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Superconductivity of Thin Film Intermetallic Compounds

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Investigations of both the macroscopic and microscopic properties of thin film superconducting materials are being carried out. Compounds under study are either technologically significant or involve possible unique mechanisms for superconductivity whose realization may extend the range of critical parameters. Under study are low carrier density superconductors, selected Heavy Fermion Compounds and Chevrel phase superconductors. High-quality superconducting films of both PbTe(Tl) and mixtures of La$_2$S$_2$-La$_3$S$_4$ have been prepared. These materials are low-carrier-density superconductors. This work is an important step in the direction of fabricating three-terminal superconducting (FET-like) devices. Films of UPt$_3$ have been produced which exhibit superconductivity. The goal of demonstrating the nature of superconducting pairing in this heavy fermion compound using tunneling and the proximity effect is in sight. Domain wall superconductivity has been demonstrated in the ferromagnetic phase of HoMo$_6$S$_8$, a Chevrel phase compound which is a reentrant superconductor.
SUMMARY

Microscopic as well as macroscopic properties of selected thin film superconducting compounds are being investigated. The particular materials being studied are either important for some aspect of superconducting electronics, such as the implementation of a superconducting FET, or involve possible unique mechanisms for superconductivity whose realization could extend the known range of critical temperatures or critical magnetic fields upward.

Under study are two types of low-carrier-density superconductors, Tl doped PbTe and the La$_2$S$_3$-La$_3$S$_4$ mixture system. The motivation for this work is the demonstration of a three-terminal superconducting device with input-output isolation and gain, which would be based on the superconducting field effect. La$_3$S$_4$ is also a high-critical field material with $H_{c2}$ the order of 20 T. The films of PbTe(Tl) have been grown by molecular beam epitaxy.

Processing of the lanthanum sulphide compound films has been carried out in a multi-source deposition system with a combination of molecular beam and electron gun sources.

Films of the heavy fermion compound UPt$_3$ have been fabricated using a dc sputtering technique. Superconductivity has been observed for the first time in films of this material. This work greatly increases the chances for being able to carry out a definitive study of the mechanism for superconductivity of the heavy fermion compounds using the proximity effect and electron tunneling. This problem is of interest because of the possibility of triplet rather than singlet pairing in such systems. The technology we have developed to produce UPt$_3$ films is also being used to
grow films of UBe$_{13}$ and CePb$_3$ which are also heavy fermion superconductors. The latter is also a high-critical field material. Our studies of polycrystalline films of HoMo$_6$S$_8$ has been completed. We have shown that the zero resistance in the ferromagnetic phase of these reentrant superconducting compounds is in part a consequence of superconductivity on the domain walls of the ferromagnetic state. Some of the supercurrent observed at low temperatures may be associated with superconductivity in the grain boundaries. In either instance there must be significant supercurrent flow through ferromagnetic material.
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I. INTRODUCTION

The investigation of thin-film superconducting compounds is an important tool in furthering the fundamental understanding of the phenomenon of superconductivity. Also thin film superconductors are very important for many technological applications of superconductivity, both on the large-scale and in superconducting electronics. In the fundamental area, the thin film geometry is useful in the characterization of both macroscopic superconducting properties such as critical fields, critical currents, and critical temperatures as well as microscopic properties such as the electron-phonon spectral function, a quantity obtained through superconducting tunneling studies. With the introduction of ultra-high vacuum thin film fabrication techniques into the processing of compounds, the promise of better materials with higher critical temperatures and critical magnetic fields for large scale devices, as well as better-controlled devices for electronic applications may indeed be fulfilled. A unique feature of research in this field is that the development of technology at a level adequate to carry out fundamental scientific studies often facilitates the applications.

This report will describe progress during the second year of a program of research on thin film superconducting compounds which began 1 September 1984. The effort is focussed on the fabrication of compounds employing techniques such as dc sputtering and electron beam co-evaporation. Materials which are currently being studied include several low-carrier-density superconductors, heavy fermion compounds, and superconducting
Chevrel phase compounds. An important aspect of the work is the correlation of microscopic and macroscopic superconducting parameters with composition and structure. Only in this way can a detailed understanding of specific properties emerge. Microscopic properties are being investigated using electron tunneling and the usual macroscopic properties such as the critical current, critical magnetic field and critical temperature are measured. X-ray diffraction analysis is the primary structure determining tool. Although Auger Electron Spectroscopy (AES), X-Ray Photoemission Spectroscopy (XPS), and electron microprobe analysis are the primary chemical tools, magnetic susceptibility analysis has been found to be useful for detecting magnetic impurity phases. A superconducting susceptometer commissioned this year has been found to be a useful tool in this regard. Morphologies are investigated using scanning (SEM) and transmission electron microscopy (TEM). A scanning tunneling microscope (STM) is being developed for routine morphological and spectroscopic (electronic) study of compounds at low temperatures.

The fundamental scientific studies being conducted under this program involve materials efforts which are intimately related to those needed for the development of superconducting technology. The problem that must be solved to optimize the superconducting properties of a film for scientific study are not unrelated to those encountered when the material or related one is to be optimized for use as a conductor in an electromagnet. Also the problems solved in preparing tunneling junctions for credible microscopic studies are closely related to the processing problems that must
be solved in the preparation of tunneling devices for superconducting electronics.

II. PROGRESS

A. Facilities

All modifications of the multi-source electron beam deposition system are fully operational. These include improvements in the sample insertion system, the noncontacting temperature sensing system and the rate monitor/controller using a Hewlett-Packard 150 computer system. Substrate fixturing which allows the loading of the system with a dozen substrates at a time is also operative.

The second dc sputtering system has been modified in a way which will permit the sputtering fixture to be isolated from the main vacuum chamber and removed to a glove box without contaminating either the vacuum chamber or the environment. This has been done to insure the safety of personnel working with intermetallic compounds containing Be.

B. Low-Carrier-Density Superconductors and the Superconducting Field Effect

This work is driven by the desire to develop a three-terminal superconducting device using the field effect. In such a device the carrier concentration in a superconducting layer would be changed by biasing a gate. This in turn would bring about a change in the superconducting transition temperature of the layer. If a three-terminal superconducting switch with isolation, high-speed, low-power dissipation and gain can be
developed, the advantages of superconducting digital electronics relative to semiconductor electronics in the areas of power dissipation, packing density and ease of interconnection might be practically realized. Also a superconducting transistor-like device could have other applications in small-scale superconductive electronics.

One route to the production of a superconducting device with FET-like characteristics is to use the field effect in a low-carrier-density-superconductor. A low-carrier density material is necessary because the field effect in ordinary metals is very weak. BaPb$_{1-x}$Bi$_x$O$_3$ would be an excellent low-carrier density material as its superconducting transition temperature is above 15 K. However, it is difficult to fabricate films in a controlled manner, and it is not a good candidate for a clear demonstration of the superconducting field effect. This is not to say that films of this compound may not be of interest in their own right, as some of the microstructural properties result in a film behaving as an array of Josephson junctions.

We have been investigating two types of low-carrier density compounds, PbTe doped with Tl, reported to be superconducting in the Soviet literature, and La chalcogenides of the Th$_3$P$_4$ type, in particular the La$_{x}$S$_{y}$ system. The compound PbTe(Tl) has been reported to be superconducting in bulk with a transition temperature above 1.4 K by Chernik and Lykov at hole concentrations of the order of 7.5×10$^{19}$ cm$^{-3}$. Although there had been reports of superconductivity on the surface of PbTe onto which Tl or Pb had been deposited, the superconductivity reported in earlier investigations of bulk PbTe(Tl) had been thought to be due to precipitated Tl or
precipitated Pb. The new Soviet work also suggests that the superconducting transition temperature was actually high relative to that of other low-carrier-density materials.

Our selection of PbTe(Tl) was thus motivated by the idea that it might be useful in demonstrating the practicality of a device, although not necessarily a useful one, because of the material's low transition temperature. We have been collaborating in this work with a group at the General Motors Research Laboratory which has served as a source of PbTe films grown using molecular beam epitaxy (MBE). We had been experiencing difficulty in reproducing the Soviet results on the bulk superconductivity of PbTe(Tl) in our epitaxially grown films. After traversing the entire range of concentrations over which superconductivity was reported in the Soviet literature, we found only a very slight indication of it at the heavily doped end of the range, where at about 0.070 K the resistance of the films was found to drop precipitously, but not to zero. Recently we have gone beyond the range of concentrations previously reported and have found superconductivity at about 0.6 K in PbTl(Tl) doped just short of a concentration which would result in the precipitation of Tl, and the possible formation of a superconducting network of Tl filaments. The resistive transition and critical field of one of the films are shown in Figs. 1 and 2.

These results do not necessarily imply that the Soviet work is incorrect although that is a distinct possibility. Alternatively there may be a difference in the way Tl dissolves in PbTe when the latter is grown from a melt, as the Russians grew it, or when it is grown from vapor as in
Fig. 1. Resistance vs temperature of a Tl$_2$-shaped PbTe film with a carrier concentration (holes) of $1.0 \times 10^{20}$ cm$^{-3}$.
Fig. 2. Critical field $B$ vs temperature for the film of Fig. 1. The upper and lower limits of the error bars denote the fields corresponding to 90 and 10 percent of the normal-state resistance.
our work. It should be noted that the carrier concentrations and transition temperatures that we find are reasonably consistent with those values reported for doped SrTiO$_3$ which is the prototypical low-carrier-density superconductor reported a number of years ago.\(^\text{11}\)

A paper describing our findings on these PbTe(Tl) films will be submitted to Solid State Communications in the near future. Even though the transition temperatures are low, we are in the process of using these PbTe(Tl) films to fabricate FET devices.

Because of initial disappointment and initial lack of success in obtaining superconducting PbTe(Tl) films, we initiated a parallel effort involving Th$_3$P$_4$ type La chalocgenides, in particular compounds in the La$_x$S$_y$ system. These materials are useful because La$_3$S$_4$ has a higher transition temperature than PbTe(Tl) and La$_2$S$_3$ is an insulator. Because the two have the same crystal structure, it may be even possible to prepare FET structures in which the base-layer and insulator are single-crystal. Furthermore, the preparation of these materials is compatible with the multisource deposition system in our laboratory in which sulfur is used to grow films of Chevrel phase compounds.

The system of compounds with La/S ratios ranging from La$_3$S$_4$ to La$_2$S$_3$ have been known for a long time. They have the unusual property that their conduction electron concentration follows the composition as La$_{3-x}$[\_]$_x$S$_4$ where [\_] denotes a vacancy and 0<\(x<1/3\).\(^\text{12}\) The important point is that these vacancies can be introduced into the La sublattice without destroying the Th$_3$P$_4$ crystal structure. This is the reason La$_3$S$_4$ and La$_2$S$_3$ can have the same crystal structure and the same lattice parameter.\(^\text{4}\) One can prepare a
continuous series of solid solutions between these two end members without any change in the crystal structure or lattice parameter. The remarkable feature of these compounds is that $\text{La}_3\text{S}_4$ is metallic and superconducting and $\text{La}_2\text{S}_3$ is an insulator. Thus the system permits a continuous change of electron concentration over a very large range and thus a wide variation of the superconducting transition temperature. The latter can be as high as 8.2 K with carrier concentrations of $1.5 \times 10^{22}$ cm$^{-3}$ and down to 1.0 K at concentrations of $5.5 \times 10^{21}$ cm$^{-3}$. Similar results have been found for the selenium and tellurium compounds. In the case of the former, the superconducting transition temperature can be as high as 10 K.

We have succeeded in preparing superconducting films of the lanthanum and sulfur compounds which appear to be well-ordered and free of impurity phases. The highest transition temperature that we have found is in excess of 8 K, which is very close to that reported for bulk material. See Fig. 3 for a curve of resistance vs. temperature and Fig. 4 for a typical X-ray pattern. Although we have not yet measured critical fields we know that they are high. The fifty-percent point of the resistive transition was reduced by 1 K in a film with a transition temperature of 8 K when a field of 4 T was applied. An account of this work will be submitted in the near future to Applied Physics Letters.

Because the multisource deposition system allows us excellent control of film composition, there is the remarkable possibility of preparing single crystal tunneling junctions with $\text{La}_3\text{S}_4$ electrodes and an insulator of $\text{La}_2\text{S}_3$. This structure could also be generalized to form a multilayer single crystal heterostructure, in which the alternating layers were superconducting and
Fig. 3. Resistance vs temperature of a La$_3$S$_4$ film which exhibits a transition temperature as high as in bulk.
Fig. 4. X-ray diffraction pattern of an La$_3$S$_4$ film. The only resolved lines are those of the Th$_3$P$_4$ structure.
insulating or semiconducting. Such a structure might have important device applications even in the normal state if it could be made with high enough quality. A technology like that of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ could in principle be developed as $\text{La}_3\text{S}_4$ can be prepared in the form of single crystals which could serve as a starting point for an epitaxial process.

C. Heavy Fermion Compounds

These compounds have been extensively studied because of the remarkable fact that their electron effective masses can be as large as $1000^{14}$ times that of the free electron effective mass. This in of itself is an important puzzle. There are a number of unusual aspects of the superconductivity of these compounds which follow from this. First, the Debye temperature of these materials can be larger or comparable to the Fermi temperature. Consequently the initial steps in the standard theoretical analyses of solids are not valid and there is a strong possibility that the usual mechanism for superconductivity involving the retarded effective electron-electron interaction moderated by phonons is not producing superconductivity. The heavy fermion compounds are believed to involve higher spin and angular momentum pairing than is the case for the usual BCS superconductor which contains singlet pairs with zero orbital angular momentum.

We have continued our efforts at preparing thin films of $\text{UPt}_3$ which may be a heavy fermion compound which may be an anisotropic superconductor. Our work has continued in the direction of preparing thin films using a sputtering technique, which is also suitable for the fabrication of
tunneling junctions. With the latter we could investigate the Josephson effect and the proximity effect between heavy fermion compounds and ordinary superconductors, with perhaps a possibility of illucidating the mechanism for superconductivity in the heavy fermions in a definitive manner. The effort to obtain high quality films has been a major one which we have described in detail in previous reports.

We have actually succeeded in preparing UPt$_3$ films which exhibit superconducting behavior, albeit at reduced temperature. In Fig. 5 we show a plot of the temperature dependence of the resistance of one of our films. We do not consider these films to be satisfactory for use in our proposed investigations and are continuing to work to improve their quality. However, at long last we believe that we understand the nature of the difficulties we have been experiencing.

Measurements of the temperature dependence of the magnetic susceptibility of our best UPt$_3$ films revealed the existence of a ferromagnetic transition at 30 K in films that became superconducting below 1 K. This was initially very surprising until we found that the compound UPt is a ferromagnet with a Curie temperature of that value. Apparently our films were being produced with a UPt impurity phase which was undetectable using any of the standard chemical and structural studies we had previously carried out, only revealing itself after careful magnetic measurements.

Extensive research in the literature has revealed phase diagrams of both the uranium-platinum and the uranium-beryllium intermetallic compound systems. From these phase diagrams we believe that we can adjust the
Fig. 5. Resistance vs temperature of a UPt$_3$ film grown on a BeO substrate at 1200°C.
composition of the uranium-platinum sputtering target and the temperature of the substrate to eliminate the unwanted impurity phase, and also that we can very easily prepare high-quality films of $\text{UBe}_3$.

Another important aspect of the fabrication of high quality films appears to be the texture of the substrate. We have concluded that substrate smoothness is very important in determining the electrical properties of the films. The best substrates in terms of low chemical reactivity with uranium are those of $\text{BeO}$. Unfortunately, that material is generally available only in polycrystalline form. The structures of $\text{UPt}_3$ films prepared on cleaved, single-crystal $\text{MgO}$ were actually more ordered than those prepared on polycrystalline $\text{BeO}$, even though the oxide impurity level of the films was much lower when the latter were used. This has prompted us to search for a source of single-crystal $\text{BeO}$. We have found a small quantity available commercially and located a larger source at the National Museum of Natural History in Washington. The latter organization makes available small stocks of synthetic minerals for researchers.

The successful fabrication of $\text{UPt}_3$ films, which we believe to be close at hand, should enable us to carry out several studies which might resolve the question of the nature of the superconductivity of these compounds. The investigation of the thickness dependence of the superconductivity and the critical fields of thin films should enable us to determine whether surfaces are pair breakers. Successful fabrication of films will enable us to embark on attempts to fabricate high-quality tunneling junctions. The measurement of the gap parameter and the Josephson effect in a heavy fermion superconductor could result in a major contribution to the fundamental
understanding of these materials. Use of the high temperature sputtering technology that we have developed on $\text{UBe}_{13}$ should also greatly enhance the chances for success in this work.

D. Chevrel Phase Compounds

We have concluded our studies of the compound $\text{HoMo}_6\text{S}_8$. For the time being we are not fabricating other Chevrel phase compounds while we devote the sample preparation facilities to the preparation of the lanthanum chalcogenides. We plan to defer to a latter date tunneling studies of the Chevrel phase compounds. Here our findings relating to the macroscopic properties of $\text{HoMo}_6\text{S}_8$ will be summarized. Films of $\text{HoMo}_6\text{S}_8$ were fabricated using an electron beam co-deposition technique. They were found to exhibit superconducting behavior below the ferromagnetic Curie temperature. Extensive measurements of the temperature and magnetic field dependences of the electrical resistance, critical magnetic field, magnetization, and critical current were carried out on this low-temperature coexistence phase. From these measurements we could conclude that the zero resistance in the ferromagnetic phase is a consequence of superconductivity on either domain walls within crystallites, or domain walls associated with grain boundaries. In either instance there must be significant supercurrent flow through the ferromagnetic material.

An account of this work has been written up and submitted for publication in Physical Review B.
E. Scanning Tunneling Microscope

We have been developing a simple scanning tunneling microscope which could be used to study superconducting compounds. The design of the microscope is based on the Virginia/Santa Barbara instrument which has a very high degree of immunity to vibrations and represents a considerable simplification of earlier designs reported in the literature. Because scanning tunneling microscopes have atomic scale resolution and can be used for spectroscopic characterization as well as imaging, they represent an important advance over conventional microscopy.

We are presently in the middle of testing such a microscope at room temperature and in air. The essential design features should be easily adapted to a low temperature environment.

The current design employs tunneling between a tungsten tip mounted in a piezoelectric element that provides motion in the x-y plane. The sample to be studied is mounted on piezoelectric bimorph that allows adjustment of the tunneling distance in the z-direction.

The x-y translation stage is a monolithic structure machined from a block of piezoelectric ceramic, which provides a rigid system with low thermal drifts. The piece is machined and then poled so as to provide independent motion in the x and y directions. The tungsten tip is produced by etching tungsten wire in an NaOH solution and makes a sliding fit into a brass collet. The collet mounts directly into the x-y translation stage. The sensitivity of the piezoelectric material is such that scans of areas roughly 0.5 μm square are possible. For the sake of stability the high
voltage source used to drive the x and y motions are low-noise, computer-programmable 0-2 kV power supplies.

The sample is mounted onto the face of a circular bimorph, which is then mounted above the tungsten tip, insulated from the x-y stage by sapphire balls. The flexure of the bimorph provides a means of adjusting the tunneling distance. Coarse adjustment of the separation is achieved with a dc motor located below the x-y stage that drives a threaded rod into the brass collet and pushes the tip up towards the sample. A 126000:1.0 ratio gearhead allows coarse adjustment speeds down to 200 A/sec. The bimorph is used for the fine adjustment as part of a proportional-integral-differential control (PID) servo arrangement. The voltage to the bimorph is adjusted so as to maintain a constant tunneling voltage for a specified tunneling current, thereby maintaining a constant sample-to-tip distance. Fast response in the z direction to changes in surface topography is obtained by using a high-voltage operational amplifier in the output stage. The sensitivity of the bimorph and the present output stage allow vertical adjustments of nearly ±1 microm. Isolation from acoustic noise is achieved using an elastic suspension system of the baseplate, on which the microscope is mounted. Further attenuation is provided by a bell jar which allows the microscope to sit in vacuum.

Collection and display of data can be handled by a computer equipped with analog input and output for monitoring and controlling the x-y position as well as the feedback voltage regulating the x-direction.

Present testing of the microscope has been using deposited thin films and graphite. Large scale structures have been resolved on grafoil with a
characteristic size of several hundred Angstroms. Vertical stability is presently at approximately 2 Å, which has prevented imaging individual atoms, which should be possible with single crystal graphite. Improvements to the vibration isolation should provide the stability necessary to resolve large scale aperiodic structures. High speed scanning techniques are being developed that will permit imaging of spatially or temporally periodic structures, even in the presence of substantial noise.

References


17. O. T. Valls and Z. Tessanovic


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IV. PUBLICATIONS AND REPORTS


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