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TUNNELING IN MAGNETIC SUPERCONDUCTING SYSTEMS

FINAL REPORT

January 31, 1985

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Supported by the Office of Naval Research Electronic and Solid

State Sciences Program under Contract N00014-78-C-0619

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ABSTRACT

The work described in this report was directed at the study of the interaction between magnetism and superconductivity, a classical problem which is important in establishing a fundamental understanding of both phenomena. This field has attracted increased attention as a consequence of the development of stoichiometric compounds which are superconducting and which contain magnetic ions. The coupling between the conduction electrons and these ions can either be ferromagnetic or antiferromagnetic. The work has had two aspects, the study of thin films of magnetic superconducting compounds using electron tunneling as a tool and the development of techniques for the fabrication of films of the Chevrel phase compounds, which, because of their high critical magnetic fields, are potentially technologically significant materials. The tunneling investigations, in addition to revealing fundamental features of magnetic superconducting materials, have also led to the development of some new techniques for the fabrication of artificial barrier tunneling junctions and have pointed out unusual possibilities for three-terminal superconducting devices.



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I. Description of the Research

A. Introduction

The work supported under this contract can be divided into several areas, fabrication and properties of thin films of magnetic superconductors of the rhodium boride family, tunneling into magnetic superconductors, artificial barrier tunneling junction fabrication and characterization, and fabrication and properties of the Chevrel phase compounds. In the following narrative the references are to works produced with support from this contract. These are enumerated in Section II of the write-up.

B. Properties of ErRh_4B_4 Thin Films

Essentially single phase thin films of ErRh_4B_4 were prepared by sputter deposition from an arc-melted target of ErRh_4B_4 .¹ This work was carried out in an ultra-high vacuum system incorporating a liquid-nitrogen cryogettering can. Optimum conditions for depositing the films were determined. Transition temperatures were found to be slightly different from those measured on bulk polycrystalline or single-crystal samples.

The critical magnetic fields of these films were investigated in some detail.² The perpendicular critical fields $H_{c\perp}$ were found to be larger than the parallel critical field $H_{c\parallel}$. These unusual results were shown to be consistent with a simple model which considers the effect of the magnetization induced in the film by the externally applied field. This was the first report of such an effect in superconductors. The measurements serve as an important probe of the internal magnetization of the magnetic ions in the superconducting state.

Techniques for the preparation of tunneling junctions with ErRh_4B_4 base electrodes and counterelectrodes of a number of metals, both superconducting and nonsuperconducting were developed.³ This work permitted the study of both Josephson tunneling and single particle tunneling in ErRh_4B_4 thin films. In the case of pair tunneling, studies were carried out on $\text{ErRh}_4\text{B}_4\text{-Lu(OH)}_3\text{-In}$ thin film junctions.⁴ The Fraunhofer-like pattern of the magnetic-field dependence of the dc Josephson current was found to split at a temperature just above the reentrant transition of ErRh_4B_4 . This result suggests the onset of a magnetic structure of semimacroscopic scale which does not break up the superconductivity of the ErRh_4B_4 electrode into disconnected domains, at least within the surface region probed by tunneling. Other features of the Josephson effect in these junctions were also investigated. All of them were consistent with the onset of strong magnetic effects at a temperature of about 1.5 K, a full half degree above the beginning of the magnetic transition. The results suggest the existence of an extended coexistence phase, perhaps connected with the polycrystalline character of the films.⁵

Single particle tunneling studies were also carried out in junctions with ErRh_4B_4 base electrodes and Sb counterelectrodes. Various features of the paramagnetic, superconducting and ferromagnetic phases were revealed in these studies. Anomalous features of the tunneling conductance in the ferromagnetic phase which persist into the superconducting state were observed.⁶ These appear to be connected with the onset of ferromagnetism in the region of coexistence of ferromagnetism and superconductivity just above the lower transition T_{c2} . Thus far they have not been explained theoretically. The general behavior of the single particle tunneling conductance and the density of states of ErRh_4B_4 as a function of temperature is very consistent with the

behavior of the Josephson effect in this material. In particular, the sub-gap conductance which decreases with temperature below 8.0 K as the quasiparticles freeze out exhibits a sharp minimum at about 1.8 K and abruptly decreases with temperature as T_{c2} is approached from above. This result is consistent with the onset of strong pair-breaking in an extended coexistence region above T_{c2} . We are convinced that this effect and corresponding features of the Josephson current are the result of the polycrystalline character of the films and the fact that small crystallites may become ferromagnetic at higher temperatures as a consequence of surface effects.⁷

C. Artificial Barrier Tunneling Junctions

In order to produce tunneling junctions with ErRh_4B_4 base electrodes we had to investigate the technology of the fabrication of artificial barrier tunneling junctions. We succeeded in developing techniques for preparing junctions with base electrodes of Nb, Nb_3Ge , Y_3Si , and ErRh_4B_4 and with counterelectrodes of Pb or In and barriers of oxidized Lu or Er.⁸ Junctions with Nb base electrodes were characterized in detail. The work showed that oxidized layers of the rare earths could be used to form artificial barrier tunneling junctions on a variety of technologically and scientifically important materials. The process is simple and fast and produces, with some base electrodes, high-quality Josephson junctions which thermally cycle.

Because oxidized layers of the rare earth metals were potentially interesting materials in their own right, we undertook investigations in order to determine the chemical composition of these artificial barriers. This was done using X-ray Photoemission Spectroscopy (XPS).⁹ The work, which was carried out in collaboration with the Surface Analysis Center of the

University of Minnesota, revealed that the barrier materials were undoubtedly rare earth trihydroxides rather than sesquioxides.

D. Tunneling Junctions with Magnetoelectric Barriers

Our development of an artificial barrier for superconducting tunneling junctions led us into serious study of the possibilities of a number of different junction configurations. We proposed a three-terminal Josephson device, which in principle could have gain and which depends on the magnetoelectric effect.¹⁰ The latter is a property of the antiferromagnetic phase of certain compounds. When an electric field is applied across a magnetoelectric material, a magnetization develops. If one junction of a two-junction, three-electrode sandwich contained a magnetoelectric barrier, a magnetic field would result if that junction were switched to the finite voltage state. This field, when coupled into the second junction, would cause it to switch from the zero-voltage to the finite-voltage state. If the second junction had a larger critical current than the drive junction, then the resultant three-terminal device would have gain.

This idea was a direct consequence of our investigations into the properties of the rare earth sesquioxides and trihydroxides, because we discovered the existence of the rare earth oxy-hydroxides which are magnetoelectric compounds. A simpler version of the device described above was conceived in collaboration with Professor T. Hsiang of the University of Rochester. In this second device the drive junction is replaced by a capacitor filled with magnetoelectric material. This permits the application of a much higher voltage than would be applied across a Josephson junction. The resultant magnetic field produced would be larger, but most importantly

the device would have field effect transistor like input characteristics. It would be a voltage controllable Josephson junction with a high input impedance. A device such as this could be very important to the future use of Josephson digital electronics.

E. Chevrel Phase Compounds

The greater part of the effort in this area was devoted to the development of a computer-controlled high vacuum evaporation system for the deposition of these compounds in a controlled manner. Such a system was successfully developed. It employed a combination of electron beam sources, resistively heated Langmuir sources and Knudsen sources. Unique features of the system included 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.

Thin films of CuMo_6S_8 have been fabricated. The CuMo_6S_8 films produced using these techniques were relatively highly ordered and pure. The HoMo_6S_8 films, as prepared, show a resistance minimum, but do not become completely superconducting. However, after they are reactively annealed they become superconducting and exhibit reentrant superconductivity similar to that described in the work on ErRh_4B_4 above. These methods have not been used successfully to form PbMo_6S_8 films because of the high volatility and short dwell time of Pb on the substrate surface.

Articles describing the fabrication system¹¹ and the results obtained with it¹² have been submitted for publication but have not appeared as of this writing.

II. List of Publications Supported by This Contract

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10. Allen M. Goldman, *Proceedings of the Applied Superconductivity Conference, 1984*, to be published.
11. R. J. Webb and A. M. Goldman, submitted for publication in *J. Vac. Sci. and Technol. A*.

12. R. J. Webb, A. M. Goldman, J. H. Kang, J. Maps, and M. F. Schmidt, Proceedings of the Applied Superconductivity Conference, to be published.

III. Doctoral Students

1. Robin Cantor, Ph.D. (Physics), 1981
Thesis Title: Single-Particle and Pair Tunneling Studies of Superconducting Compounds and Two-Dimensional Films
Current Employment: Superconductivity Group, Sperry Univac, Eagan, MN

2. Corwin P. Umbach: Ph.D. (Materials Science), 1982
Thesis Title: Fabrication of Electron Tunneling Junctions on Nb_3Ge and $ErRh_4B_4$
Current Employment: Staff Member, I.B.M. T.J. Watson Laboratory, Yorktown Heights, N.Y.

3. L-J. Lin, Ph.D. (Physics), 1984
Thesis Title: Tunneling into the Magnetic Superconductor $ErRh_4B_4$
Current Employment: Postdoctoral position, Department of Applied Physics, Yale University, New Haven, CT

4. R. J. Webb, Ph.D. (Materials Science), 1984
Thesis Title: Reactive Evaporation of Chevrel Phase Ternary Superconductors
Current Employment: 3M Research Center, St. Paul, MN

IV. Preprints of Papers Not Yet Published

- A. Proposed Three-Terminal Superconducting Device Based on the Thermoelectric Effect, to be published in the Proceedings of the Applied Superconductivity Conference.
- B. Reactive Evaporation of Chevrel Phase Superconducting Compounds, to be published in the Proceedings of the Applied Superconductivity Conference.
- C. An Evaporation System for the Preparation of Ternary Compounds, submitted to J. Vac. Sci. Technol. A.

A. PROPOSED THREE-TERMINAL SUPERCONDUCTING DEVICE BASED ON THE MAGNETOELECTRIC EFFECT

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Abstract

The development of three-terminal superconducting devices with transistor-like characteristics may be crucial for a number of applications of superconducting electronics. A three-terminal Josephson device which in principle could have gain, and which depends on the magnetoelectric effect is described. The magnetoelectric effect is a property of the antiferromagnetic phase of certain compounds. When an electric field is applied across a magnetoelectric material, a magnetization develops. If one Josephson junction of a two-junction, three-electrode sandwich contained a magnetoelectric barrier, a magnetic field would result if that junction were switched to the finite voltage state. This field, when coupled into the second junction, would cause it to switch from the zero-voltage to the finite voltage state. If the second junction had a larger critical current than the drive junction, then the three-terminal device would have gain.

Introduction

A recognized need in superconducting electronics is for a three-terminal device with transistor-like characteristics as well as ultra-low switching energies. The two-terminal nature of Josephson devices and the resultant difficulty of input-output isolation and low circuit gain have made for difficulties in the use of the high switching speed of the Josephson effect. The use of interferometers in digital circuits has provided a type of three-terminal operation, but at the expense of increased size. Various circuits using several junctions have achieved a degree of isolation using the high resistance of a switched junction. A number of devices have been reported which are based on the nonequilibrium properties of superconductors.¹ These include superconducting transistors,² controllable weak links (CLINKS),³ devices based on the quasiparticle injection tunneling effect (QUITEBONS),⁴ and three-terminal devices fabricated using submicron tunneling junctions.⁵ All of these devices are based on gap suppression and are limited by inelastic scattering times which are typically the order of 50 pS.¹

Here we present the concept of a three-terminal Josephson device which can have gain and which is based on the magnetoelectric effect.⁶ Because the magnetoelectric effect results microscopically from the sensitivity of spin-orbit coupling to electric and magnetic fields, it may be quite fast. Thus it may be possible to switch on a magnetic field using the magnetoelectric effect in a time the order of 10 pS.⁷

The Magnetoelectric Effect

The linear magnetoelectric effect is a phenomenon in which a material exhibits an induced magnetization which is proportional to an applied electric field and

an induced electric moment proportional to an applied magnetic field. The possibility of such an effect was first mentioned by Pierre Curie.⁶ It is, however, one of several classes of phenomena which until the mid-1950's were believed to be forbidden by time reversal symmetry as they are represented in the crystal Hamiltonian by a term odd in the magnetic field.

Landau and Lifshitz⁸ showed that the time reversal symmetry operation for a given crystalline geometry is not an independent symmetry element whenever the crystal is magnetically ordered, thus allowing for the possibility of a magnetoelectric effect in magnetically ordered materials. Dzyaloshinskii⁹ predicted the existence of the effect in Cr_2O_3 . The electrically induced effect was observed by Astrov¹⁰ and the magnetically induced effect by Rado and Folen.¹¹ More than thirty compounds have been subsequently observed to exhibit the magnetoelectric effect.⁶ An atomic theory of the effect was given by Rado.¹²

For purposes of subsequent discussion it is useful to consider some simple aspects of the phenomenological theory. If the thermodynamic potential of an antiferromagnet is expanded to second order in the components of the electric and magnetic fields, one obtains

$$F = -\alpha_{ij} E_i H_j + F_{\text{other}} \quad (1)$$

where the term containing the magnetoelectric susceptibility α_{ij} describes the magnetoelectric effect and the second term contains all of the other terms. The Einstein summation convention is used in the above expression. The application of standard thermodynamic relationships

$$\vec{P} = -\partial F / \partial \vec{E} ; \vec{M} = -\partial F / \partial \vec{H} \quad (2)$$

then yields the magnetoelectric contributions to the polarization \vec{P} and magnetization \vec{M}

$$P_i = \alpha_{ij} H_j ; M_i = \alpha_{ji} E_j \quad (3)$$

The symmetry properties of particular compounds are then needed to determine which terms in the magnetoelectric tensor α_{ij} are nonvanishing. These questions are considered in the various review articles and as they are not essential to the purposes of the present discussion, won't be treated here. We also will not consider the interesting work on the critical behavior of the magnetoelectric susceptibility tensor elements in the vicinity of the antiferromagnetic ordering temperature.

Experimental¹³ and theoretical¹⁴ work has shown that the critical exponent β_a of the temperature dependence of the magnetoelectric susceptibility tensor elements is identical to β , the critical exponent of the staggered magnetization of the antiferromagnetically ordered state.

Because the magnetoelectric effect results microscopically from the sensitivity of the spin-orbit coupling to electric and magnetic fields, it may be quite fast. As has been mentioned, it may be possible to produce magnetization by the application of an electric field in a time the order of 10^{-7} ps.⁷ Previous discussions of the use of the magnetoelectric effect in devices set the limit as the frequency of antiferromagnetic resonance. However, there appears to be no significant experimental literature on the response time which would be a critical parameter in the proposed use of the magnetoelectric effect in superconducting devices. If the switching time were indeed short, then the phenomenon would be extremely compatible with the requirements of Josephson technology.

There have been no practical applications of the magnetoelectric effect because of the relatively small values of observed magnetoelectric susceptibilities.⁶ Among the thirty or so magnetoelectric materials, the largest values of α are the order of 10^{-2} in Gaussian units, and are found in materials with Bv^{3+} and Pb^{3+} ions. An upper bound on the susceptibility tensor elements has been given as

$$\alpha_{ij} < (\kappa_{ij} \chi_{ij})^{1/2} \quad (4)$$

where κ_{ij} and χ_{ij} are the usual electric and magnetic susceptibility tensor elements respectively.¹⁵ The limit set by Eq. (4) is actually high in comparison with experimental values of α_{ij} , suggesting that further materials research may yield materials with more useful coefficients (see Table I for parameters of selected magnetoelectric materials).

Table I. Selected Magnetoelectric Materials

Compounds	$T_N(K)$	α (highest value)	Reference
Cr_2O_3	3.07	5×10^{-4}	(6)
$TbAlO_3$	~ 3.9	10^{-2}	(6)
$GdAlO_3$	~ 3.9	2×10^{-3}	(6)
$ErOOH$	4.1	4.5×10^{-5}	(16)
$TbOOH$	10.0	3.8×10^{-4}	(16)
$DyOOH$	7.2	9.8×10^{-5}	(16)

Josephson Devices Using the Magnetoelectric Effect

When an electric field is applied across a magnetoelectric material, a magnetization develops. If a Josephson junction can be fabricated with a magnetoelectric barrier, then each time it was switched from zero-voltage to a finite voltage of a few mV, a magnetic field would be produced in the barrier. If this junction were then formed between the top two electrodes of a three-electrode, two-barrier, double junction, with appropriately thick superconducting ground planes to direct the flux generated in the

first junction into the second, then the magnetic field produced by the first junction could switch the second from the zero-voltage to the finite-voltage state. If the lower junction had a thinner barrier and a larger critical current than the upper one, then the resultant three-terminal device would have gain. A schematic of the proposed device is shown in Fig. 1. This device would be noninverting, at least in the simple form described here. Input-output isolation would follow from the asymmetry of the structure. The particular magnetoelectric material used in the barrier would have to possess nonvanishing off-diagonal components of the susceptibility tensor so that an electric field applied across the junction would result in a magnetic field at right angles in the plane.

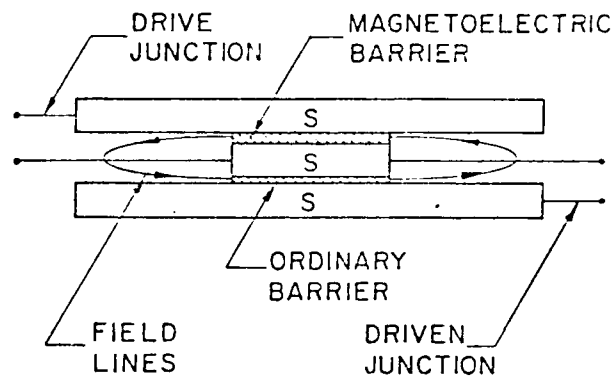


Fig. 1. Schematic of proposed three-terminal device.

A Josephson device with a magnetoelectric barrier would also have to be cooled through the Neel temperature T_N of the barrier in the presence of a magnetic field applied in the plane of the barrier and with voltage applied across it before the device could be operated in a useful way. The reason for this is that the magnitude of the magnetoelectric susceptibility depends on the product EH of the electric and magnetic fields applied to the material while it is being cooled through T_N . Field cooling, or magnetoelectric annealing, is necessary to saturate the antiferromagnetic material in a particular configuration.⁶ It has been found that without annealing the magnitude and sign of the magnetoelectric susceptibility vary from sample-to-sample and from measurement-to-measurement with the temperature dependence of the effect remaining the same. This is indicative of the existence of two or more antiferromagnetic domains. The differences in measured coefficients are evidently caused by variations in the relative volumes of the sample ordered in the different configurations. Magnetoelectric annealing saturates a given material in a particular configuration. It is possible that systematic studies of the magnetoelectric susceptibility as a function of different annealing conditions might result in an increase in magnetoelectric electric susceptibilities over currently reported values. For instance, in the case of the magnetoelectric behavior of rare earth oxyhydroxide compounds,¹⁶ electric breakdown limited the annealing conditions to a field of 4 kV/cm, which in the configuration of a junction would correspond to a 1.2 mV bias across a 30 Å barrier. The magnetic field used in the annealing process was only 900 G. Both of these numbers could be easily exceeded in the proposed configuration.

As part of the investigation of feasibility, it is useful to consider the magnetic flux generated in the magnetoelectric junction as a function of the bias current in the second junction. This is in one sense a best-case estimate, but it greatly simplifies the subsequent analysis. It is then sufficient to compute the total flux in the magnetoelectric barrier by multiplying the magnetization computed from Eq. 2 by α times the cross-sectional area of the junction in the direction of the field, which is assumed to be in the plane of the junction. For simplicity we assume that the 30 Å thick barrier, after it switches to a finite voltage, is biased at 3 mV. Then, for a coefficient α of 10^{-7} in Gaussian units the flux would be 0.02 of a flux quantum for a 1 cm wide junction. This value is clearly too small to be practical. On the other hand, for α of 1×10^{-7} the flux would correspond to 0.02 of a flux quantum for a 1 cm wide junction and 0.62 of a quantum for a junction 0.01 cm wide. Clearly the former would be a very slow device, and the latter would require the second junction to be biased separately close to its critical current in order to be switched by the applied field. On the other hand, if the magnetoelectric coefficient would be increased to 0.1, then for 0.1 cm and 0.01 cm wide junctions respectively, the flux would be 6.2 and 0.62 quanta respectively. The former would lead to workable margin requirements on the second whereas the latter would be somewhat more difficult. In any event, all of the configurations not having stringent margin requirements on the second junction would switch relatively slowly because of their large areas, unless the other dimension in the plane could be restricted dramatically. Unfortunately decreasing the thickness of the magnetoelectric junction to increase the electric field does not result in any gain in performance. Although the electric field increases linearly with decreasing thickness the flux decreases in the same manner. Increasing the thickness of the magnetoelectric junction and using all-refractory electrodes with a higher dc bias could result perhaps in a half an order of magnitude gain in the flux at the second junction.

Discussion

The extreme smallness of magnetoelectric coefficients of known materials is thus seen to be a major impediment to the potential usefulness of the proposed three-terminal device. Switching with a small magnetic field requires that the second junction be biased close to its critical current for the device to operate. It should be noted that reported magnetoelectric coefficients are far smaller than the theoretical upper limit.¹⁵ Thus systematic materials research might significantly improve the prospects for making useful devices.

An additional problem is that there have been no detailed measurements of the time constant of the magnetoelectric effect. It would have to be very short for the phenomenon to be really of significance in superconducting electronics. Thus an evaluation of the usefulness of potential devices would require systematic studies of the dynamics of the effect, preferably in the junction configuration.

The problem of fabricating the proposed structure is far from trivial. Although there have been considerable advances in artificial barrier junction technology, the barrier materials employed have been far simpler than those which exhibit the magnetoelectric effect. The potential difficulties are perhaps exacerbated by the possible need to prepare single crystal barrier materials in order to achieve

the highest possible magnetoelectric coefficients. Despite all of these difficulties, the use of the magnetoelectric effect may provide a path to a three-terminal device within Josephson technology. The proposed device, because of the extensive materials development required, must be considered to be speculative and certainly conceptually outside of the mainstream of thinking in the field at this point.

Acknowledgement

This work was supported in part by the Electronics Branch of the Office of Naval Research under contract N00014-78-C-0012. The author would like to thank M. Beasley for an important comment and T. Hsiang for useful discussions.

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B. TERNARY CHEVELL PHASE COMPOUNDS CONTAINING RARE EARTH ELEMENTS

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Abstract

Thin films of Chevrel phase compounds CaMo_6S_8 and HoMo_6S_8 have been formed using a reactive evaporation technique in which the metallic constituents are derived from either electron-beam or resistively heated sources and S vapor is obtained from a molecular beam oven. The constituents are reacted on a sapphire substrate kept at elevated temperatures. Compositional uniformity is insured by controlling the S rate and locking the rates of the other sources to it in a prearranged fashion. The evaporation system used in this work is equipped with a vacuum lock which permits substrates to be changed without reprocessing the system. CaMo_6S_8 films produced using these techniques are relatively pure and well-ordered. HoMo_6S_8 films show a resistance minimum but do not become completely superconducting as prepared, but do so after reactive annealing. These methods have not been used successfully to form PbMo_6S_8 films because of the high volatility and short dwell time of Pb on the substrate surface.

Introduction

The original investigations of ternary Chevrel phase compounds involved the study of bulk materials prepared either by arc melting or by sintering.¹ In some instances single crystals were prepared.² By and large, investigations of bulk properties have concentrated on the study of thermodynamic properties of materials such as the specific heat and susceptibility, and the investigation of the electrical resistance and its magnetic field dependence.³ Efforts at the preparation of thin film samples are driven by both technological and scientific needs. In technology there is a need to prepare ductile samples of the high-critical-field Chevrel phase compounds which may be possible by depositing these materials onto flexible tapes. On the scientific side of superconductivity there is a need to carry out quantitative tunneling spectroscopy so as to determine the mechanism of superconductivity in these materials and the nature of the interplay between magnetism and superconductivity in these compounds containing rare earth ions, which are as a consequence either ferromagnetic or antiferromagnetic at low temperatures. Thin film Chevrel phase compounds have been prepared using sputtering, and in the case of CaMo_6S_8 by vacuum

evaporation.⁴ Here we describe a procedure for fabricating thin films using a reactive evaporation technique carried out in a very clean environment which can be kept under very tight control and which is capable of producing films which are relatively ordered and compositionally pure. The long range goal of this work is to prepare high-purity tunneling junctions with individual, wide-gap electrodes.

Experimental

Films are prepared in a bakeable ultra-high vacuum system equipped with two electron-beam evaporator sources, a Knudsen cell which serves as a molecular beam source for S vapor and a resistively heated source. The vacuum system is equipped with a 400 l/s ion pump and a Varian VK-12 series helium cryopump.

Base pressures in the 10^{-8} to 10^{-9} Torr range are readily achieved. Pressures during deposition involving S vapor are in the 10^{-7} to 10^{-3} Torr range. The vacuum system, which is shown in Fig. 1, is also equipped with a sample insertion chamber and a vacuum lock which permits substrates to be transferred in and out of the deposition chamber without reprocessing the entire vacuum system.

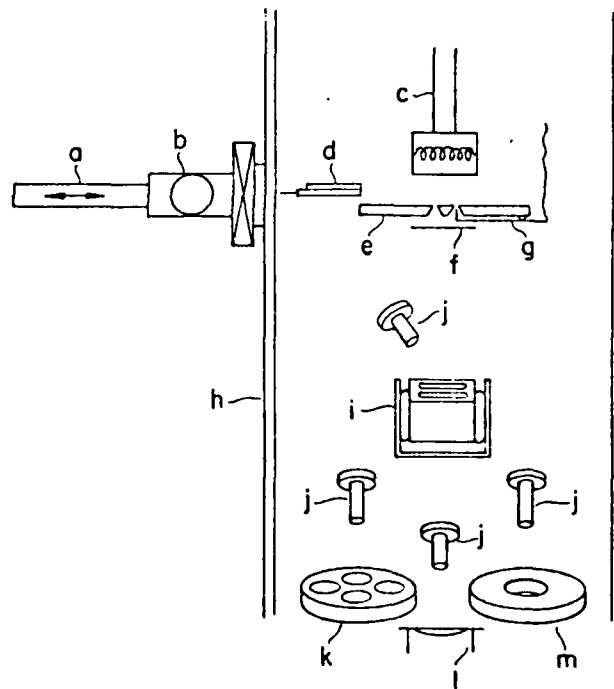


Fig. 1. Schematic of the evaporation apparatus. Its components are as follows: manipulator-a, substrate insertion chamber-h, mask-c, substrate heater-e, shutter-f, thermocouple-g, rate monitors-i, tungsten boat-k, small earth electron on-beam source-l, molecular beam oven for sulfur-m, four-beam electron gun source-n.

In contrast with previous work in which S was provided by cleaving high-purity S_8 crystals into the system, raising the pressure to the order of

10^{-3} Torr, S-vapor is produced at the substrate using the molecular beam source. The flux of S 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 effects of S in the vacuum chamber. The exterior of the molecular beam oven and a shroud around its orifice are both cooled so that any S 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. Rather than implementing three independent PID control loops for the three sources, one loop is used to control the S oven temperature. The rate set-points used to determine the error signals for the two metallic source control loops are then calculated continuously throughout the run from the measured sulfur deposition rate. The computer software is also arranged to ignore momentary excursions of the measured rate caused by any electrical transients generated in the evaporation process, although careful filtering has minimized this problem.

The films are characterized by X-ray diffraction, scanning electron microscopy and Auger electron spectroscopy. X-ray data are obtained with a diffractometer using $\text{Cu-K}\alpha$ radiation. Auger spectroscopy is carried out using a PHI Model 547 and selecting higher energy peaks for analysis. Here we will show typical X-ray data and $R(T)$ data for CuMo_6S_8 and HoMo_6S_8 films, which are a high-field material and a ferromagnetic superconductor which reenters the normal state.

Experimental Results

In Fig. 2 we show the X-ray spectrum of a 4500 Å

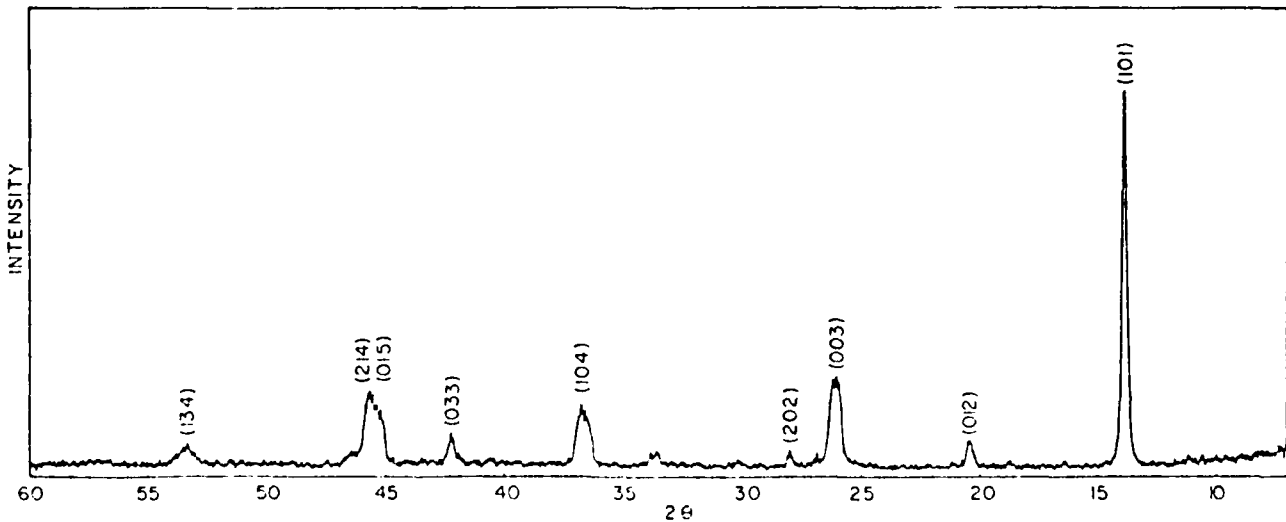


Fig. 2. X-ray intensity in arbitrary units vs 2θ for CuMo_6S_8 film. Miller indices label the various lines are shown.

thick CuMo_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 at an overall rate estimate to be 3 Å/second. In Fig. 3 we show its resistively determined superconducting transition. The width of the transition, as defined by the temperature span between 0.1 Ω and 0.9 Ω was only 0.2 K, implying that this film is a very

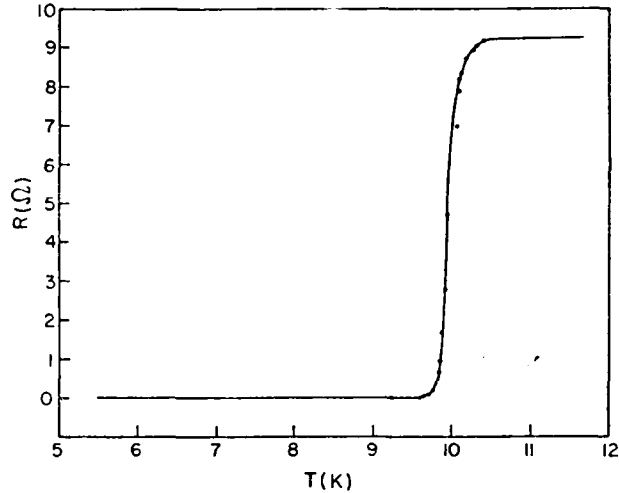


Fig. 3. $R(T)$ for the CuMo_6S_8 film of Fig. 3.

homogeneous specimen of CuMo_6S_8 . The perpendicular critical field near T_c was found to be 1.6 T/K, a value close to that of bulk material.

In Fig. 4 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

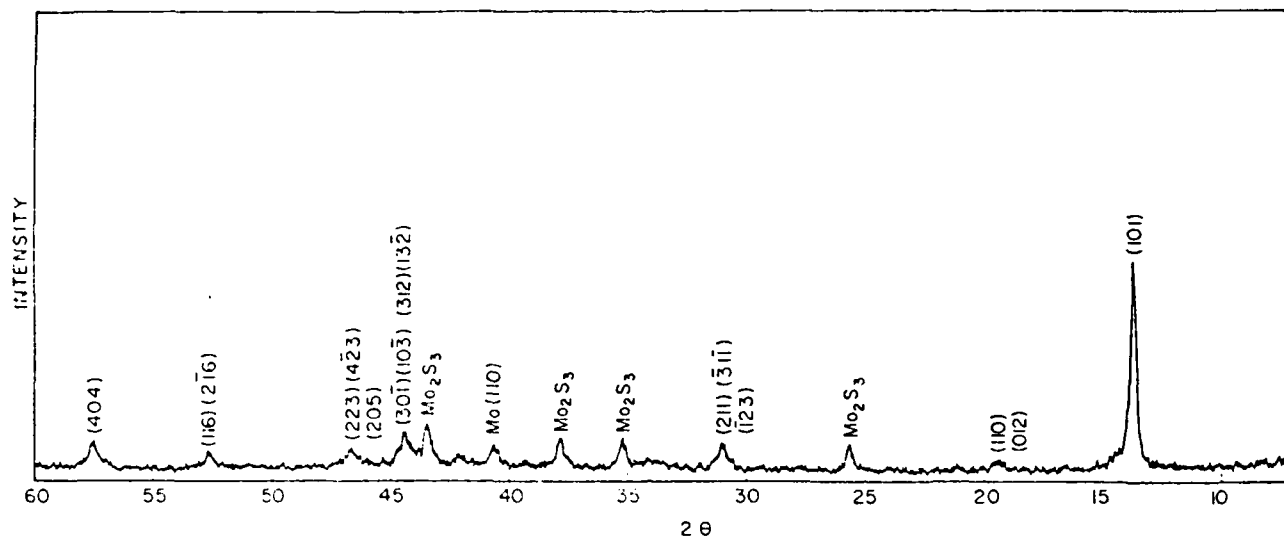


Fig. 4. X-ray intensity in arbitrary units vs. 2θ for a $PbMo_6S_8$ film, as prepared.

shown in Fig. 5. 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 $850^\circ C$ 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

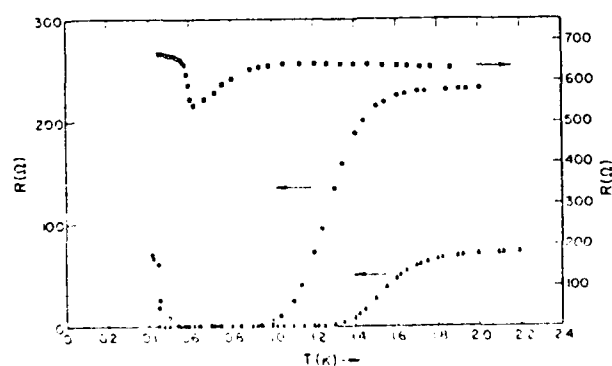


Fig. 5. $R(T)$ for the $PbMo_6S_8$ film of Fig. 4. The points are for the as-prepared film. The circles and squares are measurements on cooling and heating, respectively, after one hour of annealing and open triangles are measurements on cooling and heating respectively after the second anneal.

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 results, as we have interpreted them, are consistent with work on $ErRh_4B_4$ in which T_{c2} of polycrystalline samples, both bulk and thin-film was consistently higher than that of single crystals. If the annealing process results in the growth of large crystallites of $PbMo_6S_8$, a similar reduction of T_{c2} might be expected.

Discussion

These 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 $PbMo_6S_8$ 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 it was necessary to anneal the films, either to produce the correct phase or control the surface, 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 technique with Pb as was used with sulfur to produce $PbMo_6S_8$, thus getting around the difficulties we described above.

Acknowledgments

The authors would like to thank Fred Moore and David Smock for their assistance in the early stages of this project. This work was supported in part by the National Science Foundation through a grant to the University of Illinois at Urbana-Champaign.

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C. 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.

* Supported in part by the ONR under contract N00014-78-0619

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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 sputtering¹ 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 materials³ 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 targets⁵ 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 schematically 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 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 tantalum. 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 μ H 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 algorithm⁸

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

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

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

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

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

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 equation⁹

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

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 \AA 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

$$N = p/\sqrt{2\pi mkT} \quad (5)$$

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 compounds⁴ by coevaporation techniques, sulfur vapor is projected at the substrate using the molecular beam source rather than by bleeding high purity H₂S 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 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 $\text{Cu}_x\text{Mo}_6\text{S}_8$ 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 $3 \text{ \AA}/\text{second}$, 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 $R_{300\text{K}}/R_{15\text{K}}$ 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

The authors would like to thank R. Cantor, F. Moore and D. Kinosky for their assistance in the early stages of this research. Dr. J. Maps and J. Kang performed the low temperature measurements. Some of the equipment was originally purchased under a Grant from the National Science Foundation.

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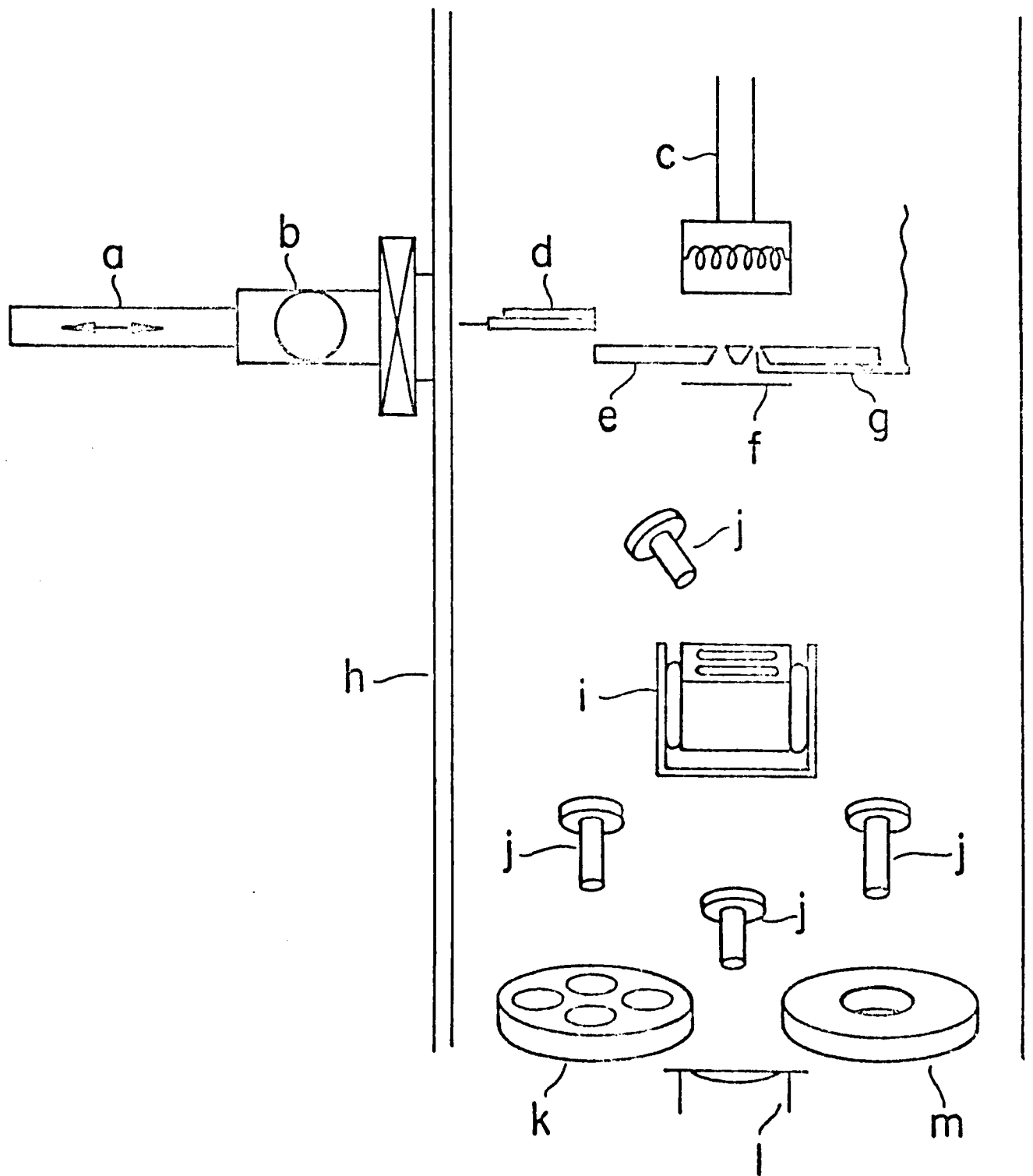
Figure Captions

- Fig. 1. Schematic of the Evaporation Apparatus. The letters denote the following components: a. linear motion manipulator, b. vacuum lock chamber, c. niobium heater block, d. substrate holder, e. mask carousel, f. shutter, g. thermocouple, h. liquid nitrogen shroud, i. sulfur molecular beam oven, j. crystal rate monitors, k. four hearth electron beam source, m. single hearth electron beam source.
- Fig. 2. Detail of substrate holder. The letters denote the following components: a. niobium heater block, b. boron nitride insulator, c. substrates, d. stainless steel frame with niobium bottom sheet, e. boron nitride mask, f. linear motion manipulator, g. stainless steel mask carousel.
- 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



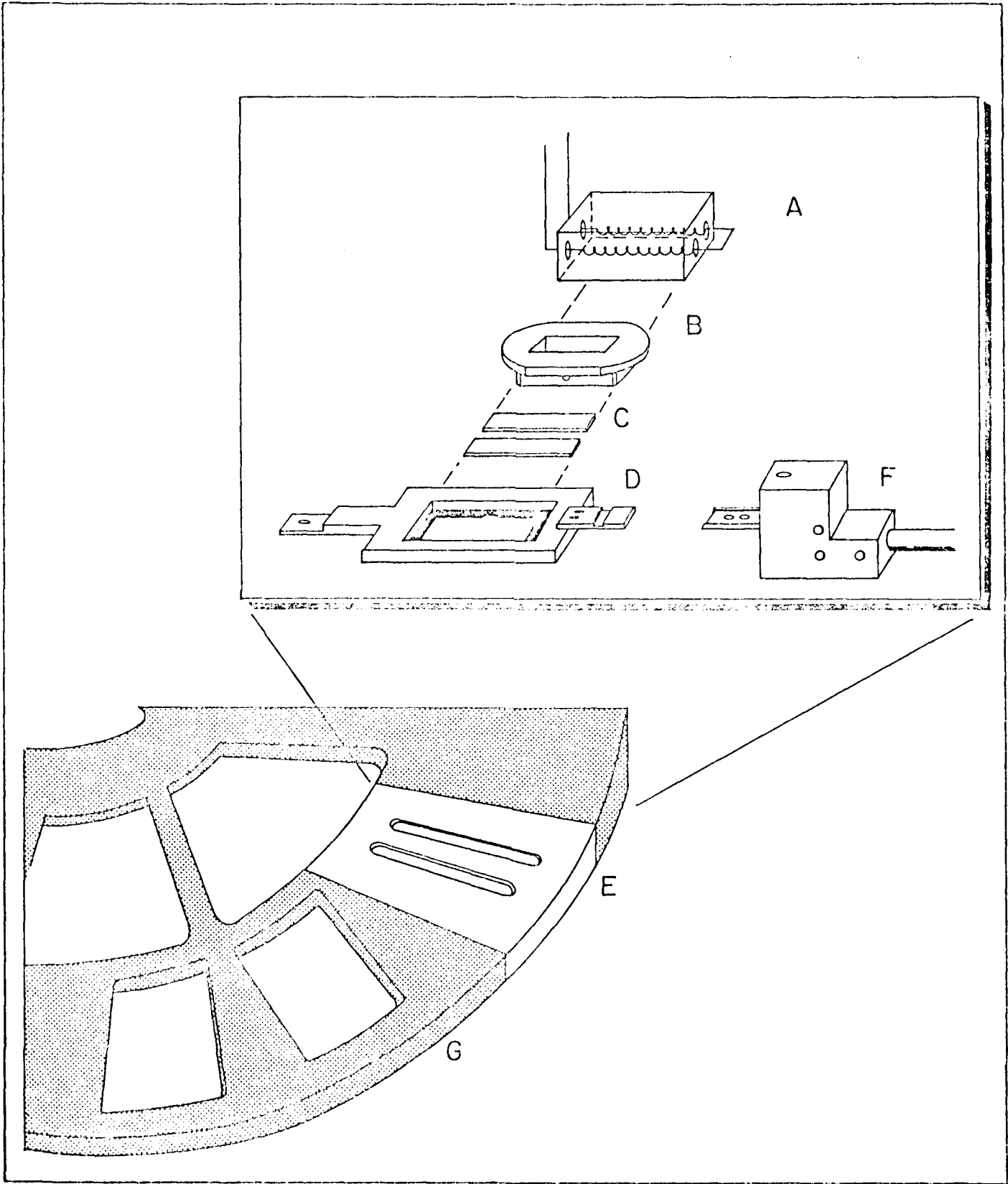


FIG. 2

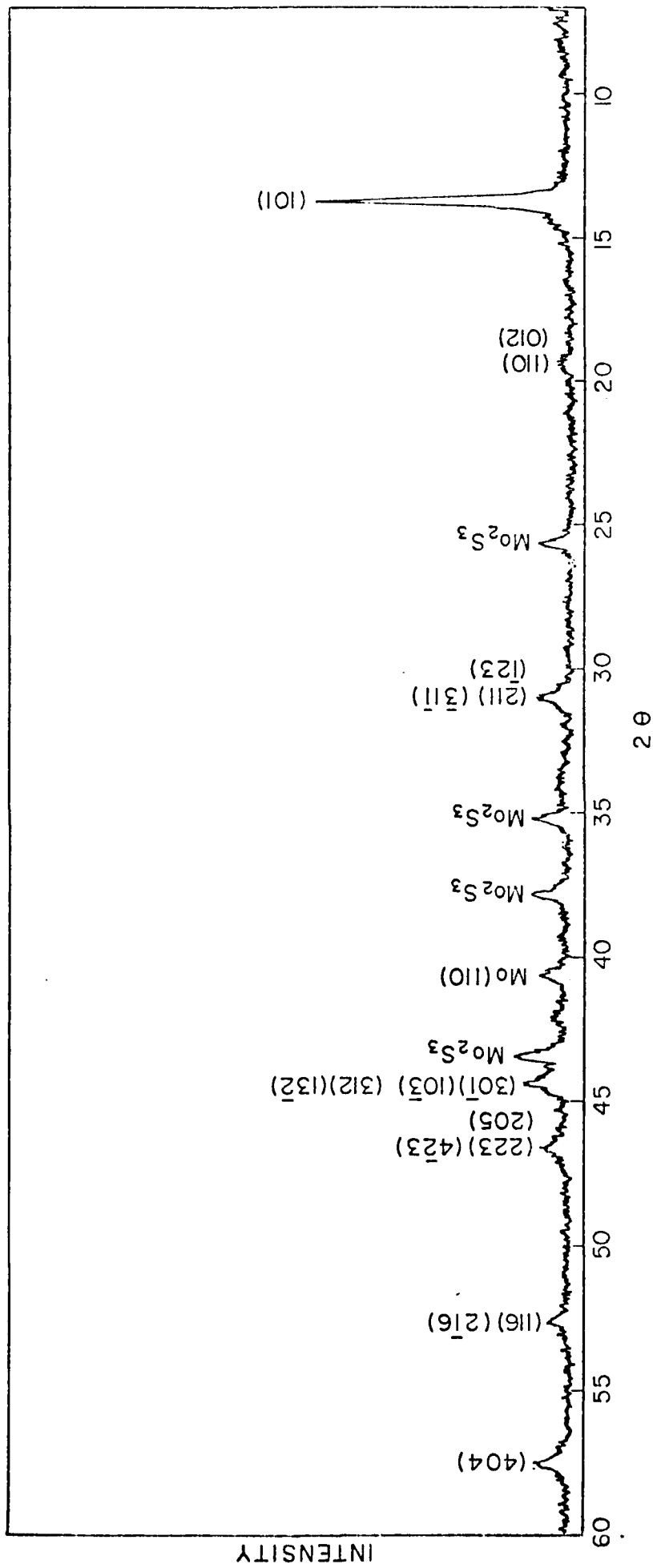
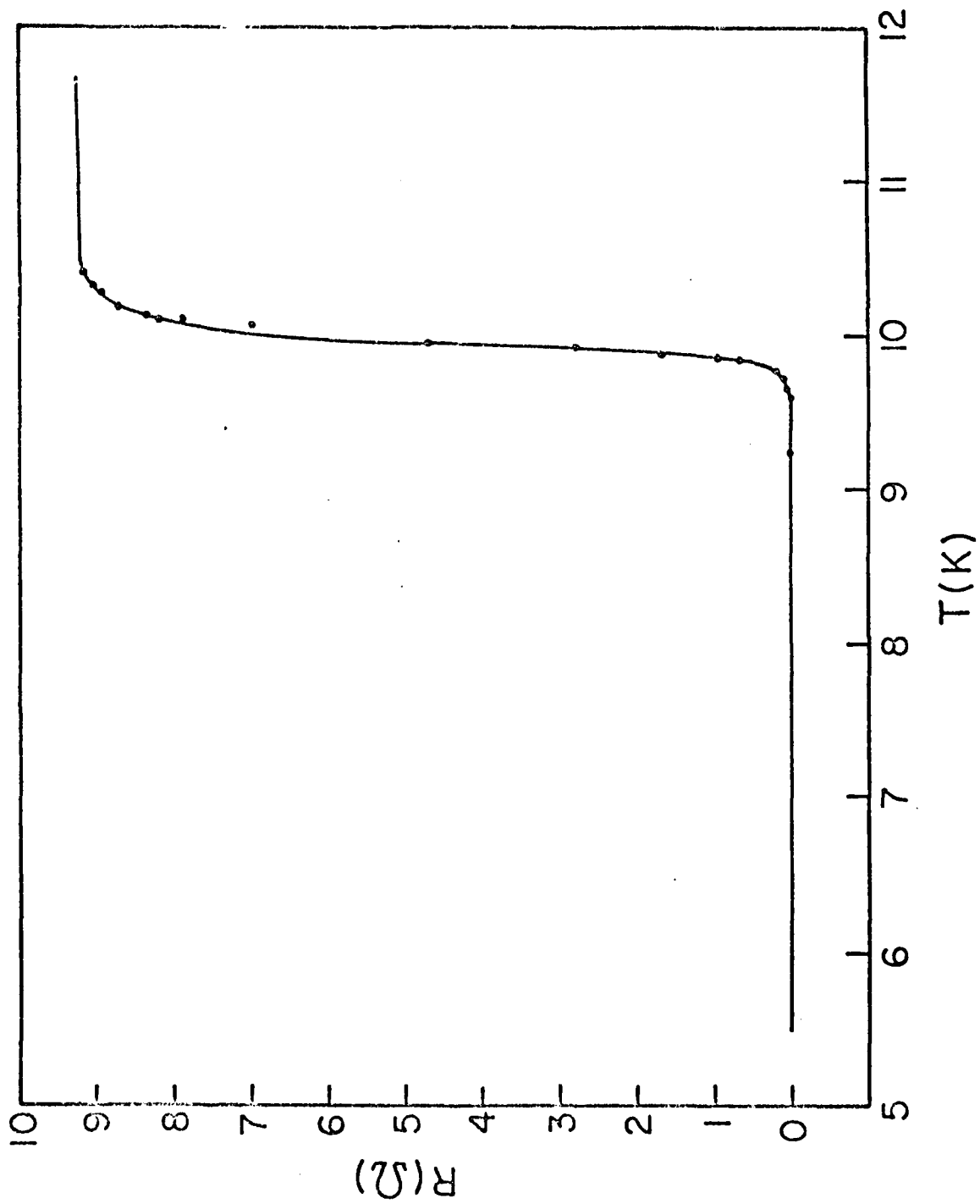
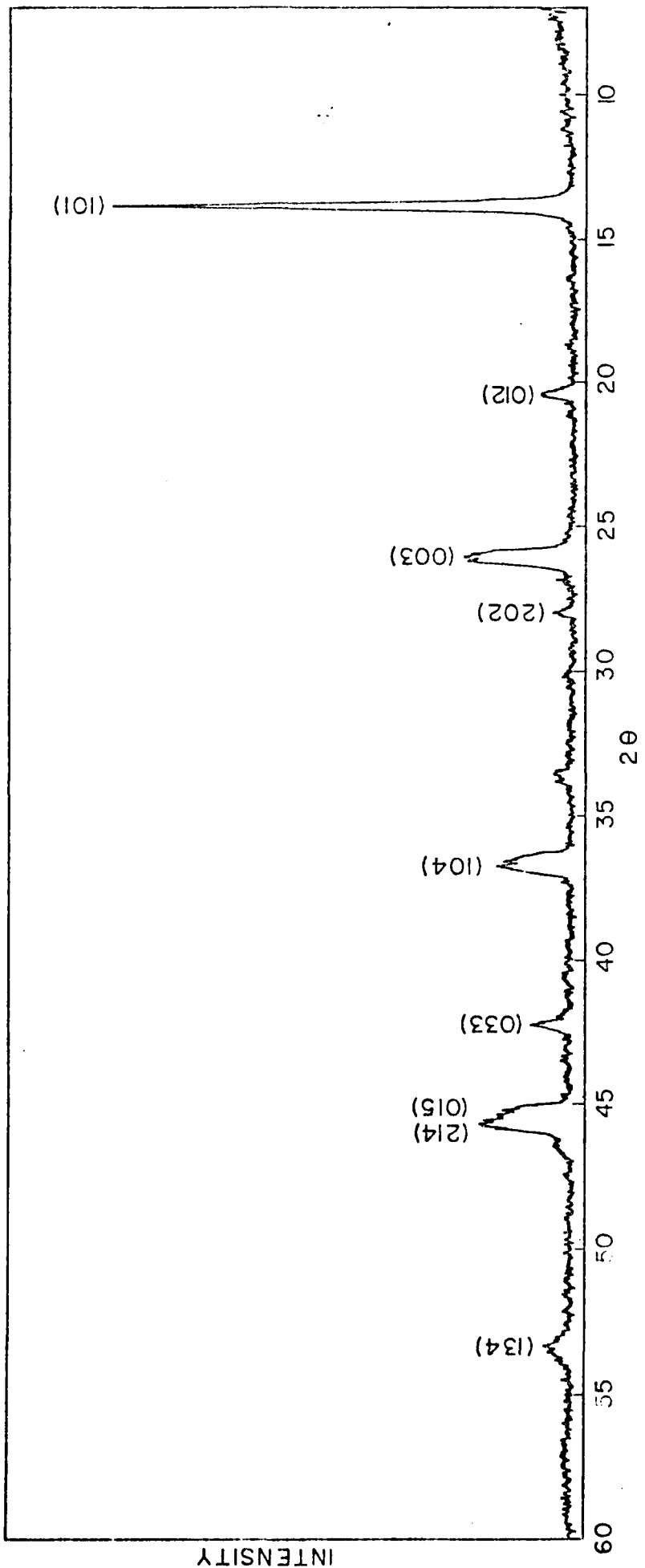


FIG 3





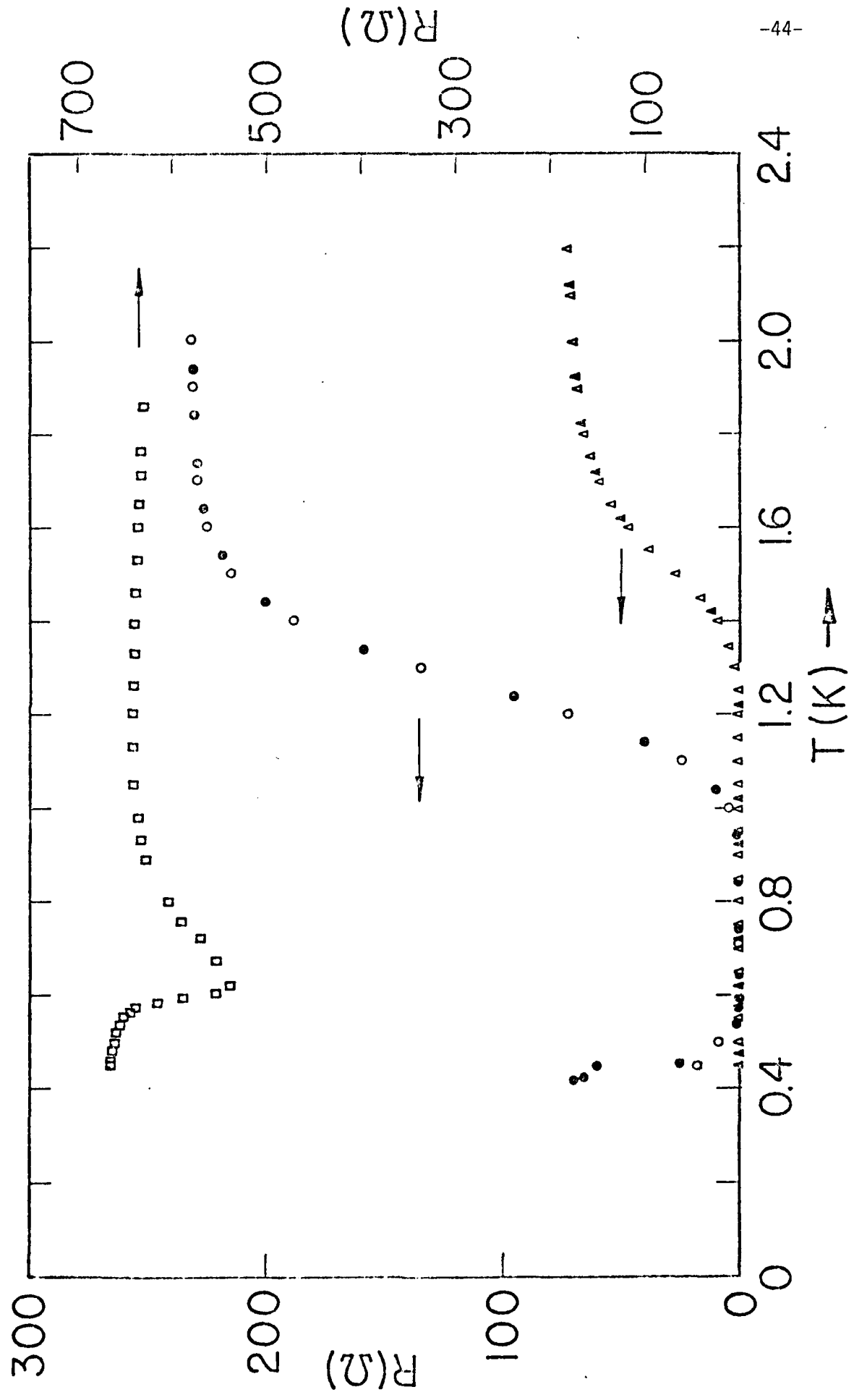


Fig 6

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