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Superconductivity

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SUPERCONDUCTIVITY

1

Plenary Topics

A Survey of Superconducting Materials

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Introduction

This paper provides an overview of superconducting materials for nonspecialists in this currently very active field of research. Several new classes of materials have emerged in the past two or three years, and some of them offer promise of higher critical temperatures—although new records have not yet been achieved. Several of the hydrides of the transition metals have recently been found to be superconducting, for example, thorium hydride, Th_4H_{15}, discovered by Satterthwaite and co-workers[1] at the University of Illinois. Hydrogen has also been introduced into palladium by ion implantation; the system becomes superconducting close to 10°K.[2] Another interesting class of superconductors involves layer compounds, such as tantalum disulfide, which were shown to have very interesting asymmetric superconducting characteristics by Geballe and co-workers at Stanford.[3] Recently Matthias and co-workers[4] have discovered a new ternary group, typified by $LiTiS_2$, in which critical temperatures as high as 17°K have already been achieved. All these materials are discussed elsewhere in this volume and we shall not elaborate on them here.

We have chosen instead to focus most of our attention on the β-tungsten or A15 group of superconductors, for two reasons. First, these materials still offer the highest critical temperatures known at the present time. Second, they offer a fascinating set of electronic, lattice, crystallographic, and defect properties which impact directly upon superconductivity. These properties have been investigated to a greater extent than for any other class of superconducting compounds. We can expect to find similar behavior in other high-T_c compounds as more detailed studies are made, but for the most part this has not yet been done.

In order to obtain a proper perspective on superconducting materials, it is also necessary to have some idea of potential uses. Therefore, we include a few comments on what has to be done to go from a raw superconducting material to a wire or cable which is of value to electrical technology.

A simplified historical overview of the subject is provided by Fig. 1. By about 1940 most of the high-T_c elements had been identified and some pioneering work on sodium chloride-structure carbides and nitrides had been done by Meissner and Franz[5] in Germany. In 1950 Matthias and Hulm[6,7] began some experiments which led to the discovery of the high-T_c A15 superconductors, such as V_3Si and Nb_3Sn, and also superconducting alloys of transition metals, typified by niobium–titanium.*

*See Ref. 7 for a detailed list of references on high-T_c materials.

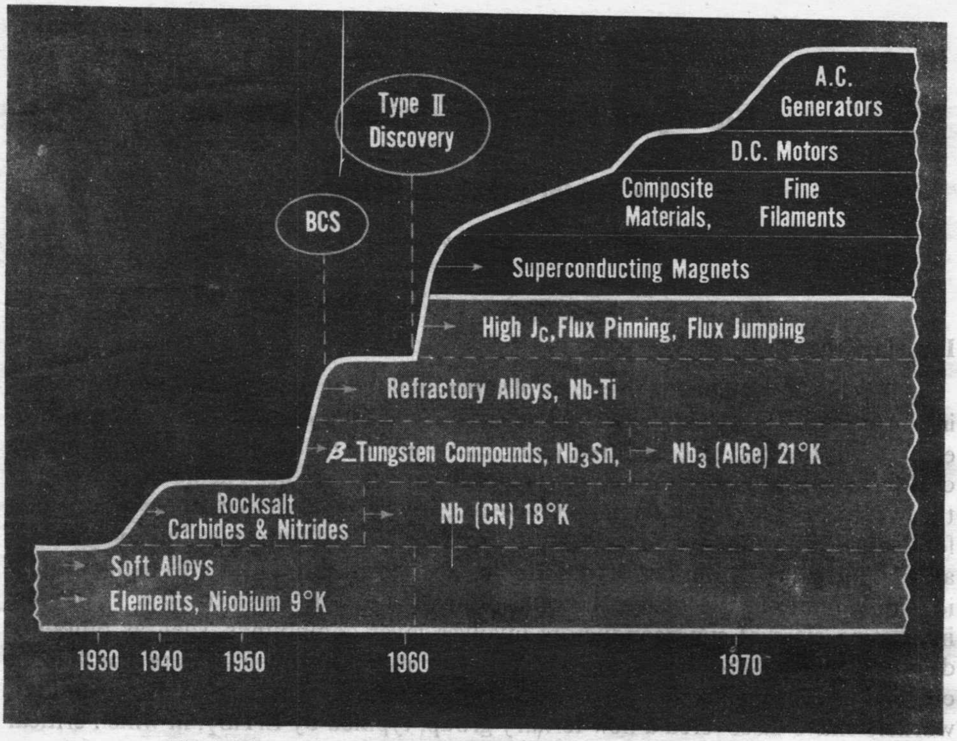

Fig. 1. History of superconducting materials and their applications.

A study of the magnetoresistance properties of Nb_3Sn by Kunzler and co-workers[8] in 1961 revealed the dramatic high-field and high-current-density properties of this class of materials, and triggered a whole new field of technology.

After 1961 the role of metallurgical defects in controlling the critical current density of type II materials was explored and the concept of flux pinning by defects became well known. The first application of these materials was in the construction of superconducting magnets. In this connection it was found to be good practice to form the superconductor into a composite structure with a good normal conductor such as copper. A further improvement was obtained by dividing the superconductor itself into a large number of fine filaments. The resulting "filamentary composite" conductors have proved to be eminently satisfactory for large magnet construction.

Recently an application of much greater industrial importance has emerged. In May 1972 it was reported at the Applied Superconductivity Conference in Annapolis that several prototype ac generators of a few MVA capacity were under construction. At the recent Cryogenic Engineering Conference in Boulder the successful completion and testing of a 5-MVA, 60-Hz generator was reported by Westinghouse.[9] The way is now clear for the construction of a much larger machine, in the 50–75-MW class. It appears that with a major effort a prototype machine of this class could be placed in a central power station by the middle or late seventies. At last superconductivity is on its way to practical application in a major industrial market. We may anticipate a large return on the investment in basic research which has already taken place, and a greater willingness to fund more research in the future.

Superconducting materials appear to hold great promise for future technological development. As far as ac machine applications are concerned, it would be useful to have materials with much higher critical temperatures, say 25 or 30°K. This would certainly ease refrigeration requirements. At the same time it must be emphasized that we have not yet been able to fully exploit the 21°K critical temperature already available to us. Present technological developments are based upon ductile alloys with T_c's around 10°K. This restriction is primarily due to the poor mechanical properties of the higher T_c compounds.

As far as basic understanding is concerned, the primary aim is, of course, to determine why certain special materials and certain crystal classes are favorable to the occurrence of high critical temperatures. Over the years some progress has been made toward this goal. Following the advent of the BCS theory, the theory of superconducting interactions was gradually refined. It is now possible to make reasonably good calculations of T_c for certain simple materials. For the most part, however, theory has tended to lag well behind experiment in this field.

The reasons for theoretical difficulty are not hard to find. High-T_c materials are really quite complex systems. Their electronic and lattice structures are quite inaccessible experimentally, and they are rarely well characterized in a materials science sense. This is not to imply any "alchemical" attributes to these materials, but merely to say that we seldom have exact knowledge of factors such as composition, secondary phases, vacancy content, degree of long-range ordering, and so on. These parameters are known to affect T_c, and sometimes even dominate it.

We believe that the creation of a satisfactory general theory for all materials is an illusory goal. Progress will best be made by painstakingly building up a series of quasiempirical models specialized to various material situations. Our aim here is to discuss some of the experimental factors which seem to be important in influencing T_c and which should presumably enter into such models. We hope to indicate some of the areas of ignorance and to give some guidance as to what might be done in future experimental work to close these gaps.

High-T_c Superconductors

Due to their restricted numbers, the elements are of quite limited interest from a superconducting materials viewpoint, and we have to deal mainly with alloys or compounds. Superconducting binaries and ternaries are readily formed all over the periodic system, but as far as high T_c is concerned, the greatest interest is centered around the transition metals, in particular niobium and vanadium.

The most prominent transition metal systems are: (1) body-centered cubic alloys such as Nb–Ti, $T_c \sim 10$°K; (2) B1 (rocksalt) structure compounds such as NbN and Nb(C,N), $T_c \sim 18$°K; (3) A15 (β-tungsten) structure compounds such as V_3Si and $Nb_3(Al,Ge)$, $T_c \sim 21$°K.

The first two classes have been discussed quite extensively in recent reviews,[7,10] and will not be further analyzed here. We have chosen instead to focus our attention upon the third group, which has so far offered the most spectacular examples of