as lead would be expected to dissociate into the mixed state in a field. The reason why this would be expected is as follows: If the superconductor in a field $H_0 < H_C$ were to break up into infinitesimal sheets of normal phase separated by superconducting layers thin enough to be penetrated by the field, the excluded flux would enter

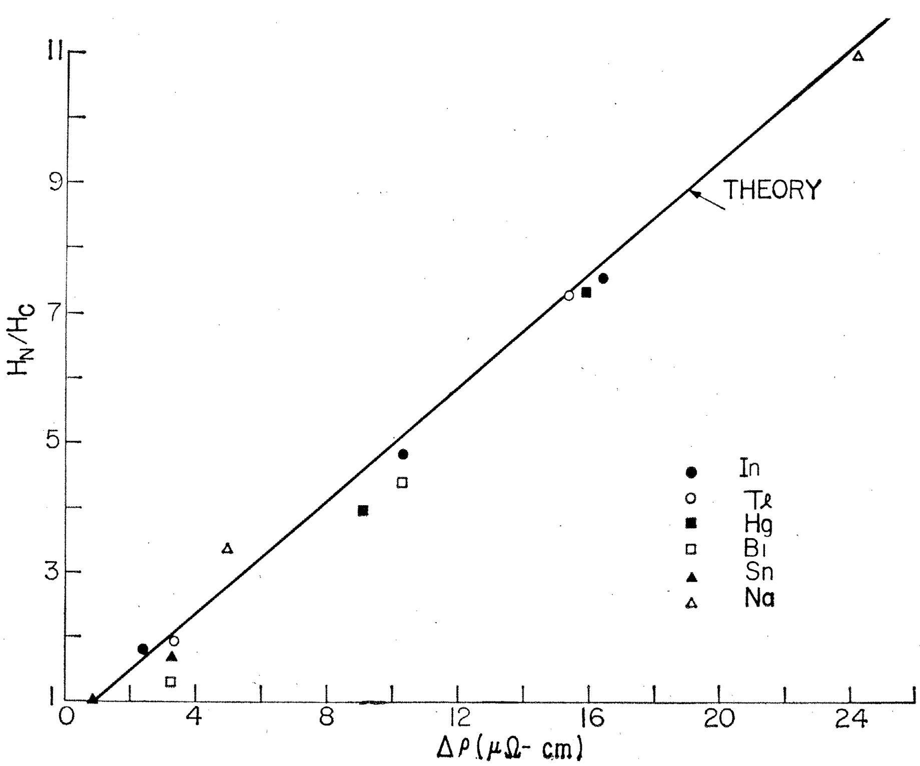


Fig. 7. The properties of mixed-state superconductors as a function of the resistivity in the normal state (*50*). The ratio, H_N/H_C, of the upper critical field to the thermodynamic critical field for various lead alloys is plotted against the extra resistance, $\Delta\rho$, introduced by alloying. The solid line is derived from the theory of mixed-state superconductors, with no adjustment of parameters.

through the normal sheets and spread out through the thin superconducting layers. Thus, the field energy due to flux expulsion would be eliminated, and this would cost only the condensation energy of the infinitesimal amount of superconducting material that would be converted to the normal state.

The structure is one that maximizes the area of interface between superconducting and normal regions while minimizing the volume of normal phase; because of field penetration into the superconducting phase the surface energy between normal and superconducting phases is negative! The exclusion of field from a region bounded by a surface enclosing only superconducting phase costs energy of $H_C^2/8\pi$ per unit volume of that phase. But because the field can penetrate by an amount characterized by λ, the energy of flux expulsion is changed by $-(H_C^2\lambda/8\pi)$ per unit area of interface. As ideal superconductors do not dissociate into the mixed state, there must be a positive interfacial energy that outweighs this negative London term, and the total surface energy may be written:

$$\alpha_{ns} = \frac{1}{8\pi}\left(H_C^2\,\xi - H_C^2\lambda\right) \qquad (8)$$

In ideal superconductors from which flux is completely excluded in fields of less than H_C, ξ must be larger than λ.

The distance ξ is called the range of coherence; it exists because the state of electronic order represented by the superconducting phase cannot change abruptly into that of the normal phase. The London theory improperly assumes that this change is spatially discontinuous. In 1950, two proposals were put forward to account for the positive surface energy, one by Pippard (*55*) in England, the other by Ginzburg and Landau (*15*) in Russia. These two theories, which at first seemed quite different, lead to similar conclusions about the surface energy (*39*): it is positive in ideal superconductors because the distance needed for the electronic configuration to change from that of the superconducting phase to that of the normal phase is larger than the penetration depth λ. Measured values of ξ are of the order of 10^4 angstroms in a pure material, while λ is usually a few hundred angstroms.

The idea of a positive interfacial energy explains why ideal superconductors do not dissociate into the mixed state and also points the way to converting an ideal material into a mixed-state material: the range of coherence, ξ, must be made less than the penetration depth λ. This is accomplished by adding impurities or alloying elements to the base metal, because these impurities scatter electrons and shorten the distance over which it is possible for a change of electronic configuration to occur (*56*). Scattering by impurities governs the resistivity of metals in the normal state at very low temperatures, hence one would expect the interfacial energy, α_{ns}, the field for onset of the mixed state, H_{FP}, and the field for complete flux penetration, H_N, to be related to this resistivity. This expectation is confirmed by experiment. Figure 7 shows the ratio H_N/H_C as a function of the residual resistivity of a series of lead alloys and demonstrates that the field, H_N, for the final transition from the mixed state to the normal state in this series is fixed by the residual resistivity (*50*). The line marked "theory" in Fig. 7 is calculated (*57*) from the theory of Abrikosov (*17*), and there are no adjustable parameters in fitting the curve to the data. The agreement is remarkable. Abrikosov's work, based on the ideas of Ginzburg and Landau (*15*) supplemented by the theoretical results of Gor'kov (*58*), suggests a structure for the mixed state in which the field pierces a regular array of threads running parallel to the field and spreads out into surrounding material. An alternative approach to the theory of the mixed state has been to assume it to be a laminar structure of alternating thin superconducting and thinner normal regions (*59*), a structure originally proposed by H. London (*38*). The two views are alike in their major conclusions, although Abrikosov's results agree better with detailed experimental measurements.

If, in Eq. 8, ξ is less than λ, then flux is completely excluded only up to field intensity $H_{FP} = H_C(\xi/\lambda)^{1/2}$, which is less than H_C. At this field intensity flux begins to enter, the mixed state occurs, and there is a gradually dimin-

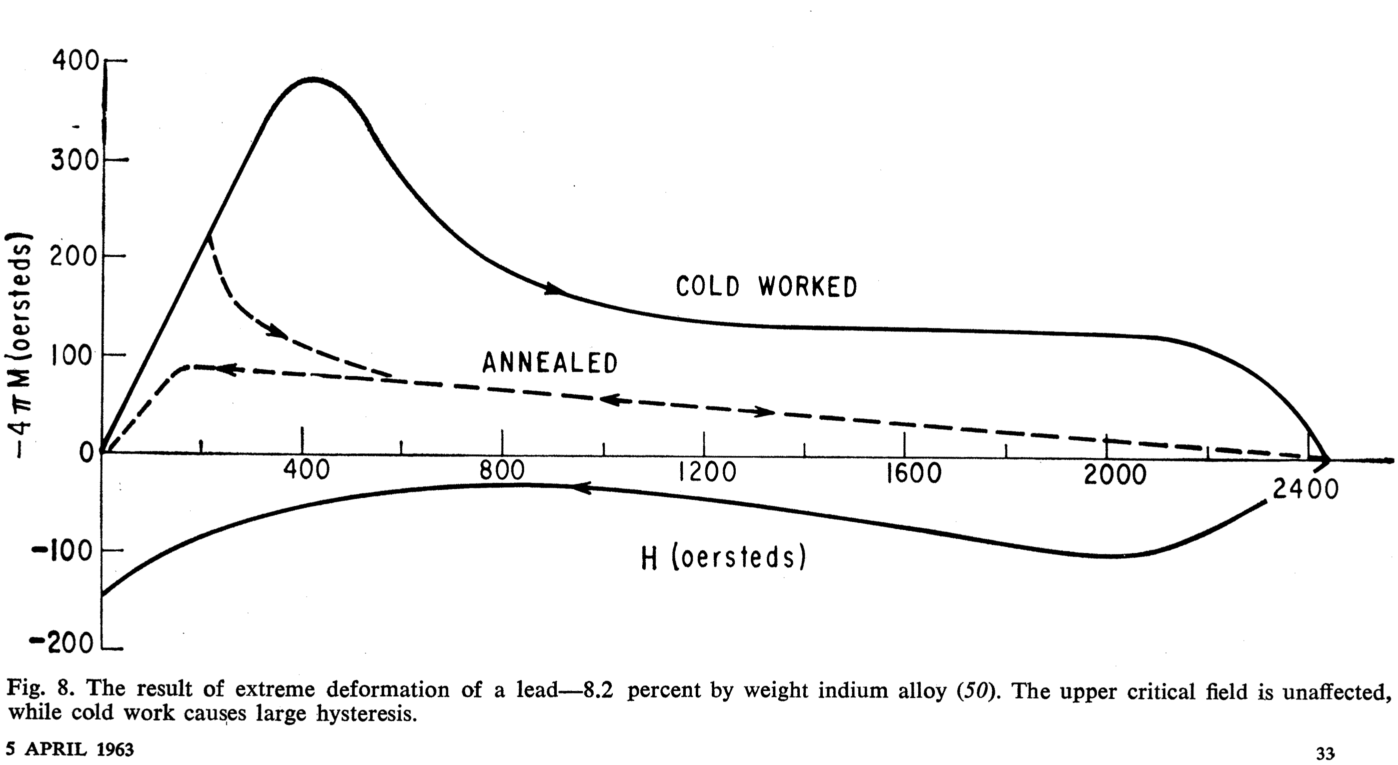


Fig. 8. The result of extreme deformation of a lead—8.2 percent by weight indium alloy (*50*). The upper critical field is unaffected, while cold work causes large hysteresis.

ishing flux exclusion until the sample becomes completely normal at $H_N > H_C$. The theory of the mixed state therefore also predicts a magnetization curve like that of Fig. 5*b*, a curve which is reversible in contrast to the one of Fig. 5*a* for a filamentary material.

Each of the two models is sufficient to explain the persistence of superconductivity in very high fields, and each depends ultimately on the fact that magnetic fields can penetrate slightly into the superconducting phase. Beyond that, the models lead to different predictions about properties. The ultimate critical field, H_N, is fixed by filamentary dimensions on the one hand, by electronic structure and electronic mean free path on the other. The magnetization is hysteretic and size-dependent in one type of material, reversible and size-independent in the other type. These contrasts should make it simple to decide which model is applicable to each high-field superconducting material, but there are complexities that obscure this clear-cut distinction.

Real Materials

The filamentary model predicts the magnetization properties of large samples of V_3Ga, but specific-heat measurements at high fields show that more of the sample remains superconducting than would be expected on the basis of this model. These contradictory observations emphasize the fact that although the broad principles of high-field superconductivity may be known, application of those principles to real materials is incomplete. Nevertheless, a beginning has been made.

Intermetallic compounds such as V_3Ga, Nb_3Sn, and alloys such as Nb-Zr and Mo-Re, as commonly prepared, contain composition fluctuations or other phases and are full of defects. Even if these materials would be mixed-state superconductors in a pure, homogeneous, undeformed state, their properties would be changed by flaws and inhomogeneities. But should we expect them to resemble filamentary materials, as they seem to?

Experimental evidence favoring this conclusion is shown in Fig. 8, from the work of J. D. Livingston (*50*). An annealed sample of lead-indium alloy shows the behavior expected of a mixed-state superconductor. But, upon deformation, the magnetic hysteresis becomes large, like that of a filamentary material, and implies high critical current densities. These currents disappear at exactly the same field as that at which the mixed-state disappears. In further experiments Livingston showed that annealing restored the properties of the relatively pure mixed state. This result is similar to the behavior of the niobium-zirconium alloys shown in Fig. 1, where the upper critical field is unaffected by deformation while the current density is greatly increased (*60*).

Granted that intrinsic mixed-state behavior may be concealed by irreversibilities due to flaws, is there a way to reveal the nature of the underlying material? As stated earlier, the magnetization of a filamentary material is a function of sample size and its hysteresis diminishes with size, whereas the magnetic properties of the mixed state are independent of size. Therefore, if the filamentary model is applicable to inhomogeneous, imperfect, mixed-state materials, their hysteresis should diminish with size, and measurements on fine particles or thin films should reveal their intrinsic nature. P. S. Swartz (*61*) has studied powders of Nb_3Sn, Nb_3Al, V_3Ga, and V_3Si, and J. Hauser (*62*) has studied films of V_3Si; each found that the magnetization of these small samples approaches the curve characteristic of a mixed-state superconductor. Also, B. B. Goodman (*63*), by analyzing the specific-heat data on V_3Ga, extracted the reversible magnetization curve and concluded it was that of a mixed-state material.

The evidence gathered so far suggests that many of the practical high-field superconductors are intrinsically mixed-state, and that their upper critical fields, H_N, are therefore determined by their electronic structure and normal-state resistivity. However, in the usual condition of preparation, the magnetic properties are those one expects from the filamentary model.

It is possible that this apparent contradiction can be easily resolved. The threads of flux that compose the mixed state must, in the course of magnetization, come through the outside surface of the specimen. If there is any impediment to their motion, such as bits of a nonsuperconducting phase, the threads of flux will tend not to move until they are pushed along from behind by more threads of flux. The threads of flux interact only over very short distances because the superconducting currents that compose them extend only to the depth of penetration. Consequently, the net applied force on a given flux thread is proportional to the local gradient of the density of flux threads. If the resisting force of the distributed imperfections is constant throughout the specimen, the gradient of the density of flux threads—that is, the gradient of field—will be a constant. According to Ampere's law this is equivalent to a uniform critical current density. Hence, the magnetic properties will be exactly those calculated earlier for the filamentary model. It is too early to state whether this or related points of view (*64*) are correct, but the importance of the problem of the interaction of flux threads and material imperfections is clear.

Summary

The recent burst of effort in the area of high-field superconductors has led to the construction of 70,000-oersted coils and the expectation that 100,000-oersted fields will be attained in the near future. The general theory suggests that fields above 300,000 oersteds are conceivable and that current densities of millions of amperes per square centimeter may be attained. Theory and experiment suggest that the upper critical field of materials such as Nb_3Sn and $Nb_{.75}Zr_{.25}$ is determined by their tendency to form a mixed state, and that a crucial question concerning their other properties is that of the interaction of this mixed state with imperfections. Lastly, it is possible to make a synthetic high-field superconductor by mechanically subdividing an ideal superconductor.

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News and Comment

Graduate Aid: Poll of Educators Suggests That Needs Vary Widely in Scientific Disciplines

In the debate over how this country can produce more scientists and engineers, two conflicting articles of faith endure side by side: graduate support is now so abundant that even a mindless warm body finds the government ready to foot the bill for an advanced degree; and lack of financial assistance prevents many qualified students from continuing their studies.

The latter point of view is held by the President's Science Advisory Committee (PSAC), which last December recommended a financial aid program aimed at achieving an "abrupt increase" in the percentage of undergraduate science and engineering majors going on to graduate study. The committee said the increase could be achieved without a decline in quality, principally by removing financial barriers to graduate training (*Science*, 21 Dec. 1962). The proposal was attacked by a number of scientists and educators on the grounds that just about anyone capable of absorbing graduate training can now find fairly generous support, and that an abrupt increase was to be had only by accepting students of questionable ability.

Since the debate, unfortunately, is accompanied by a remarkable dearth of reliable statistics, *Science* thought it might be useful to ask the chairmen of undergraduate science and engineering departments (i) how their students were faring in obtaining assistance for advanced studies, and (ii) what governmental steps they would propose to expand the nation's supply of scientists and engineers. Accordingly, questionnaires were sent to 750 undergraduate chairmen in the so-called EMP (engineering, mathematics, and physical sciences) fields, covering every such department that turned out more than ten majors in these fields in the 1959–60 academic year. Within a month, 347 usable replies came back, providing a fund of information that suggests that a great deal of the debate simply has not been dealing with reality. After paying due homage to the perils of polling, it appears that the adequacy of support varies widely among the disciplines, and that a shotgun approach to graduate aid would justify the fears of the critics.

The key question in the poll ran as follows: "In recent years, the number of graduate fellowships from various sources has increased. Based on your own experience with recent students at your institution, has the increase been sufficient to insure that all of your qualified and interested graduates desiring assistance for graduate study have been able to obtain it?"

The 347 replies can be tabulated as follows:

	Yes	No	Uncertain
Mathematics	46	38	7
Engineering	28	61	5
Chemistry	87	7	
Physics	43	25	
Total	204	131	12