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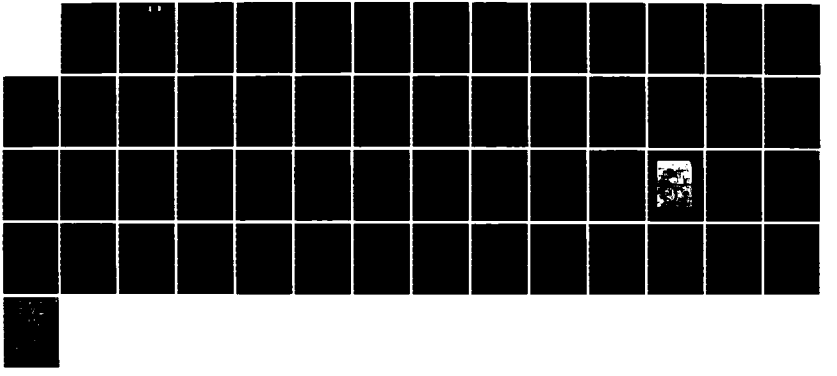

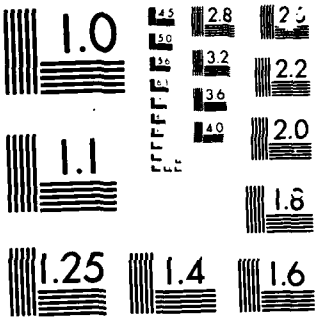

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SUMMARY

The macroscopic as well as microscopic properties of selected thin film superconducting compounds are being investigated. The materials being studied are either members of technologically significant systems or involve possible unique mechanisms for superconductivity whose realization should extend the range of critical parameters to either higher temperatures or higher critical fields. Materials under study are the superconducting Chevrel phase compounds, selected Heavy Fermion compounds and a low carrier density superconductor, Tl doped PbTe. The latter is being investigated with an idea to understanding the superconducting field effect. Processing of the Chevrel Phase compounds is carried out in a multi-source deposition system. The latter has been upgraded and improved during the grant period. The electrical and magnetic properties of the reentrant superconductor $HoMo_6S_8$ have been investigated in some detail with the magnetic and superconducting character of the low-temperature phase found to be dependent on the degree of disorder in the film. Single crystal films of the Heavy Fermion compound UPt_3 have been prepared. Although these films are highly ordered they have not been found to be superconducting, perhaps because they are off stoichiometry by as little as one percent.

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Superconductivity of Thin Film Intermetallic Compounds

Grant No. AFOSR-84-0347

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School of Physics and Astronomy, University of Minnesota

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Principal Investigator: Allen M. Goldman

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I. INTRODUCTION

The study of thin-film superconducting compounds has become an important frontier of the Science of Superconductivity for a number of reasons. 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. In addition, this geometry is frequently technologically important for both large-scale and small-scale applications of superconductivity. With the introduction of modern ultra-high vacuum techniques into research on the preparation of compounds, the promise of better materials with higher critical temperatures and critical magnetic fields for large scale applications, and better devices for small scale applications may indeed be fulfilled. The remarkable feature of this research area is that the technology required to carry out fundamental scientific investigations is frequently the same as that needed to facilitate the applications.

This report will describe progress in the first year on a program which began 1 September 1984. The effort was designed to take advantage of the control of chemical composition and morphology possible using thin film techniques such as sputtering and electron beam co-evaporation. Materials which are being investigated include the superconducting Chevrel phase compounds, the Heavy Fermion Compounds, and low carrier density compounds. A critical aspect of this work is the correlation of microscopic and macroscopic superconducting parameters with composition and structure. Microscopic

properties are being determined using electron tunneling, and macroscopic properties are found by measurements of the critical field, critical current and critical temperature. X-ray diffraction analysis is the primary structure determining tool, and Auger Electron Spectroscopy (AES), X-Ray Photoemission Spectroscopy (XPS), and electron microprobe analysis are the primary chemical tools.

It cannot be overemphasized that the fundamental scientific studies being conducted involve materials efforts which are intimately related to those needed for the development of technology. The optimization of the superconducting properties of a film for scientific study is not unrelated to the optimization of the material for use as a conductor in an electromagnet. Certainly problems of preparing a tunneling junction for credible microscopic studies are closely related to the processing problems in the preparation of practical tunneling devices.

II. PROGRESS

A. Facilities

The multi-source electron beam deposition system which is used to prepare many of the ternary and pseudoternary compounds that are being studied under the program has been upgraded. A sample insertion system with a vacuum lock has been added. The latter is pumped by a turbomolecular pump. This permits very rapid roughing out of the entire system as well as rapid sample insertion.

The vacuum system has been equipped with a noncontacting temperature sensing system which permits accurate determination of substrate temperatures. The system, supplied by Williamson[1], determines temperature by computing the ratio of radiant energies emitted from a surface in two adjacent wavebands. The signals are processed through a single silicon detector which views the substrate surface through a fiber optic link. The measurements are independent of the emissivity of the surface, but are affected by the general brightness in the vacuum system. Thus, this instrument is used either to calibrate thermocouples which measure temperature during depositions, or is used to control temperature during high temperature annealing when the electron guns are not operating.

The DCC-116 computer for evaporation rate monitoring has been replaced by a system which uses a Hewlett-Packard 150 computer. More importantly, a capability for extremely accurate measurement of the frequency of a crystal oscillator thickness monitor using sampling times shorter than are possible using pulse counting has been implemented. "Smart" frequency counters are used. These determine frequency by careful measurement of period rather than by counting in a fixed gate time. Resolution of one-tenth of a Hertz of 5 MHz signals, using sampling times of one-tenth of a second rather than a second is now possible. We have four independent channels of measurement and control. This new system will permit tighter rate control of processes involving very slow evaporation rates. As soon as sufficient results are available to warrant publication, a short note on this innovation will be submitted to an appropriate technical journal.

An additional change in the multisource deposition system has been the augmentation of the substrate fixturing to accommodate simultaneously twelve

separate samples with independent masking of each. This will greatly facilitate the fabrication of tunneling junctions in subsequent phases of the work as well as speed up the exploratory phases of the development of new thin film materials. Now the system can be loaded with up to a dozen substrates and a whole series of depositions made without disturbing the vacuum environment.

We have augmented our facilities in another manner. Using a UHV system given to us a number of years ago by Professor Peria we have set up a second dc sputtering system to operate in tandem with the one we have used for a number of years. This new system has fixturing identical to that of the older one and can use common instruments. The reason for establishing a second system was to increase the throughput of investigations that are possible using sputtering.

B. Chevrel Phase Compounds

Experimental work in this area has been concentrated on the study of $HoMo_6S_8$ films prepared during the fall and on new films prepared using a modification of the original techniques which will be described below. $HoMo_6S_8$ is being investigated because it is an excellent model system for the study of the interplay between ferromagnetism and superconductivity.[2]

A technique which we have called reactive annealing has been developed and is described in a publication which will appear in the October issue of the Journal of Vacuum Science and Technology.[3] The idea behind the technique is that a film can be re-introduced into the vacuum system after it has been initially prepared and studied and then annealed in the presence of a flux of

sulfur vapor. The process can be repeated many times if necessary. In the case of $HoMo_6S_8$ films it was discovered that as-prepared films were not superconducting, and that a few annealing cycles resulted in a film reentering the normal state. On the other hand, continued annealing, although resulting in an improvement of the resistivity ratio of a film, destroyed the reentrance into the normal state. Other investigators in Europe and Japan have prepared films of $HoMo_6S_8$ which never reentered.[4,5] Our films are the only ones in which reentrant behavior has ever been found.

The results of measurements of R(T,H) have been made to determine the nature of the nonreentrant, low-temperature phase of $HoMo_6S_8$. The results are particularly intriguing because the critical field curves of nonreentrant $HoMo_6S_8$ resemble curves reported for antiferromagnetic rather than ferromagnetic superconductors.[6] The only explanation for nonreentrant behavior advanced thus far has been that it is due to superconductivity in the grain boundaries of an essentially ferromagnetic material.[7] This explanation has really not been tested in a definitive manner. It is claimed, however, that the existence of large ferromagnetic domains are responsible for the extremely long time constants in response to a changing magnetic field which have been observed in the vicinity of 0.1 K. These are the order of hours in the case of our films which are the order of 1/2 μm thick.

An alternative explanation of these long time constants is the possible transformation by disorder of the RKKY interaction responsible for ferromagnetism to an antiferromagnetic interaction.[8] This appears to be supported by the critical field data. A third explanation is the possibility that an antiferromagnetic state is a consequence of the thin film geometry.[9] This prediction follows from the tendency for ferromagnetism to nucleate on

surfaces. We are attempting to distinguish between these various alternatives by studying the magnetic susceptibilities of films at low temperatures using a SQUID, and by investigating the properties of films as a function of thickness and disorder. The latter is a function of the degree of annealing.

Reactive annealing was reported at the APS March Meeting and the work on the long time constants was presented at the Conference on Superconducting Mechanisms and Materials at Ames, Iowa in April. An account of the work will be published in the proceedings of that conference.[10]

The improvement of the substrate temperature control in our vacuum system resulted in a minor setback in our production of Chevrel phase films, which, when resolved, ultimately led to an improvement of our fabrication process. The optical temperature monitor did not function correctly when the electron guns were operating because of the very bright glow from those sources. This forced us to change our process. Stoichiometric ratios of the constituents were deposited onto cold substrates and the reactive annealing process was then carried out after the film was formed. After a bit of experimentation it was found that very high quality films could be formed using this procedure in a highly reproducible fashion. The films, in addition, have smooth surfaces which should greatly enhance the chances for producing tunneling junctions. This new procedure appears generalizable to the other Chevrel Phase compounds which are of interest to us.

C. Heavy Fermion Compounds

These materials are of interest because of the remarkable fact that their electron effective masses can be the order of a thousand times greater

than the free electron effective mass.[11] A consequence of this is that the Debye temperatures of some of these materials can be comparable or even larger than the Fermi temperatures. Thus the usual approximations employed in conventional solid state theory are no longer valid. In addition, it is hard to understand how the superconductivity of these materials can be produced by the conventional electron-phonon mechanism in which the attractive interaction is a result of an "over-screening" of the repulsive Coulomb interaction. In essence an electron outruns its screening cloud. This cannot happen if the electrons are "slow" and cannot "outrun" their screening.

Thus from a fundamental point of view the heavy fermion compounds are important because of the large values of their effective masses, and because of unusual magnetic properties in the normal state which we have not discussed. Their superconductivity is unusual because it involves heavy mass electron quasiparticles and may involve either triplet pairs or some sort of spatially anisotropic pairing state.[12]

Although these materials have low transition temperatures, they exhibit remarkable high critical magnetic fields, and one heavy fermion compound, $CePb_3$, exhibits field-induced superconductivity at the 12 T level!![13] Its superconductivity begins at field levels where the superconductivity of most high field materials is beginning to disappear!

Our work on these materials has thus far been focussed on UPt_3, which is the best candidate for triplet superconductivity. Our efforts at preparing thin films of UPt_3 have continued along the lines indicated in our March report. We have succeeded in growing extremely well-ordered <u>single crystal</u> films using MgO substrates. The films are prepared using low-voltage dc sputtering with the substrates held at 1200°C. The presence of UPt_3 and the

absence of other phase, to the five percent level, have been determined from X-ray diffraction patterns which are extremely sharp. The patterns are sharper than those obtained from a single-crystal provided by J. Smith and Z. Fiske of Los Alamos Scientific Laboratory. The latter sample is known to be stoichiometric and superconducting. However, despite the highly ordered character of the structure of the films they have not been observed to be superconducting down to 0.050 K.

At first we thought that this difficulty was a consequence of strain resulting from the difference between the expansion coefficients of UPt_3 and the MgO substrates. We then developed a technology for floating films off of their substrates and annealing them in ultra-high vacuum at 1200°C. We then measured the properties of these free-standing films at low temperatures. This direction of research has also proved not to be useful.

Recently, we have carried out careful electron microprobe studies of both our single crystal films and the Los Alamos single crystal. These experiments have revealed about a 1.0% excess in the Pt concentration of our films relative to that in the single crystal. We are at present attempting to adjust the composition slightly, hopefully producing nearly ideal specimens of UPt_3. The resultant ordered thin film configuration should be ideal for developing definitive tests of the microscopic nature of the pairing and the mechanism for superconductivity in this material.

In addition, when we finally succeed in preparing superconducting UPt_3, the understanding of the absence of superconductivity in the samples we have prepared thus far should shed additional light on the mechanism for superconductivity in this remarkable material. This will require continued thorough structural and chemical characterization of the samples.

We have decided to prepare $CePb_3$, in addition to UPt_3, using dc sputtering in the same fashion. As was mentioned above, $CePb_3$ is a material which enters the superconducting state at a field of approximately 12 T. Its preparation using sputtering should be an easier problem than the preparation of UPt_3 because the requirements on crystalline perfection appear to be less stringent. We have commissioned a second sputtering system, as mentioned above, which will be used for this work. The goal will be to produce high quality thin films, and measure their macroscopic properties in the high-field superconducting state. In particular, we will be interested in critical currents and critical fields which may be easier to determine in thin film samples than in bulk. It may be possible to produce better samples than have thus far been studied in bulk. The latter have Pb precipitated at grain boundaries. As a result, their normal state properties can only be studied in a field large enough to quench the superconductivity to Pb.

Work on all of these areas will be reported in the literature as soon as it has reached a sufficient level of maturity.

D. Low Carrier Density Superconductors and the Superconducting Field Effect

As we mentioned in our report in March, the demise of the superconducting computer project at IBM was in part a consequence of the absence of a three-terminal switching device with FET-like characteristics. We suggested that it might be possible to achieve such a device using the field effect in low-carrier density systems. We filed an invention disclosure with the University and set out to fabricate such a device using Tl doped

PbTe, which has been reported by Soviet workers[14] to be a low-carrier density superconductor. Subsequent to the initiation of this effort we became aware of the work of two Japanese groups[15,16] demonstrating field effect superconducting devices based on the proximity effect driving an inversion layer into the superconducting state. Also, Hebard and Fiory at AT&T Bell Laboratories[17] demonstrated the field effect in thin films of indium/indium oxide. (The first work on the field effect was actually done by Glover and Sherill[18] and by Stadler[19] in the early and mid 1960s.) Also, a talk on the field effect in superconductors was given at the Gordon Conference on Superconducting Films held in August 1985.

With a high level of effort nationally and internationally in this area, and with the patent picture certainly cloudy, we decided not to develop PbTe doped with Tl in our own laboratory. We have instead arranged a colloboration with a group at General Motors Research Laboratory which is a source of PbTe films with epitaxially grown insulating overlayers. We are attempting to study the superconducting field effect using this material which is actually the best PbTe in the world.

The expitaxially grown overlayers are actually quite important as a major impediment to the use of the field effect to modulate the transition temperature of a superconductor will be the presence of traps in the insulating layer. These will collect charge that must be induced in the superconducting film if the field effect is to produce a significant change in T_c. Thus even though PbTe(Tl) is not a high-T_c material, studying the superconducting field effect using it will be useful because the insulating layer separating the film from the gate can be trap-free. Our collaborator at General Motors Research Laboratory is Dr. Dale Partin. We are in the process

of working with him to obtain the correct Tl doping of PbTe so as to attain superconductivity. Dr. Partin grows the material using Molecular Beam Epitaxy (MBE). He is also the developer of the technology for growing epitaxially a highly ordered oxide layer containing Eu on top of the PbTe. This material is the highly desirable insulator described above. Dr. Partin has thus far supplied us with samples that are doped with Tl to about 50% of the level reported by the Soviet group as being superconducting.[14] Our measurements of these indicate that they are indeed normal down to 0.05 K. We expect a shipment of more heavily doped material by the end of September. If this material is indeed a superconductor, then a primitive three-terminal device suitable for testing can be prepared rather quickly.

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III. PERSONNEL

A. M. Goldman, Professor of Physics and Principal Investigator

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IV. PUBLICATIONS AND REPORTS

1. "An Evaporation System for the Preparation of Ternary Compounds," R.J. Webb and A.M. Goldman, J. Vac. Sci. Tech., to be published 10/85.
2. "Reentrant Superconducting Behavior of $HoMo_6S_8$ Thin Films," J. Maps, R.J. Webb, J.H. Kang, and A.M. Goldman, Bull. Am. Phys. Soc. 30, 321 (1985), abstract of a presentation at the APS March Meeting.
3. "Superconductivity of $HoMo_6S_8$ Thin Films," J. Maps, J.H. Kang, and A.M. Goldman, to be published in the Proceedings of the Conference on Mechanisms and Materials of Supercondictivity, Ames, Iowa, 1985.

V. APPENDICES

Appendix A

An Evaporation System for the Preparation of Ternary Compounds*

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Abstract

A computer-controlled high vacuum evaporation system has been constructed for the fabrication of ternary compounds such as the Chevrel phase materials. The latter are formed on a substrate held at high temperatures with the constituent elements being deposited from some combination of electron beam sources, resistively heated Langmuir sources and Knudsen sources. Unique features of the system include the techniques employed to handle sulfur in a high vacuum environment, and the monitoring and control system used to ensure the formation of stoichiometric compounds with a high degree of compositional uniformity.

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I. Introduction

The preparation of superconducting compounds in the form of thin films is motivated in part by the relative ease of characterizing the macroscopic superconducting properties of materials in the form of thin films, and the possibility of studying microscopic properties using electron tunneling techniques. By and large the technology of forming binary superconducting compounds such as the A15 compounds using sputtering[1] or electron beam co-evaporation techniques is well developed.[2] The study of these materials is now in a highly quantitative phase. On the other hand, the investigation of the superconductivity of thin films of ternary superconducting compounds such as the Chevrel phase materials[3] is far less developed because of the difficulties of preparing high-quality samples of controlled composition and microstructure.[4] Chevrel phase materials which are of interest in superconductivity are of the form MMo_6S_8 where M is a metal ion. These compounds can also be formed with Se replacing S and depending upon M the compounds are either high-critical-field superconductors, magnetic superconductors, or magnetic compounds.

The fabrication of thin films of the Chevrel phase compounds containing sulfur as a constituent, is particularly difficult as a result of the essential incompatibility of sulfur with the ultra-high vacuum environment needed to prepare high quality films. Some progress has been made in the preparation of either these materials employing sputtering techniques using compound targets[5] or by reactive coevaporation techniques,[4] together with annealing in a sulfur atmosphere. However, these methods appear not to be totally compatible with the surface processing requirements for the fabrication of tunneling junctions.[6] It is with the latter in mind that we have developed

the system described below. As many of the features of the system involve standard technology, this discussion, in addition to providing an overview, will concentrate on the unique features of the apparatus which contribute significantly to its success in the fabrication of Chevrel phase compounds. In Section II we will describe the vacuum system. Section III will be concerned with the substrate mounting and heating. Section IV will treat the evaporation sources, concentrating on the special Knudsen source developed for the deposition of sulfur. Section V will contain a discussion of rate monitoring and Section VI will treat the problem of process control. The last section will contain a discussion of results and of an annealing technique which appears to be highly successful.

II. Vacuum System

The substrates, evaporation sources, and rate monitors are contained within an ultra-high vacuum chamber, the components of which are shown in the photographs which are in Fig. 1. This main chamber is pumped by a Varian VK-12 closed-cycle, helium-refrigerated cryo-pump, with a speed of 1000 liters per second. In addition, there are ion pumps with a combined speed of 400 liters per second. The chamber is lined with a thin-walled stainless steel shroud, which is filled with liquid nitrogen during the evaporation, in order to provide extra pumping and to capture stray evaporant. The chamber is also fitted with heating collars which allow it to be baked at a temperature of approximately 150°C.

A separately pumped antechamber is attached to the main chamber, via a gate valve, and is used to change substrates between evaporations. This antechamber precludes the necessity of opening the main chamber to atmosphere

between runs. Using the antechamber, changing the substrates takes about one hour, and background pressures before a run are typically about 5×10^{-9} torr.

III. Substrate Mounting and Heating

The evaporant materials are deposited onto single crystal Al_2O_3 substrates which are polished so as to be scratch free on one side when examined in a microscope with a magnification of 70X. The substrates are 2.54 cm by 0.625 cm by 0.05 cm thick, and are oriented with the c-axis in the plane which ensures that no substrate lines appear in an X-ray diffractometer scan. The objective in designing a substrate holder is to be able to measure the substrate surface temperature while thermally insulating the substrates from the rest of the apparatus. The holder must also have the capability of heating the substrates to high temperatures during a deposition. It is also necessary for the substrate holder to be compatible with a substrate changer with which insertion and removal from the vacuum system is accomplished.

The substrate holder is shown in Fig. 2. It consists of a stainless steel frame with a thin niobium bottom which holds the substrates. When in place, inside the main chamber, it is sandwiched between two boron nitride insulators. The top insulator separates the steel holder from the heater block, while the bottom one has the film masking pattern cut into it. The substrates are heated radiatively by the niobium block to temperatures between 700 and 1100°C. The block itself is heated by filaments which run through it.

The holder has an ear which mates to spring clip on the end of a magnetically-coupled, linear-motion feedthrough, used to insert and withdraw

the substrates from the main chamber. An indexing hole in the holder is engaged when the heater block is lowered. This positions the substrates relative to the mask disc. This feature is especially important for multiple processing, such as fabricating tunneling junctions.

Using the above-described substrate changing apparatus, it is not possible to have a thermocouple attached directly to the substrate which is the optimum way to measure substrate temperature. The thermocouple is, instead, supported in an alumina tube which presses it against the substrate surface. This method is susceptible to errors due to uneven contact pressure and conduction losses through the support arm. A non-contact, optical sensor will be installed in the future. An optical sensor should give a more accurate temperature reading as it does not rely on a pressure contact and will not suffer conductive losses.

IV. Evaporation Sources

There are four evaporation sources mounted in the main chamber, one four-hearth electron gun, a single hearth electron gun, a resistively heated dimpled tungsten boat and a molecular beam oven.

The molecular beam oven, which is shown in the photographs of Fig. 1, provides a clean, well controlled mechanism for handling sulfur in the ultra-high vacuum environment. It consists of a central crucible, made of copper, which is supported inside a copper water jacket by four thermoelectric heating elements. The water jacket is fed by a closed-cycle heating and cooling unit which is temperature controlled at all times. The jacket protects the crucible from radiative heating by the other sources, and is also used to bring it up to a quiescent temperature of about 80°C prior to a run. When the

oven reaches this temperature, the thermoelectric heaters are activated to further warm the crucible to its operating point, typically between 100 and 108°C. The power to the thermoelectric heaters is adjusted in order to control this temperature precisely. The temperature of the crucible is measured by a platinum resistance thermometer affixed to it with Torr-seal epoxy. All copper parts of the oven are gold plated to prevent attack by the sulfur.

Because the oven is a Knudsen cell or molecular beam oven,[7] it provides a well controlled stream of evaporant directed at the substrates. This feature precludes the necessity of having a high partial pressure of sulfur in the system, which is advantageous both from the standpoint of cleanliness, and because excess sulfur can cause operating problems for the electron gun sources.

There are two electron beam sources in the system. A single crucible electron beam source and a four-hearth source. One of the four crucibles of the latter is in use at any given time, and they can be switched without breaking vacuum. This allows, for example, using one crucible to evaporate a constituent of the Chevrel phase, and then using another to evaporate the barrier material for a tunneling junction. These electron beam sources are powered by an Airco model CV-14 14 kW power supply. Electromagnets in the sources can be coupled to an oscillator and programmable power supply to raster the beam. This is necessary when evaporating a refractory metal such as molybdenum at a low rate in order to prevent local melting of the pellet, which will eventually cause a hole to form in the charge. This hole collimates the evaporant stream, thus changing the distribution of evaporated material in an uncontrolled manner.

As mentioned previously, sulfur in the system can cause operating problems for the electron beam sources. These problems arise because sulfur deposits on the insulators of the high voltage gun filament feedthroughs, and causes them to arc. This problem has been eliminated by keeping the feedthroughs warm at all times, thus causing any sulfur which is deposited to desorb immediately.

In the present mode of operation, the electron beam sources are used to evaporate the metallic constituents of the Chevrel phase materials. These sources can also be used to evaporate insulators, such as Al_2O_3, which may be necessary for the in-situ fabrication of tunneling junctions.

The fourth source is a Langmuir, or open source, which is a resistively heated, dimpled boat made of either tungsten or tantulum. This source, which is powered by an Airco model CR-4 SCR controller and transformer, is used for evaporating materials, such as holmium, which sublime at a fairly low temperature. The boat heats the entire charge evenly, as opposed to the electron beam sources which heat the charge locally.

V. Rate Monitors

The deposition rate from each source is measured by a standard quartz crystal rate monitor. Each monitor has also been calibrated by carrying out a test evaporation and measuring the deposited thickness at the substrates using either an interferometer or profilometer to determine a correction factor.

The crystals have a finite lifetime. When material has been deposited to a sufficient thickness, the oscillations become damped or "hop" between different modes. This limitation was a factor in the operation of the sulfur molecular beam oven. In practice, the oven is pre-heated for approximately

two hours prior to a run in order to stabilize the sulfur evaporation rate. This soak time, coupled with the necessary high sulfur evaporation rate, loads the crystal to near its limit in a single run. To get around this problem, the sulfur monitor is fitted with a nichrome wire heater which warms the holder between runs and causes the sulfur on the crystal to desorb, returning it to its original condition.

During the course of an evaporation the crystals are maintained at a constant temperature by water circulated through lines which are silver-soldered to the holders. Because of the particular cut of quartz used in these crystals, the characteristic frequency of the crystals does not change appreciably with temperature in the region from 0 to 65 °F. Therefore, chilled tap water is adequate for temperature control.

A unique feature of the present system is that each crystal monitor is fitted with a "snout" aimed at the particular source being monitored. This snout helps prevent cross-talk between the sources, therefore ensuring independent control of the individual evaporation rates.

The electrical connection from the crystal holders to the feedthroughs on the vacuum chamber is made via a teflon insulated conductor which is doubly shielded with copper braid. This shielding is necessary to prevent interference from rf emission during the operation of the electron beam sources. These lines are also filtered externally with 1 μH inductors to block high frequency noise.

VI. Evaporation Process Control

The evaporation rates from each source are monitored and controlled by a NOVA-1200 compatible mini-computer. It is planned to replace this fairly

elaborate system with a personal computer with appropriate interfaces in the near future. The control program is written in BASIC and uses a simple proportional-integro-differential algorithm[8]

$$E(k) = E(k-1) + A_0 e(k) + A_1 e(k-1) + A_2 e(k-2) \quad (1)$$

where e(k) is the difference between the desired and measured rates at the $k^{\underline{th}}$ interval, and E(k) is the correction signal generated. The constants in the above equation are given by

$$A_0 = K_p(1 + \frac{T}{T_i} + \frac{T_d}{T}) \quad (2)$$

$$A_1 = -K_p(1 + 2\frac{T_d}{T}) \quad (3)$$

$$A_2 = K_p(\frac{T_d}{T}) \quad (4)$$

where K_p is the loop proportional gain, T_i is the integral time, T_d is the derivative time, and T is the period of the measurement. The above algorithm is obtained from the continuous time PID equation[9]

$$E(t) = K_p e(t) + \frac{1}{T_i}\int e(t)dt + T_d \frac{de(t)}{dt}$$

The parameters K_p, T_i, and T_d are adjusted to provide stable control of the evaporation sources. Factors which affect this adjustment are the type of

source in use, the material being evaporated, and the desired evaporation rate. The optimum parameters are determined by observing the source control voltage as the computer executes a step change in the evaporation rate. The proper parameters are those which execute the change in the least amount of time, with a minimum amount of overshoot, and without driving the control voltage into oscillation. Typical sets of loop parameters for a variety of materials and sources are given in Table 1.

The computer performs several different functions during the course of an evaporation. The sequence of steps performed depends on the type of source. The electron beam and resistive boat sources require three segments of control. During the first segment, the source power is increased slowly up to a pre-determined level. This warms the evaporant material and allows it to outgas in a controlled way, thus preventing large pressure excursions. The second segment maintains the source power at this level for a set time. The source material is warmed evenly throughout, and its evaporation rate becomes stable. At this point, the computer shifts to "rate mode" and, from then on, controls the evaporation rate with the rate monitor and the above algorithm.

Control of the sulfur oven is accomplished by using the crucible temperature to determine the operating point. The deposition rate from the sulfur oven is monitored at all times as it may change from run to run, even if the crucible is at the same temperature. This occurs because the sulfur is in granular form and the heat distribution is not constant throughout the charge. The capability of controlling the sulfur oven by its evaporation rate has been built into the control program, but it is not used because of the slow response time of the oven.

The control program is configured to operate in either of the two modes. In the first mode the desired deposition rates from each source are pre-set and the program controls each source independently. Because of the oven response time limitation, a second mode is used, whereby the oven is first warmed to its operating point. The program then averages over the five preceding sulfur rates to determine rate from which the rates required of the other sources are calculated. This calculation is performed continuously and maintains the relative composition of the evaporant stream, despite shifts in the sulfur rate. This feature helps to ensure compositional uniformity throughout the deposited film. The computer also prints out the individual rates every three seconds as the run progresses.

An important feature of the control program is that it limits the range of possible rate readings from each source. The program ignores spurious rate readings above a given value and any negative readings. These readings can be induced by interference from the electron beam sources. The output lines from the computer to the electron beam power supply are also filtered to minimize interference. These filters, plus those on the rate monitor lines, have been completely effective in stopping unexpected halts in the execution of the control program which had been observed prior to their installation.

The system has been operated with overall rates the order of 3 to 10 Å per second, or essentially one layer of unit cells of the Chevrel phase compound per second. The gate time, the time during which the rate monitors count, is one second. Therefore, any short term fluctuations in the rates are averaged over one layer of unit cells.

This method of using a slow overall rate and carefully controlling the relative amounts of material deposited is in contrast to the technique

employed by Hammond in fabricating A15 compounds.[2] That technique relies on high evaporation rates, 100 to 200 Å per second, and fast control, which is necessary because of fluctuations in the rate created by turbulence in the molten charge materials. These fluctuations may lead to inhomogeneity in the composition of the samples. This problem in the present instance is avoided by evaporating at a slow rate because the charge material remains stable. Another advantage of using a slow rate is that because the constituents react at the surface, bulk diffusion is not required to ensure sample homogeneity.

Perhaps one of the most important features of the present system is its cleanliness, which is necessary for producing consistently high quality Chevrel phase materials. An estimate of the number of impurity atoms incorporated into a film can be made from simple kinetic theory. The number of atoms impinging on a surface is given by

$$N = p/\sqrt{2\pi mkT} \tag{5}$$

At an operating pressure of 5×10^{-9} Torr, and an overall evaporation rate of 10 Å per second, the above expression leads to an impurity of about .05%, which is lower than that of most starting materials. Because of this, it is not necessary to rely on a high evaporation rate to produce clean samples.

VII. Results and Discussion

It is first useful to summarize the unique aspects of this deposition system and its use in the preparation of ternary compounds. In contrast with previous attempts to fabricate Chevrel phase compounds[4] by coevaporation techniques, sulfur vapor is projected at the substrate using the molecular beam source rather than by bleeding high purity H_2S or hot S gas into the system, raising the pressure to the order of 10^{-3} Torr. The flux of sulfur incident on

the substrate is the primary control parameter in determining the rate of formation of the films. Great care is taken to minimize the contaminating of effects of sulfur in the vacuum chamber. The exterior of the molecular beam oven and a shroud around its orifice are both cooled so that any sulfur vapor emitted from the oven, even when it is at ambient temperature, is not scattered about the interior of the stainless steel bell jar. Nevertheless, it was found necessary to heat the high-voltage vacuum feedthroughs of the electron beam sources to prevent arcing during deposition as some sulfur collects on the insulators.

A key feature of the operation of the system is the unique evaporation rate monitoring and control system. Each source is monitored with a collimated crystal-oscillator thickness rate transducer. The computer software is also arranged to ignore momentary excursions of the measured rate caused by any electrical transients generated in the evaporation process, a necessary step even though careful filtering has been carried out to minimize the problem.

We now discuss representative results obtained using this system. In Fig. 3 we show the X-ray spectrum of a 4500 Å thick $Cu_xMo_6S_8$ film. As can be seen, this film is nearly single phase with only traces of MoS_2 and free Mo. It was deposited at a substrate temperature of 800°C on an overall rate estimate to be 3 Å/second. In Fig. 4 we show its resistivity determined superconducting transition. The width of the transition, as defined by the temperature span between 0.1 RN and 0.9 RN was only 0.3 K, implying that this film is a very homogeneous specimen of $CuMo_6S_8$. The temperature derivative perpendicular critical field near T_c was found to be 1.6 T/K, a value close to that of bulk material.

In Fig. 5 we show the X-ray pattern of a $HoMo_6S_8$ film, also deposited at a rate of 3 Å/second, and which is approximately the same thickness as the $CuMo_6S_8$ film described above. The plot of R(T) is shown in Fig. 6. It should be noted that the as-prepared film did not exhibit reentrant superconductivity and had a resistivity ratio R_{300K}/R_{15K} of about unity. The film was then returned to the vacuum system and annealed for an hour at 850°C in the presence of a flux of sulfur vapor identical to that used during the original deposition. The resistivity ratio then rose to 2 and reentrant superconductivity was observed. A subsequent annealing for an additional two hours under the same conditions resulted in a further reduction of the room temperature resistance and an increase of the resistivity ratio to the order of 3. In this instance reentrant behavior was not observed in zero magnetic field. In a field of a few hundred Gauss the resistance was observed to increase towards the low end of the obtainable temperature range, suggesting that the final annealing steps served to lower T_{c2}, which is the temperature at which the material reenters the normal state. Further studies at lower temperatures will be required to determine in detail the effect of the final annealing step.

The above results are presented to demonstrate the versatility of the apparatus used to prepare thin film Chevrel phase compounds. Adjustment of the evaporation parameters is guided by observation of the impurity phases present in each film and their relative stabilities. Thus in the case of $PbMo_6S_8$ we were not successful as Pb is very volatile and has a very short dwell time on the substrate at high temperatures as shown by the absence of any Pb or Pb-based phases in the as-deposited films. The annealing process which was used to produce reentrant $HoMo_6S_8$ is potentially very useful in

preparing these materials in a manner consistent with fabricating high quality tunneling junctions. In contrast with previous work in which annealing, either to produce the correct phase or control the surface was carried out in a separate chamber or in pyrex or quartz tubes, the annealing here is carried out in an environment compatible with subsequent processing to form a tunneling junction. It may be possible to use the same trick with Pb as was used with S to produce $PbMo_6S_8$, thus getting around the difficulty we described above.

Acknowledgements

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Figure Captions

Fig. 1. Photographs of the Evaporation Apparatus. The larger view on the left shows the two electron gun sources and the resistively heated boat. Standard commercial components have been used. In the photograph on the right the molecular beam oven is the structure above the electron guns. The four small cylindrical devices are collimated crystal oscillator rate monitors. The circular disks are mechanically operated shutters. The molecular beam oven is a heated box with a three slit opening at its top.

Fig. 2. Detail of substrate holder. The substrates (C) are supported by a .020 inch thick niobium sheet which is in turn attached to the bottom of a .25 inch thick stainless steel frame (D). The substrates are held in place by a boron nitride insert (B) which also serves to insulate the holder from the heater block (A). This block is a hollow piece of niobium 1.2 by 1.0 by 0.5 inches. Boron nitride and caps support two tungsten filaments within the block. It is attached to the end of a vertically oriented linear motion feedthrough. When the substrate holder is in place, the block is lowered and an indexing pin (not shown) positions the holder with respect to the mask carousel (G). The carousel includes a mask insert of boron nitride (E) which is used for elevated temperature depositions. The substrates are changed between runs using horizontally oriented standard linear motion manipulator (F). A spring clip on the end of the manipulator engages a tab on the substrate

holder. The assembly is inserted into the system through a vacuum lock, the indexing pin and heater block are lowered, and the manipulator is withdrawn. The opposite procedure is used to remove the substrates.

Fig. 3. X-ray intensity in arbitrary units vs. 2θ for a $CuMo_6S_8$ film. Miller indices labeling various lines are shown.

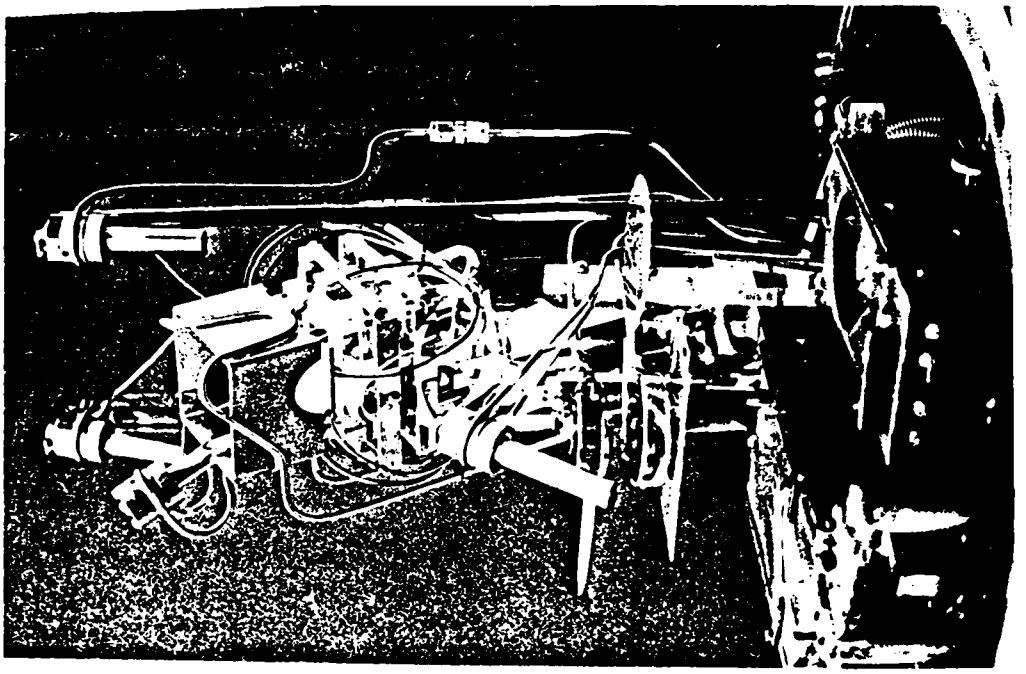
Fig. 4. R(T) for the $CuMo_6S_8$ film of Fig. 3.

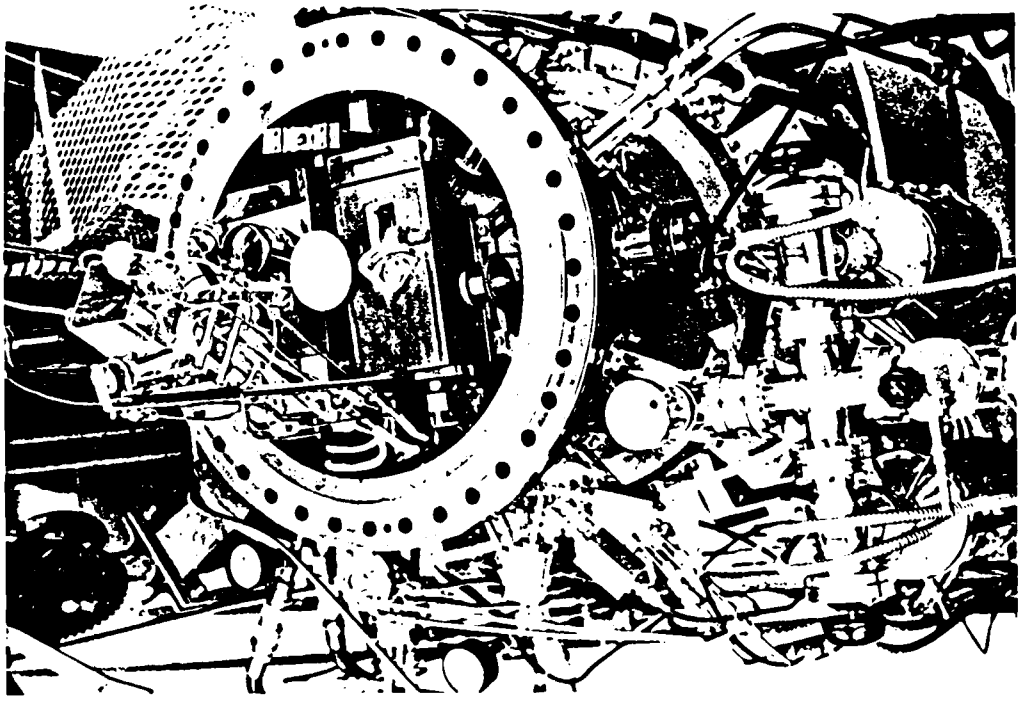
Fig. 5. X-ray intensity in arbitrary units vs. 2θ for an $HoMo_6S_8$ film as-prepared.

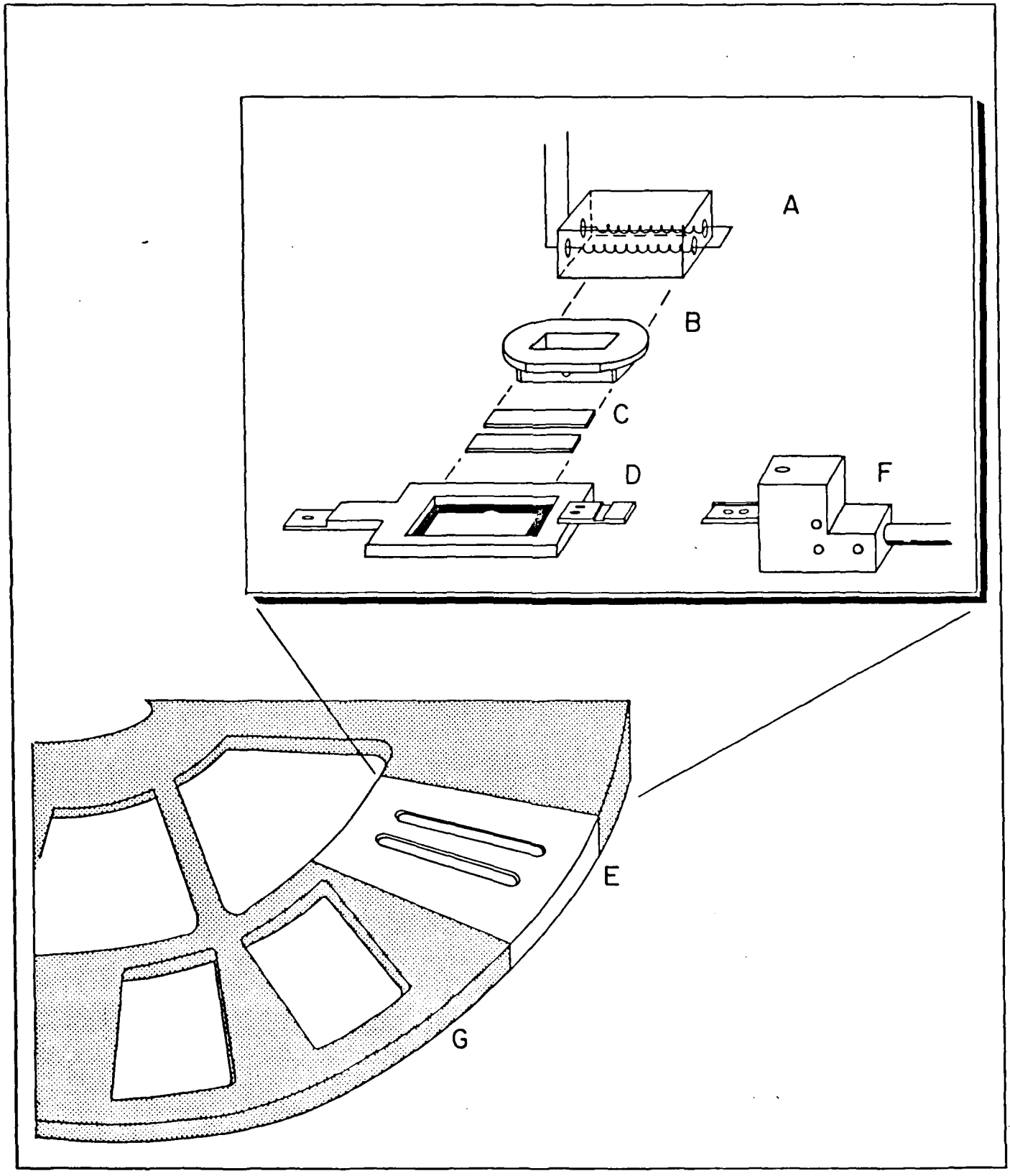
Fig. 6. R(T) for the $HoMo_6S_8$ film of Fig. 5. The rectangles are for the as-prepared films. The closed and open circles are for measurements on cooling and heating after one anneal. The closed and open triangles are measurements on cooling and heating respectively after the second anneal.

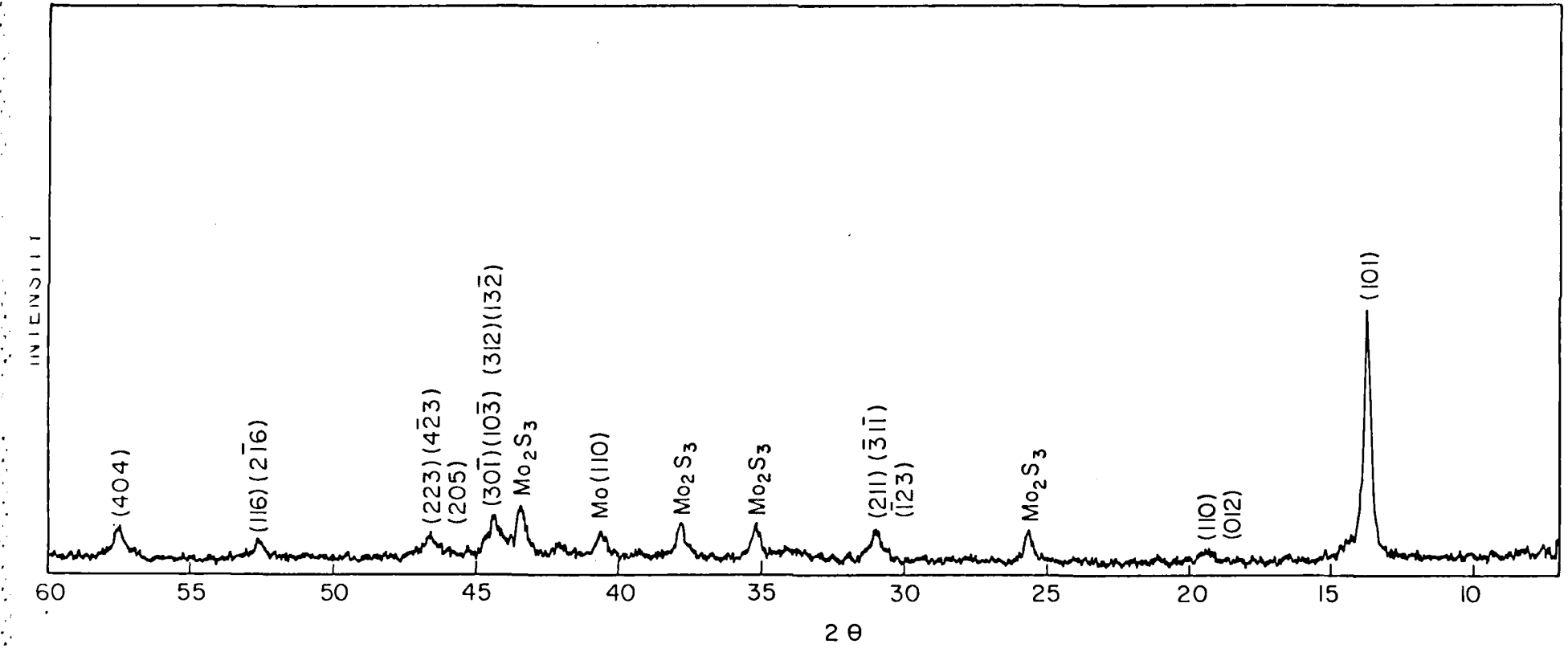
Table I. Proportional-Integral-Differential Control Loop Parameters

MATERIAL	SOURCE	RATE Å/sec.	K_p	T_i sec.	T_d sec.
S	oven	5	1	700	.01
Mo	e-beam	2	150	10	.1
Cu	e-beam	2	150	35	.1
Ho	boat	2	100	35	.1
Pb	e-beam	100	150	10	.1
Pb	e-beam	2	1	.01	.01
Gd	e-beam	2	150	35	.1






A
B
C
D
F
E
G


INTENSITY
(404)
(116) (2$\bar{1}$6)
(223) (4$\bar{2}$3)
(205)
(30$\bar{1}$) (10$\bar{3}$)
(312) (13$\bar{2}$)
Mo_2S_3
Mo (110)
Mo_2S_3
Mo_2S_3
(2$\bar{1}$1) (3$\bar{1}\bar{1}$)
($\bar{1}$23)
Mo_2S_3
(110)
(012)
(101)
60
55
50
45
40
35
30
25
20
15
10
2 θ

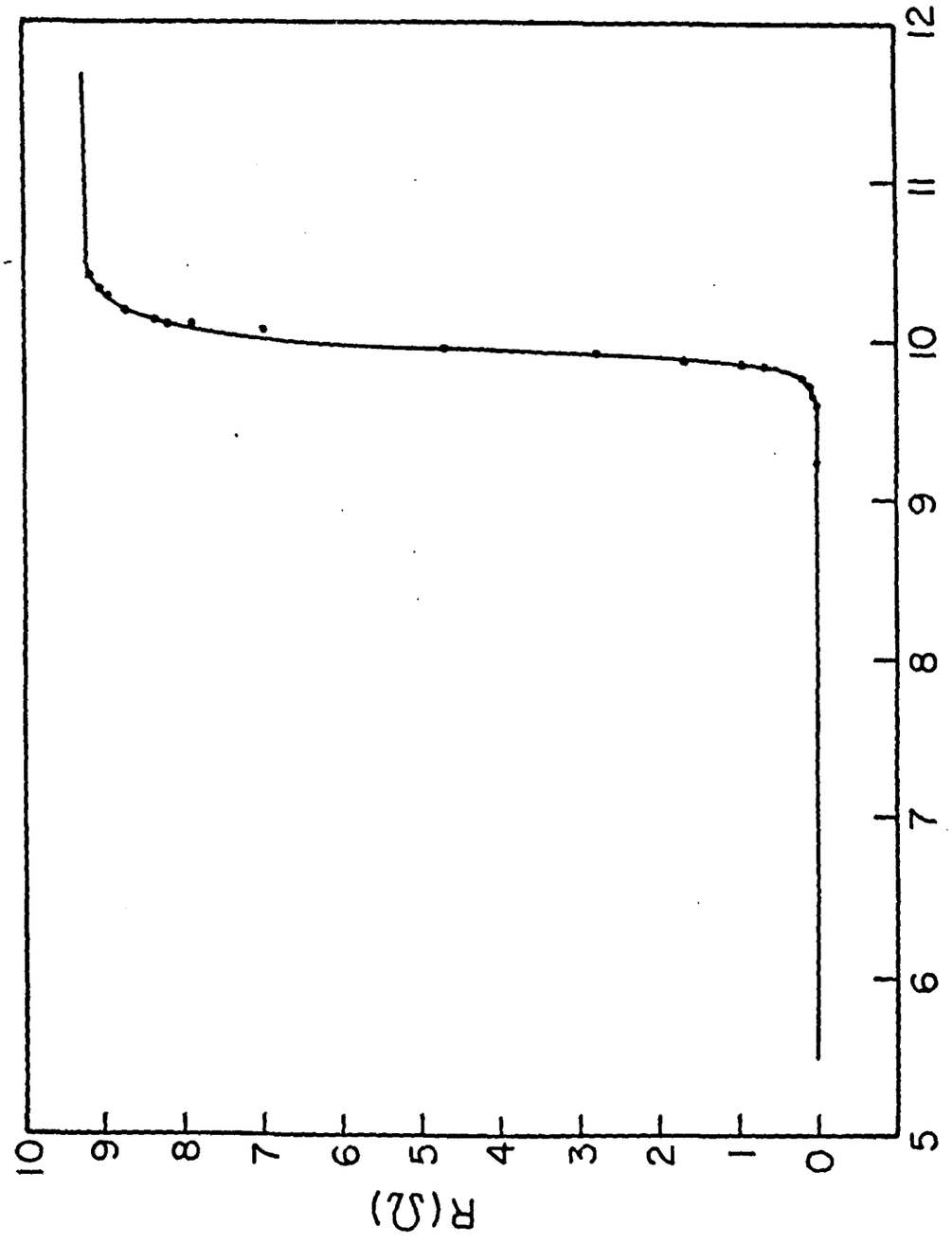
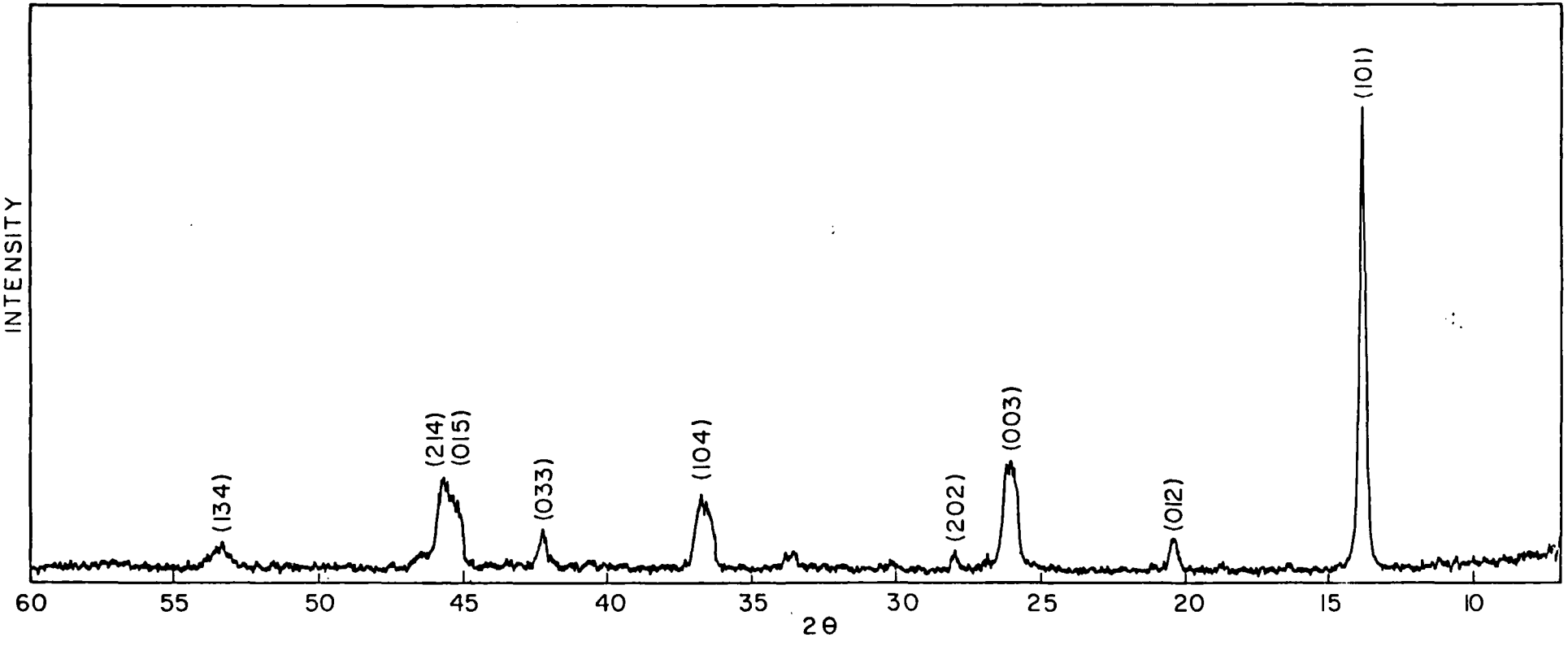


Fig 4


INTENSITY
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(015)
(033)
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(012)
(101)
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55
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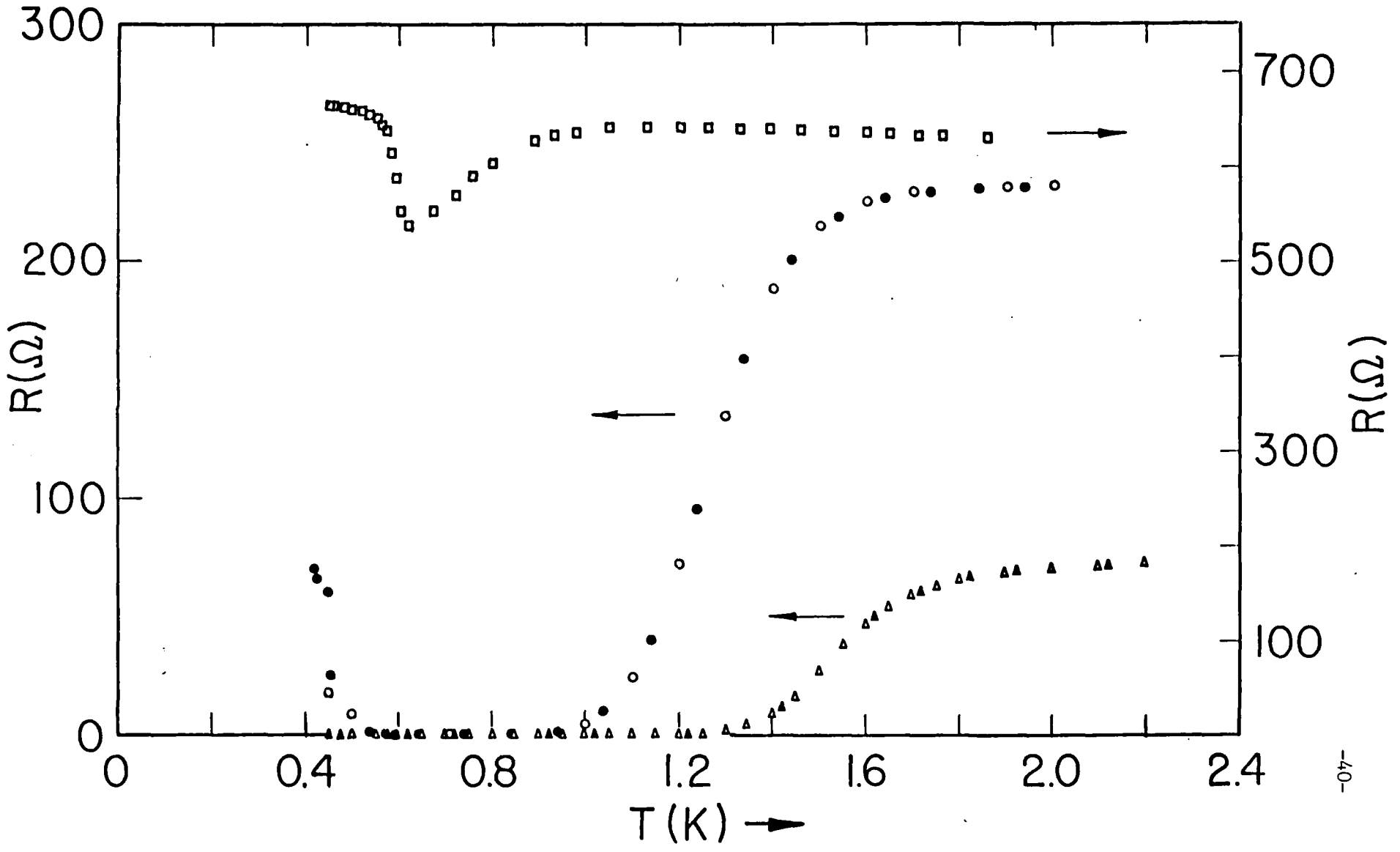
45
40
35
30
25
20
15
10
2θ


300
200
100
0
R(Ω)
700
500
300
100
R(Ω)
0
0.4
0.8
1.2
1.6
2.0
2.4
T(K)

Appendix B

Superconductivity of $HoMo_6S_8$ Thin Films

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Key words: Magnetic Superconductors

Thin Films

Critical Fields

Running Title: $HoMo_6S_8$ Films

ABSTRACT

Films of $HoMo_6S_8$ approximately 0.5 micron thick have been prepared by co-deposition of the elements on a substrate held at an elevated temperature. As-prepared films do not exhibit superconductivity. Annealing in the presence of a flux of sulfur vapor for about one hour at 850°C lowers the resistivity, raises the resistivity ratio and brings about reentrant superconducting behavior similar to that observed in bulk polycrystalline samples. Subsequent annealing suppresses the reentry into the normal state even though the resultant film has a higher resistivity ratio and appears to have a sharper upper resistive transition. These results are discussed in the context of both domain wall superconductivity and possible antiferromagnetism rather than ferromagnetism of the low temperature phase.

The superconducting intermetallic compound $HoMo_6S_8$ is a Chevrel phase system which reenters the normal state at a temperature T_{c2} below the ordinary superconducting transition temperature T_{c1}. In the vicinity of T_{c2} a periodic spin structure has been observed in neutron diffraction experiments. Similar observations have been made in the reentrant superconductor $ErRh_4B_4$. These two materials are important model systems for the study of the interplay of ferromagnetism and superconductivity.[1] The preparation of these compounds in the form of thin films is motivated in part by the relative ease of characterizing the macroscopic superconducting properties of films, and the possibility of studying microscopic properties using electron tunneling techniques.

The fabrication of thin films of the Chevrel phase compounds containing sulfur as a constituent is particularly difficult as a result of the incompatibility of sulfur with the ultra-high vacuum environment needed to prepare high quality films. We have developed procedures for the formation of films by co-deposition of the elemental constituents onto hot substrates, typically at temperatures the order of 850°C. Details of the computer-controlled deposition apparatus and the fabrication techniques have been given elsewhere.[2] The $HoMo_6S_8$ films of the present investigation were formed at a rate of 3 Å/second with the vacuum system pressure in the 10^{-7} Torr range. Low temperature measurements were made initially with a ^3He refrigerator and extended to lower temperatures with a dilution refrigerator, with preliminary thermometry calibration made against CMN.

A plot of resistance vs. temperature of a $HoMo_6S_8$ film is presented in Fig. 1. The crosses are the data for as-prepared films. The diagonal crosses are the data obtained after annealing the film for one hour at 850°C in the presence of a flux of sulfur vapor identical to

that used during the original deposition. The resistivity ratio after this first anneal increased from one to about two. Reentrant superconductivity was observed in this film. A subsequent annealing for an additional two hours under the same conditions resulted in a further reduction of the room temperature resistance and an increase of the resistivity ratio to the order of three. In this instance reentrant behavior was not observed in zero magnetic field. Comparison of the X-ray diffraction patterns of the film after various annealing steps indicated that in addition to improving the electrical properties of the film the effect of annealing was to reduce the Mo_2S_3 impurity concentration.

In Fig. 2 we show the resistance as a function of temperature in zero field and in fields of 500 and 1000 Gauss. A magnetic field of 200 Gauss resulted in reentrant superconductivity with a return to the normal state at about 0.6 K. This data was taken with the magnetic field applied parallel to the film plane.

In Fig. 3 we show three curves corresponding to the fields and temperatures at which the resistance of the film was 0.1, 0.5, and 0.9 of its normal state value. Data was obtained with both parallel and perpendicular magnetic fields although only the results for the parallel field are shown. It was found, in agreement with previous results on $ErRh_4B_4$ films, that the perpendicular critical fields were always larger than the parallel fields.[3]

An important feature of measurements on the magnetic field dependence of the resistance, which we have not illustrated in the figures, was the observation of very long time constants in the electrical response of the system to changes in temperature or magnetic field at low temperatures. As an example, if the sample were cooled

down in a field of 2.0 T to about 70 mK, and the field turned off, it would take several hours for the resistance to decay to zero, the value which would be obtained by cooling in zero magnetic field. Such a long time is far longer than the thermal time constant of the film. These measurements were carried out in such a way as to maintain thermal equilibrium and avoid eddy current heating resulting from changing the magnetic field.

If the magnetic field were cycled back and forth through zero at low temperatures, hysteresis in the resistance vs. field was observed. It was even possible to establish conditions in which superconductivity below 0.1 K was established by the application of a magnetic field.[4] The observed long time constants made the process of data acquisition below the nominal lower transition T_{c2} a very tedious process.

The present results are reminiscent of a number of features of data on polycrystalline, single crystal, and thin film samples of $HoMo_6S_8$ reported by a number of investigators.[4,5,6] Long time constants have been found in all three types of samples. Magnetic field induced superconductivity has been observed in both polycrystalline and single crystal samples of $HoMo_6S_8$.[4] The present results are different from previously reported work on $HoMo_6S_8$ films in that an electrically reentrant superconducting state is actually found, although on subsequent annealing the film was found to be fully superconducting down to low temperatures.[6]

The relatively low resistivity ratios of all of the films and the fact that the as-prepared films are not actually ever fully superconducting indicates that these materials are significantly disordered even after annealing. The most obvious qualitative explanation of the data is that the films, when sufficiently ordered

after the second annealing step, don't return to the normal state because of percolating paths across the sample exhibiting domain wall superconductivity.[7] After only one annealing step, the network is not actually percolating so that reentrant behavior is observed. The long time constants characterizing the electrical response of the sample to changing the magnetic field or varying the temperature would then be consistent with the hindered motion of semimacroscopic magnetic domains.[4]

Despite the attractiveness of the above explanation, it is by no means unique, and certainly cannot be considered to have been tested in a critical manner in any of the work reported to date. Because the critical field curves shown in Fig. 3 resemble those of antiferromagnetic superconductors, it is possible that the twice annealed film of $HoMo_6S_8$ is an antiferromagnet coexisting with superconductivity[8] and not a ferromagnet with domain wall superconductivity at low temperatures. Resolution of these issues will require further experiments investigating the effect of this order on the superconductivity and magnetic behavior of $HoMo_6S_8$ films.

The authors would like to thank Professor E. D. Dahlberg for helpful discussions. This work was supported by the Air Force Office of Scientific Research under Grant AFOSR-84-0347.

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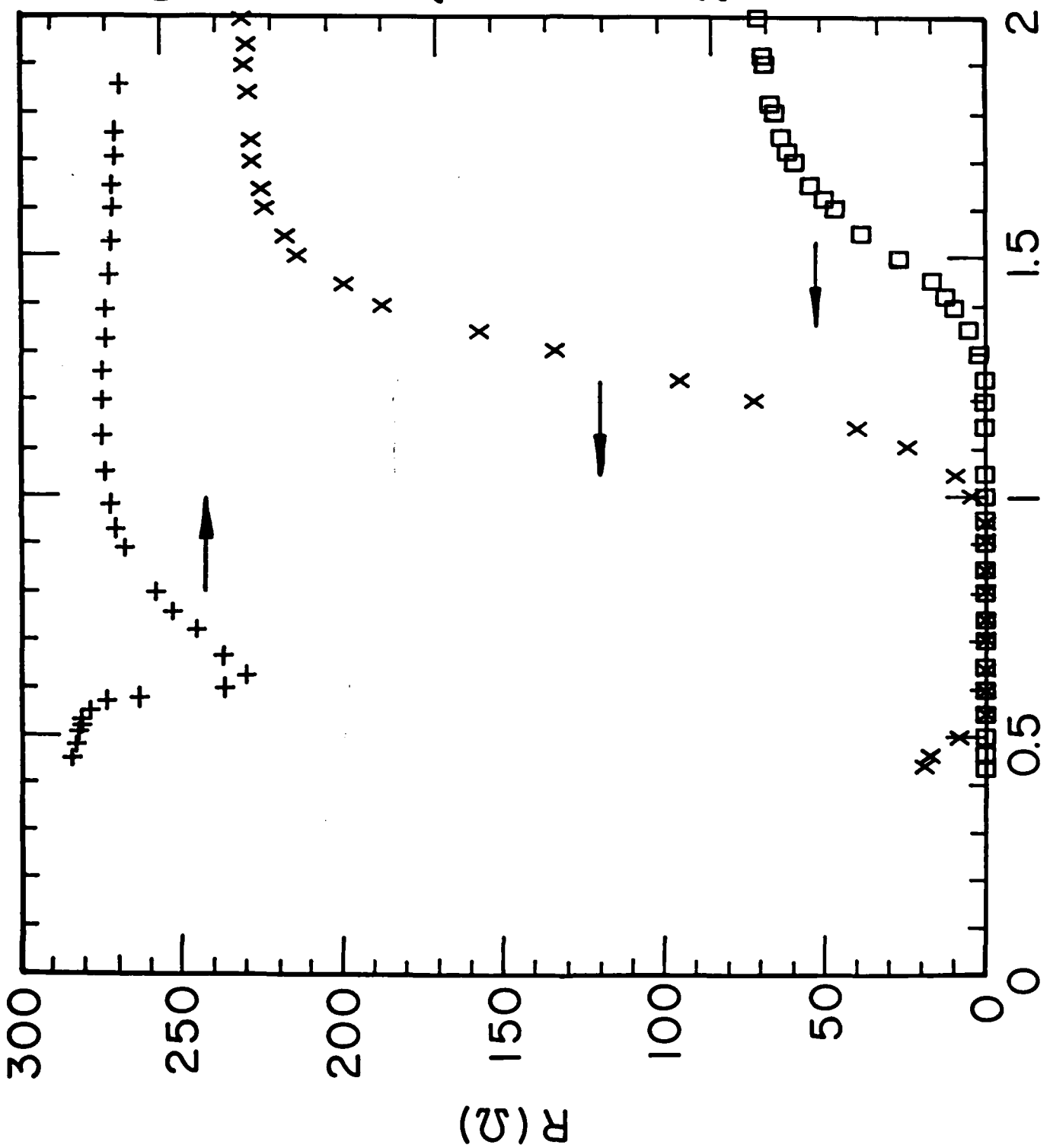
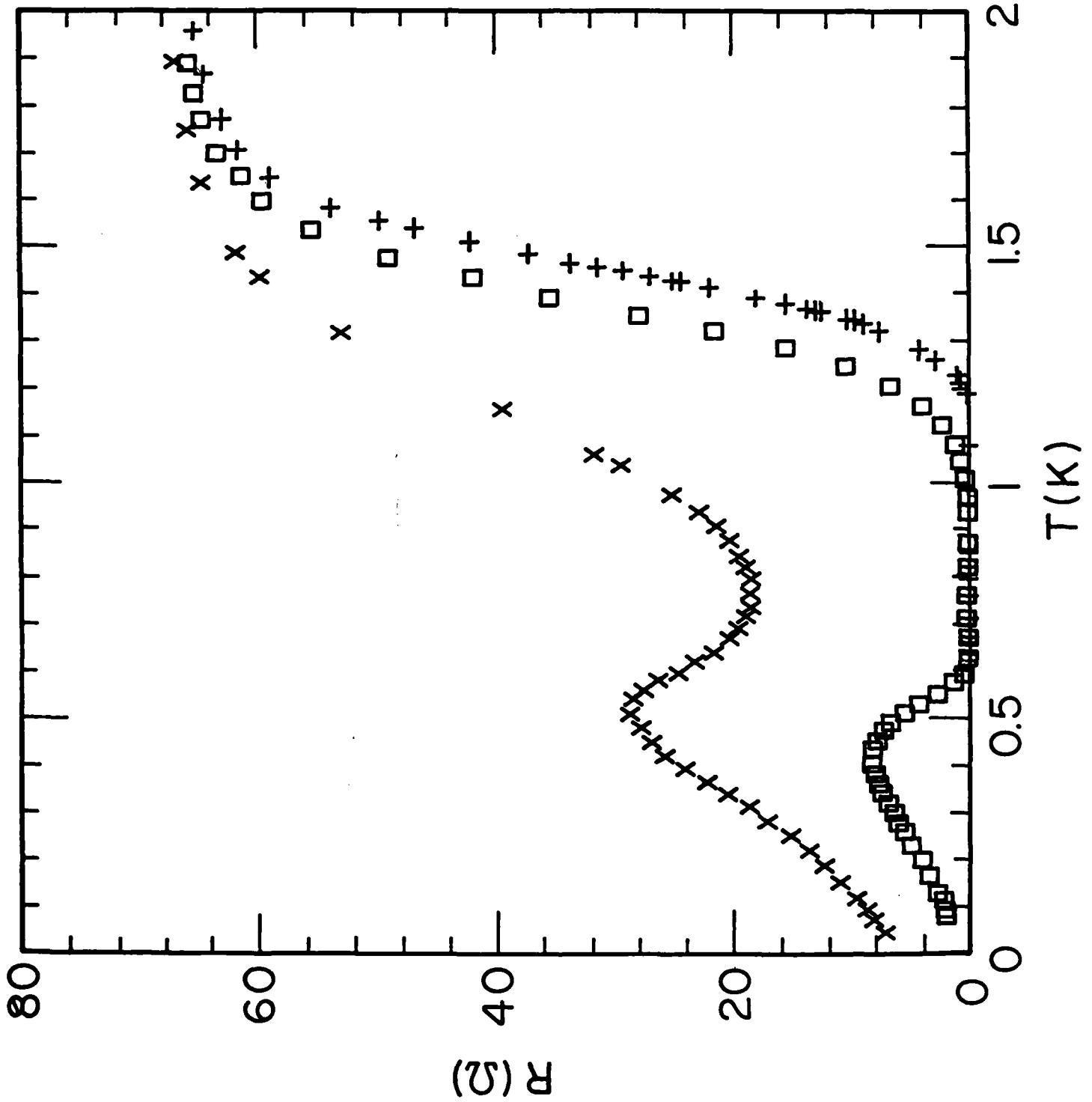
Figure Captions

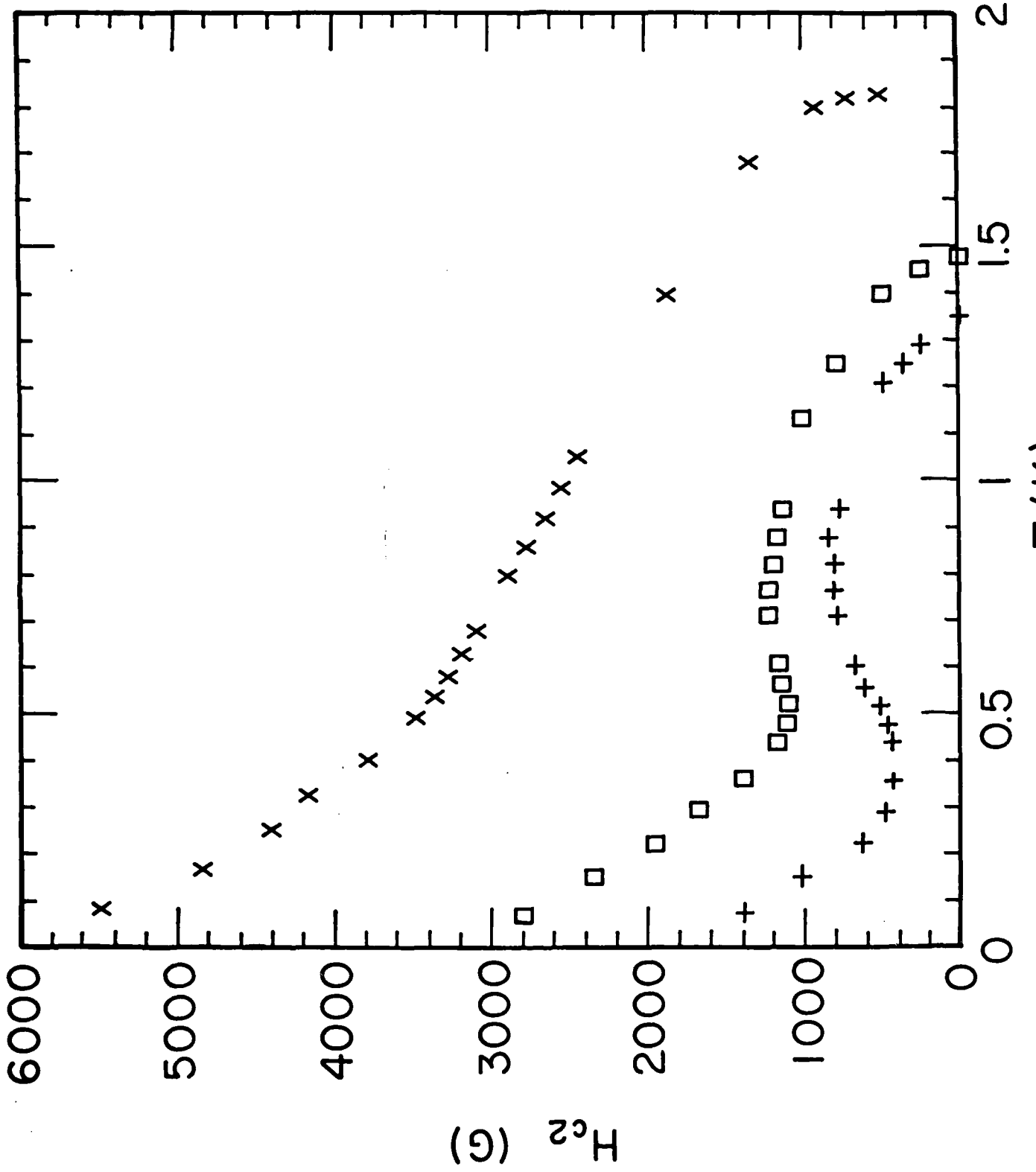
Fig. 1. Resistance vs. temperature for a film as prepared (+) and after successive annealing (x,).

Fig. 2. Resistance vs. temperature of annealed sample showing no re-entrance in zero magnetic field (+) and re-entrance in applied fields of 500 G ( ) and 1 kG (x).

Fig. 3. Magnetic field as a function of temperature required to restore resistance to 0.1 (+), 0.5 ( ), and 0.9 (x) of the normal state resistance.


R(Ω)
600
400
200
0
2
1.5
1
0.5
0
T(K)
R(Ω)
300
250
200
150
100
50
0


R (Ω)
80
60
40
20
0
0
0.5
1
1.5
2
T(K)


6000
5000
4000
3000
2000
1000
0
H_{c2} (G)
0
0.5
1
1.5
2
T (K)

END

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