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SUPERCONDUCTIVITY IN METALS AND ALLOYS

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FOREWORD

This report was prepared by the RCA Laboratories under USAF Contract No. 33(616)-6405. The contract was initiated under Project No. 7371, "Applied Research in Electrical, Electronic and Magnetic Materials," Task No. 73711, "Applied Research on Conductor and Semiconductor Materials." The work was administered under the direction of the Central Directorate of Advanced Systems Technology, Wright Air Development Division, with Mr. R. A. Wolf acting as project engineer.

This report covers work conducted from May 15, 1959 to November 15, 1960.

G. D. Cody of RCA Laboratories was project engineer for the work reported. F. D. Rosi of RCA Laboratories was project supervisor.

ABSTRACT

Methods have been developed for the measurement of the interphase energy in superconductors. A description of the method is given along with preliminary results on thin foils and films of tin.

A proposed examination of the thermal contact resistance (Kapitza resistance) between metals and liquid helium is described. The apparatus is designed to measure changes in this contact resistance at the superconducting transition as well as in the normal state.

Measurements of the effect of hydrogen and deuterium on the superconducting transition temperature of lanthanum have revealed that they both depress the transition temperature; hydrogen depresses the transition temperature more than deuterium.

Measurements have been made of the transition temperatures in the system $(Nb, Ta, V)_3Sn$. The transition temperatures range from 2.8°K to 18°K and can be related to a simple mass and volume dependence. Critical field measurements indicate behavior similar to that in other "hard" superconductors. Resistance measurements have revealed a resistance anomaly near 100°K which can be related to an existing theory.

It has been found possible to prepare films of Nb_3Sn by a transport reaction.

Alloying experiments indicate ambiguities in the electron-to-atom ratio ascribed to various elements.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Jules I. Wittebort

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I. INTRODUCTION

The object of this contract has been: 1) to study the structure sensitive factors affecting the kinetics of the transition between the normal and superconducting states of selected metals, metal alloys, and intermetallic compounds and 2) to explore the area of intermetallic compounds and compound alloys for new superconductors. This report is intended to give an interim summary of the progress achieved in meeting these objectives.

The second section of the report concerns research on the superconducting transition. The transition from superconducting to normal phase is similar, in many respects, to phase transitions in more familiar systems. In the absence of applied magnetic fields or currents the transition is of second order occurring at a definite critical temperature, T_c, and exhibiting a characteristic specific heat anomaly. Such a transition is very similar to that occurring at the Curie temperature of ferromagnetic materials and to the order-disorder transition of certain alloy crystals. On the other hand, in the presence of an applied magnetic field or current the transition is of first order and similar, in many respects, to solid-liquid transformations. It is characterized by a latent heat of transition and a volume change, and the kinetics of the transition are governed by the nucleation of one phase in the presence of the other, followed by a growth of the new phase at the expense of the old.

The nucleation and growth aspects of the kinetics are the subjects of the present studies. The factor which exerts a major influence on the nucleation process is the surface energy (or surface tension) which exists at the boundary between normal and superconducting phases. The major effort in transition studies over the past year has been an investigation of this parameter.

In addition to controlling the nucleation, the surface energy also influences the rate of growth of the new phase by determining the shape of the boundary between the two phases. Electrodynamic interactions, however, are also important influences on the growth process. In 1950, Pippard(1) proposed a model for the growth of the normal phase at the expense of the superconducting phase. In this model, the velocity of a boundary between phases is such that the applied magnetic field plus that field due to the eddy currents induced in the normal phase, is just equal to the critical magnetic field at the boundary. Thus if the normal phase growth were slower than a certain value, flux would tend to pile up at the boundary and the field would tend to exceed the critical value; on the other hand, if the growth were faster than this value, flux would be unable to pile up at the boundary fast enough to maintain the magnetic field at the critical value. Hence a unique velocity of boundary motion was obtained. The validity of this model has been adequately demonstrated by the work of Faber(2) and that of Ittner(3).

However, in addition to electrodynamic processes there are thermal processes which can, under certain circumstances, influence and even dominate the growth rate of the new phase. As has been shown in earlier work at RCA(4), current-induced transitions are often completely dominated by the evolution of joule heat in the normal parts of the superconductor. Even in field-induced transitions, joule heat generated by eddy currents in the normal phase and the evolution of the latent heat can influence the growth rate. Thus the mechanisms by which heat is transported between the superconductor and the helium bath also play a role in the kinetic processes of the transition. In addition to the heat conductivities and heat capacities of the superconductors, the helium bath, and, in the case of thin films, the substrate, other factors are important. One is the thermal contact resistance between two dissimilar materials which is responsible for the so called "Kapitza jump" in temperature at a boundary and is important in determining the thermal coupling between the bath and the superconductor. Studies of the thermal contact resistance between liquid helium and superconductors are underway and will be reviewed in a later section.

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The third section of the report concerns materials research which has been directed toward an understanding of the nature of superconductivity in compounds and compound alloys. The present interim report on materials is concerned with five areas of research: The behavior of particularly simple alloys where valences are rather well defined, e.g. alloys of hydrogen with rare earth and transition metals; secondly, the dependence of the transition temperature on mass and volume in isoelectronic and isomorphic substances, e.g. alloys of the β-tungsten compounds Nb_3Sn, V_3Sn, and Ta_3Sn; thirdly, the investigation of the valence to be associated with transition metals in superconducting compounds, e.g. the valences associated with the components of such ternary alloys as gold-rhodium-zirconium; fourthly, the electrical and magnetic behavior of selected compound superconductors and possible correlations with the superconducting properties; finally, the preparation of compound superconductors in single crystal, film or whicker form.

The well known rules of Matthias(5) have furnished a guide to the formation of superconducting alloys and compounds. Matthias was able to correlate regularities in the superconducting transition temperature of compounds with the total number of valence electrons per atom. These rules achieved a more fundamental basis when it was noticed that the transition temperature can also be related to another parameter, the density of states, which is also a function of the electron-to-atom ratio.(6) Pines(7), moreover, was able to relate the Matthias' rules to a semi-free electron model of a superconductor based on the Bardeen, Cooper, Schrieffer(8) theory of superconductivity. Unfortunately, despite the great value of these deductions and generalizations, it should not be thought that one has even a qualitative understanding of superconductivity in compounds and alloys. The electron-to-atom ratio is certainly not the only parameter to be considered. The average mass, specific volume of the compound, and crystal structure must, and do, affect the transition temperature as strongly as the electron-to-atom ratio. One can point to several isoelectronic and isomorphic compounds the transition temperatures of which vary by a very large factor. Indeed it is sometimes very difficult to define what should be considered the "valence" electrons. For example, do low lying shells, although unfilled, contribute to the valence electrons? The answer would appear to be obvious in the case of the rare earth metals, not so obvious in the case of the transition metals. Finally, the effect on the transition temperature of magnetic interactions, as in rare earth compounds, and the effect of atomic disorder in alloys, should surely be taken into account in any consideration of the superconducting states.

With the present theory of superconductivity limited to an oversimplified semi-free electron model, it would be surprising to expect theoretical guidance in the complicated realm of superconducting compounds and alloys. Rather one should hope that sufficiently accurate experimental work could point possible directions in which the theoretical work should proceed.

The fourth section presents a summary of the progress to date and the proposed future experimental program. In the appendix some of the experimental techniques used for the measurements are described in more detail.

II. STUDIES OF THE SUPERCONDUCTING TRANSITION

A. INTERPHASE SURFACE ENERGY STUDIES

1. SUPERCOOLING

The existence of a positive surface energy was implied by the observation of hysteresis in the magnetization curves of superconductors as early as 1936(9). A typical magnetization curve for a superconductor having zero demagnetizing coefficient is shown in Fig. 1, where the arrows indicate the curve to be followed for increasing and decreasing fields. H is the value of the magnetic field, H_c is the critical field, H_e the value of the field for the spontaneous growth of superconducting nuclei in the normal material, and I is the (average) magnetic moment per unit volume of material. This type of hysteresis is called supercooling because of the similarity of this phenomenon to that occurring in, say, the water-ice transition. A simple thermodynamic argument shows that one should expect supercooling in the presence of a positive surface energy. To show this, the Gibbs free energy of a normal specimen with a single superconducting nucleus must be calculated. Let

g_n = Gibbs free energy per unit volume in the normal state $(H = 0)$

g_s = Gibbs free energy per unit volume in the superconducting state $(H = 0)$

α = Surface free energy at a normal-superconducting boundary.

Thus

$$g_s = g_n - \frac{{H_c}^2}{8\pi} + \frac{H^2}{8\pi} \qquad \text{and} \tag{1}$$

$$G = g_n(V - v) + \left(g_n - \frac{{H_c}^2}{8\pi} + \frac{H^2}{8\pi}\right) v + \alpha A_{ns} \tag{2}$$

where G is the total free energy of the specimen, $-\frac{{H_c}^2}{8\pi}$ is the lowering of the free energy due to the condensation of the superconducting electrons and $\frac{H^2}{8\pi}$ is the increase in free energy due to the magnetization of the superconducting volume. V is the volume of the specimen, v is the volume of the nucleus, and A_{ns} is the area of the surface of the nucleus. It should be pointed out that we have assumed that the nucleus has a zero demagnetizing coefficient which is certainly incorrect. However certain simplifications are obtained without seriously affecting the generality of the conclusions. Then

$$G = g_n V - \left(\frac{{H_c}^2 - H^2}{8\pi}\right) v + \alpha A_{ns} \tag{3}$$

and in general A_{ns} is proportional to $v^{2/3}$ so that

$$G \approx g_n V - \frac{({H_c}^2 - H^2) v}{8\pi} + a v^{2/3} \tag{4}$$

Figure 2 is a plot of G as a function of v for different values of H less than H_c. As can be seen, when the volume of a nucleus grows from a very small value, the total free energy must increase because of the surface energy, before it can decrease. Thus the specimen must be "supercooled" by lowering the

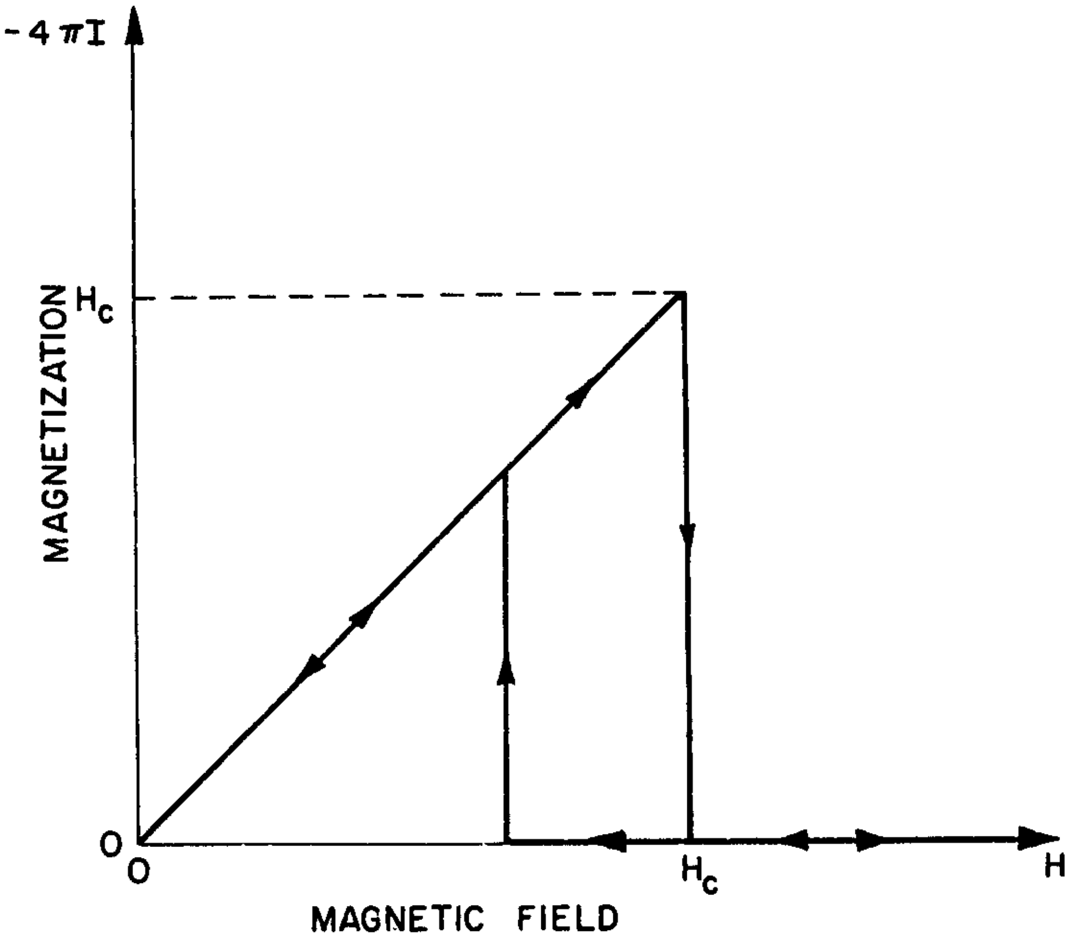


FIG. 1 TYPICAL MAGNETIZATION CURVE FOR A SUPERCONDUCTOR HAVING ZERO DEMAGNETIZING COEFFICIENT

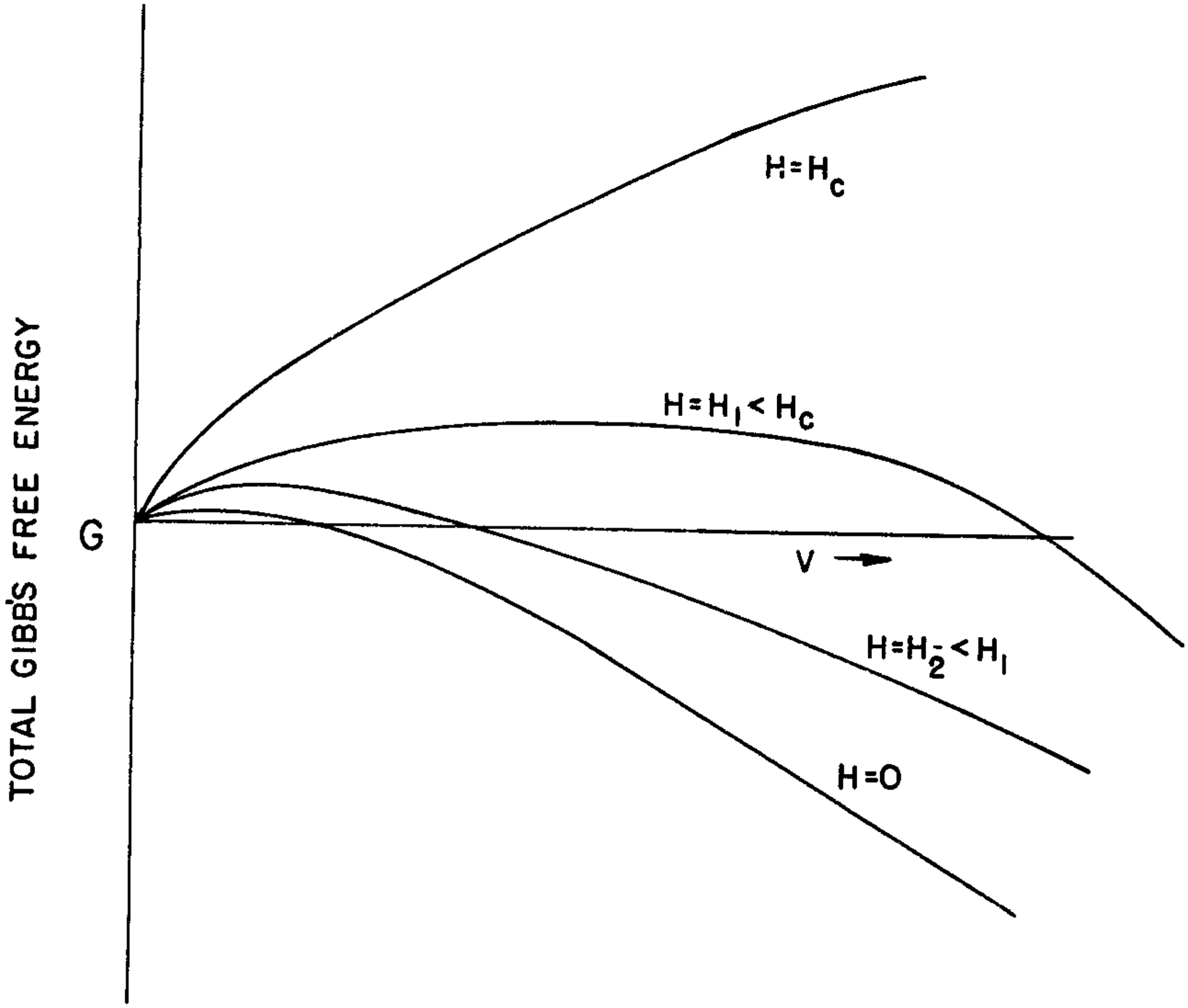


FIG. 2 FREE ENERGY OF A NORMAL SPECIMEN AS A FUNCTION OF VOLUME OF SUPERCONDUCTING NUCLEUS FOR DIFFERENT MAGNETIC FIELDS

field sufficiently below the critical value to lower the maximum value of the free energy enough to permit a thermal fluctuation in the volume to readily overcome the barrier. That this high degree of supercooling is rarely, if ever, attainable is discussed by Faber(10) in some detail.

It was our original intent to use the phenomena of supercooling in order to deduce the effect of concentration of the solute atoms in solid solution alloys on the surface energy. For the measurement an ac method was chosen. A long superconducting rod was surrounded by a many-turn pickup coil and an ac solenoid. An external dc magnetic field was applied parallel to the axis of the rod and was produced by means of a large nitrogen-cooled solenoid which surrounded the liquid helium dewar. The field current was controlled by a transistor regulator. The earth's magnetic field was canceled using three mutually perpendicular sets of Helmholtz coils. A high gain, frequency-selective amplifier and a phase-sensitive detector were used to observe the transitions.

The results indicated that great pains would have to be taken to remove flaws and strains, even in the purest of specimens, in order to obtain accurate surface energy measurements. Since the problems were expected to multiply many-fold when alloys were investigated it was thought that another approach to the problem should be sought. The method used at present involves the study of the intermediate state of thin foils. A discussion of the method and the present state of the measurements follows.

2. INTERMEDIATE STATE STUDIES

The intermediate state is, in a sense, a misnomer. A superconductor in this state is actually composed of a fine-grained mixture of normal and superconducting regions which arises in the following way. When a superconducting body having a non-zero demagnetizing coefficient is immersed in an otherwise uniform magnetic field, the field on the surface of the body varies from point to point. Thus, as the applied field is increased from a small value, the field at some points on the surface reaches the critical value H_c sooner than does the field at other points on the surface and sooner than does the applied field. For all values of the applied fields greater than the value for which this occurs and less than H_c, at least in the absence of an interphase surface energy, the specimen breaks up into the mixture of normal and superconducting regions. The volume fraction of the material which is normal at any applied field in this range is such that the average field inside the specimen is H_c. In fact the size of these regions is determined by the surface energy. This was first discussed by Landau(11) in 1937. Using a method analogous to the Bitter powder technique, Schawlow(12) and later Faber(13) actually deduced values for the surface energy by measuring the size of these domains.

Because of the positive surface energy, the value of the magnetic field for the onset of the intermediate state is higher than that given in the earlier discussion. The smaller the specimen dimension in the field direction, the larger is this threshold field. Landau(14), Andrew(15), and Kuper(16) have discussed, in detail, the dependence of this threshold field on surface energy and specimen dimensions.

There is another threshold field which is dependent on surface energy. This field will be called the upper threshold as contrasted with the one discussed in the above paragraph which will be called the lower threshold. The upper threshold field is that magnetic field for which the specimen becomes completely normal. From an experimental point of view the upper threshold field is to be preferred because it does not require (in the case of foils or films) a precise knowledge of the demagnetizing coefficient of the specimen as a whole. That this upper threshold field should be less than H_c can be easily seen. A bulk specimen in a magnetic field somewhat less than H_c will have a lower volume free energy than a normal specimen. However, a thin film, if it contains one or more superconductive regions, will have a higher total free energy than if it were all normal, because of the positive interphase surface energy. Davies(17) gives a much oversimplified thermodynamic argument to relate this upper threshold field to the surface energy and the thickness of a foil which has been subjected to a magnetic field perpendicular to its surface. One can conclude, however, that the function

$$\Phi = \frac{H_c^{\,2} - H_t^{\,2}}{H_c^{\,2}} = f(\Delta/d). \tag{5}$$

here H_t = the threshold magnetic field
d = the foil thickness
Δ = the surface energy parameter, which is defined by relation $\alpha = \frac{H_c^{\,2}}{8\pi}\Delta$. Thus Δ has the units of length.

Although the exact form for $f(\Delta/d)$ is not known, Davies shows that changes of Δ with temperature and other parameters can be obtained empirically. While our measuring technique differed considerably from that used by Davies, our method of data analysis was essentially the same.

The experimental arrangement is described as follows. A sandwich was formed by placing the film or foil to be studied between two flat spiral coils which were formed by photo-etching copper evaporated on glass. Thin sheets of mica insulated and protected the sample from the coils. The sandwich was held together with a phosphor bronze coil spring. The assembly was placed in a cryostat so that a dc magnetic field could be applied parallel or perpendicular to the plane of the film. With a small 500 cps current present in one of the spirals the signal from the other was observed as a function of the dc magnetic field at temperatures below the critical temperature. The observed signal when the sample was normal was as much as 1½ orders of magnitude larger than when the specimen was superconductive. H_c was determined by observing the transition when the external field was applied parallel to the surface of the specimen; the upper threshold field H_t was determined by observing the transition when the external field was applied perpendicular to the surface. Figure 3 is a diagramatic representation of the experimental arrangement. The area of the coils was made small compared with the film area thus reducing edge effects. Preliminary results on three pure tin specimens, two rolled foils 60.7 microns and 12.5 microns thick and an evaporated film 0.5 microns thick, will be summarized. Figure 4 is a plot of Φ as a function of the reduced temperature, $t = T/T_c$, for the three specimens. From these data, $\log_{10}\Phi$ vs. $\log_{10}(1/d)$ was constructed for different values of the reduced temperature. The resulting family of curves is shown in Fig. 5. Since Φ is a function of (Δ/d) only, as one moves along a Φ = constant line, such as $A\text{-}A'$ in Fig. 5, the argument (Δ/d) must not change. Thus the difference in the $\log_{10}(1/d)$ values at two different temperatures must be equal to the difference in the logarithms of the surface energy parameter at the two temperatures. Thus $\frac{\Delta(t)}{\Delta(t_o)}$ can be deduced from these curves. In Fig. 6 are shown a collection of points from such a calculation and the curve $\Delta\alpha(1 - t^{3/2})^{-1/2}$ which was obtained by Davies(17), Faber(18,19), and Sharvin(16) independently. It should be noted that each curve of Fig. 4 was determined by three points only (one point for each specimen) and, therefore, a large experimental error should be expected. However the agreement with earlier results is sufficiently good to extend the method to impure specimens to determine the variation of Δ with impurity concentration and electronic mean free path. To this end sixteen impure specimens containing assorted impurities in solid solution in concentrations varying from 0.1 atomic percent to 1.0 atomic percent are being prepared. Each specimen is in the form of a disk 20 mm in diameter and 25 microns thick. Data from these specimens should be available in the near future.

B. THE THERMAL CONTACT RESISTANCE

The phenomenon of thermal contact resistance between two dissimilar materials was first observed by Kapitza(21) in 1941 and has been investigated by many others since. Most recently Lee and Fairbank

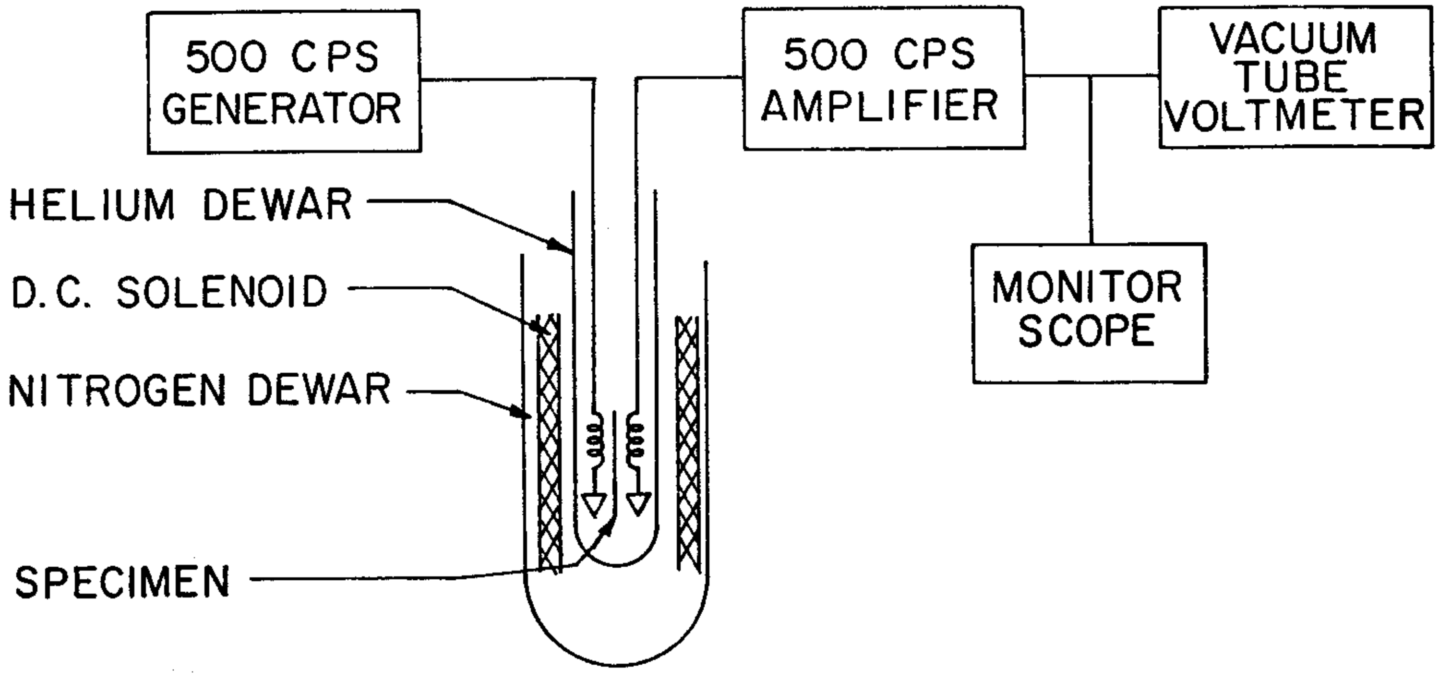

500 CPS GENERATOR
500 CPS AMPLIFIER
VACUUM TUBE VOLTMETER
MONITOR SCOPE
HELIUM DEWAR
D.C. SOLENOID
NITROGEN DEWAR
SPECIMEN

FIG. 3 EXPERIMENTAL ARRANGEMENT FOR OBSERVING THE NORMAL-SUPERCONDUCTING TRANSITION IN THIN FILMS AND FOILS

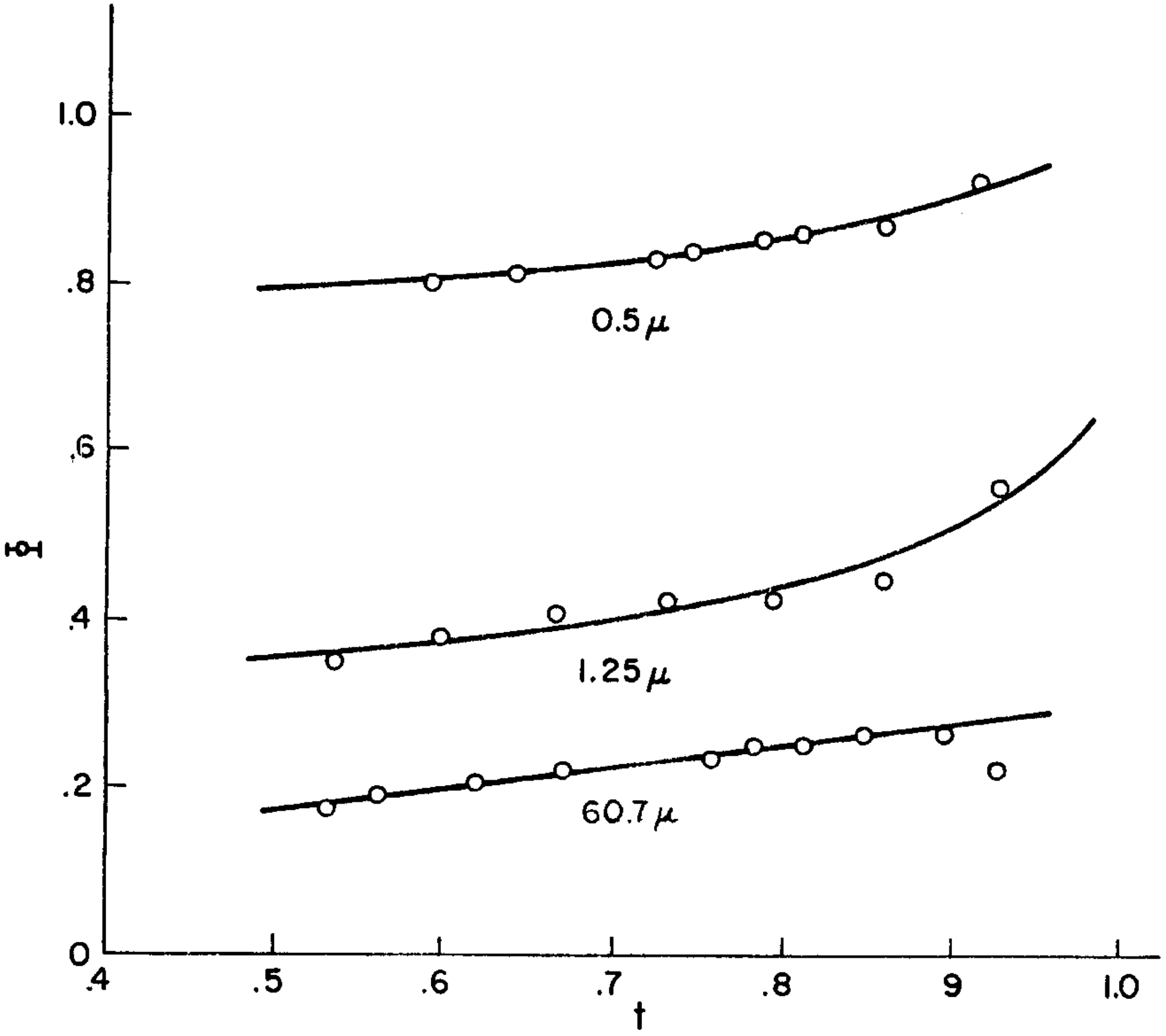


FIG. 4 $\xi = \frac{H_c^2 - H_t^2}{H_c^2}$ VS $t = \frac{T}{T_c}$ FOR THREE SPECIMENS HAVING DIFFERENT THICKNESSES

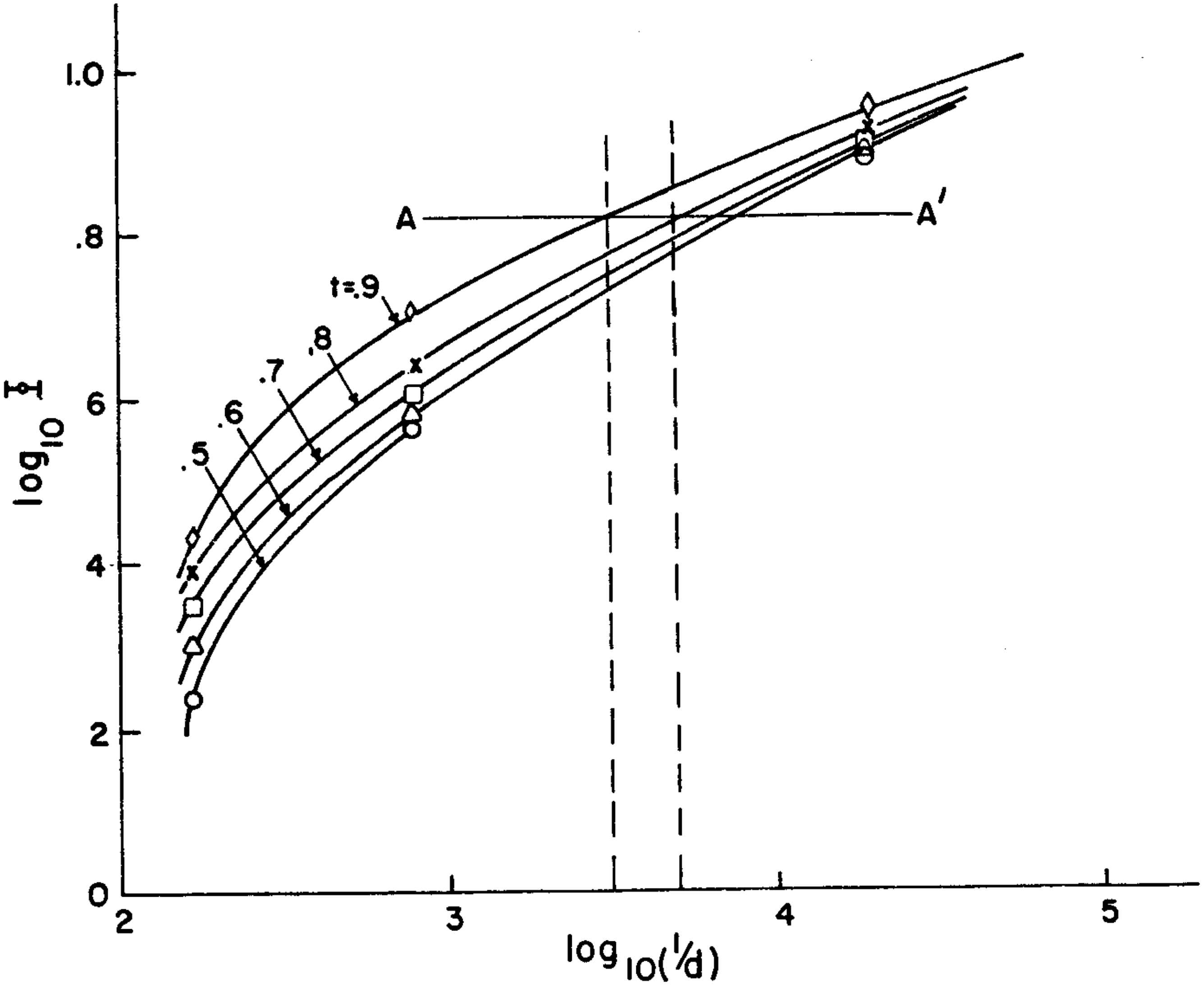


FIG. 5 $\log_{10} \frac{I_0}{I}$ vs. $\log_{10} (1/d)$ FOR THREE TIN SPECIMENS

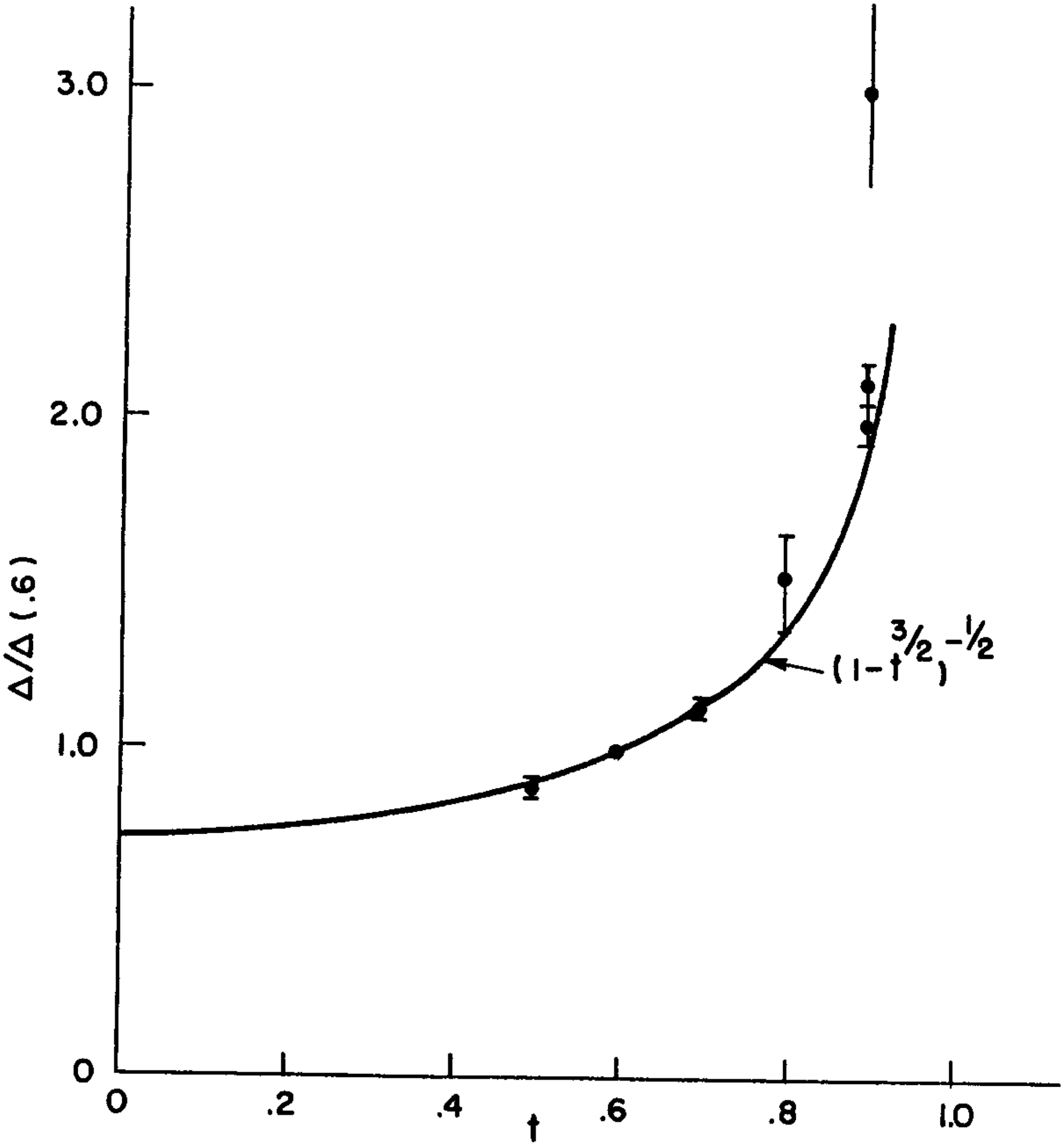
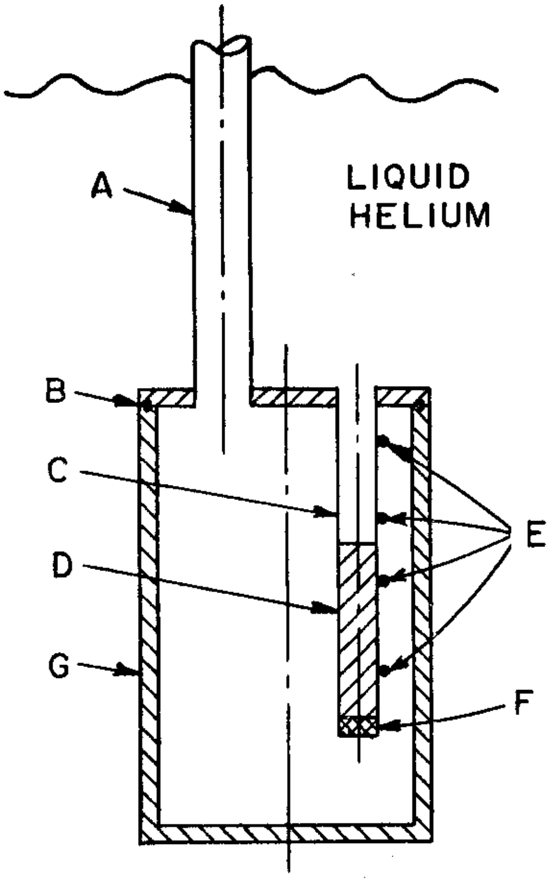


FIG. 6 SURFACE ENERGY PARAMETER, Δ, AS A FUNCTION OF REDUCED TEMPERATURE FOR TIN

have measured the contact resistance between copper and He^4 below the λ-point(22) and between copper and He^3 (23). Little(24) has made a theoretical calculation of the heat transport across a boundary by considering the scattering of phonons due to discontinuities of the elastic constants at the boundary. The results of the calculation seem to be in good agreement with measurement on solid-solid interfaces but yield figures which appear to be about two orders of magnitude too small for copper-liquid helium interfaces. Furthermore, although the earlier work of Ambler(25) tended to confirm the temperature dependence predicted by Little(24) and others(26,27), the work of Lee and Fairbank(22,23) was in definite disagreement. To quote Lee and Fairbank, "It would appear that further work on this problem, both experimentally and theoretically, is in order." Little(24) has offered as a possible explanation for the discrepancy a relatively large contribution to the heat transport on the part of surface waves. He also suggests the existence of a direct interaction between the electrons of the metal and the surface phonons. If this were true, a difference in the thermal contact resistance between a superconductor and liquid helium can be expected when the metal is in the normal state and when it is in the superconducting state.

Measurements of the thermal resistance between tin and liquid helium II have been started. A schematic of the conductance cell is shown in Fig. 7. This arrangement should prove capable of providing accurate data at temperatures below the λ-point (2.19°K). Above the λ-point the apparatus will have to be modified to shorten the helium column because of the poor thermal conductivity of He I. Initially, however, much valuable information can be obtained in the lower temperature domain where the superfluid He II with its very high effective heat conductivity is the stable phase. The apparatus for these measurements was recently finished and preliminary measurements are being made.



A - STAINLESS STEEL PUMP LINE & ELECTRICAL CONDUIT.
B - GOLD "O" RING
C - THIN WALL STAINLESS STEEL TUBE
D - SPECIMEN
E - THERMOMETERS - 1/10 WATT ALLEN-BRADLEY RESISTORS
F - HEATER
G - GOLD PLATED BRASS RADIATION SHIELD

FIG. 7 SCHEMATIC OF THERMAL CONDUCTANCE CELL

III. SUPERCONDUCTING COMPOUNDS AND ALLOYS

A. LANTHANUM-HYDROGEN AND LANTHANUM-DEUTERIUM SYSTEMS

The work of several investigators on various alloy systems has shown that such concepts as electron-to-atom (e/a) ratio, average mass, atomic volume, electronic spin, and electronic mean-free path play an important role in superconductivity. The dependence of the superconducting properties of metals on these parameters is not well defined and requires further studies. In particular, the real significance of the e/a ratio, other than its definition, is obscure, since it is difficult to define the valence of most of the elements present in alloys. The effect of the average mass in superconducting alloys and compounds appears to be vastly different than that in superconducting pure elements. Moreover, it is sometimes difficult to separate volume effects from those due to variable e/a ratio. Although the dependence of the superconducting transition temperatures of alloys can be quantitatively represented by an empirical equation the qualitative dependence is far from understood.

The study of the lanthanum-hydrogen and lanthanum-deuterium systems was undertaken to assist in an understanding of superconductivity in alloy systems. The reason for the selection of these systems is that hydrogen and deuterium appeared to be particularly simple solutes which are absorbed in fairly large quantities by lanthanum. They enter into lanthanum interstitially and are probably completely ionized if one extrapolates from other transition metal-hydrogen systems.(28) Moreover, the large mass difference between the two isotopes could provide a direct comparison of the mass effect of the solute on superconducting transitions.

There are several disadvantages to the lanthanum-hydrogen system which had to be overcome in this work. One of them is that lanthanum exists in two allotropic forms at low temperatures, a hexagonal form having a transition temperature of about 4.8°K, and a face centered cubic form having a transition temperature of about 5.9°K.(29) In ordinary lanthanum both forms coexist at low temperatures although only the hexagonal form is thermodynamically stable. The face centered cubic form is the desirable form for this study since it can be stabilized by small amounts of hydrogen and by quenching from high temperatures. Another difficulty connected with this system is that there are two phases in the lanthanum-hydrogen system,(30) namely, a phase consisting of the solution of hydrogen in the metal and a lanthanum hydride phase. According to Ziegler(31) the hydride phase is not superconducting, hence the study of the superconducting properties of this system is limited to a rather narrow range of concentration of hydrogen (or deuterium) in lanthanum. At room temperature the solubility of hydrogen in lanthanum is less than 1 atomic percent whereas at 600°C the solubility increases to about 8 percent. Since it was desired to study the effect of dissolved hydrogen in the alloys over a large concentration range, such alloys had to be annealed at 600°C and then quenched to retain hydrogen in the dessolved state.

The specimens were prepared in an apparatus represented schematically in Fig. 8 using the following method. Weighed specimens in the shape of bars with approximate dimensions of $2.5 \times 2.5 \times 20$ mm (weight ≈ 0.5 g) were placed in a quartz ampules which were attached to the hydrogenating apparatus. The samples were subsequently heated at 550°C for 15 minutes in a vacuum. During this time the specimens degassed sufficiently so that the final pressure in the system was about 5×10^{-6} mm. A calculated amount of hydrogen was then generated into a calibrated bulb *C* by heating uranium hydride (in tube *A*) prepared previously. The pressure of hydrogen was measured by means of a McLeod gauge, which was connected to the hydrogenation apparatus through a cold trap *E*. The specimens were hydrogenated for ten minutes at 550°C and they were then sealed off in quartz tubes. The specimens were subsequently annealed from 600°to 700°C, for 12 to 24 hours and then, while still sealed in the ampules, were quenched in water or silicone oil at 0°C. The total error in the amount of hydrogen in the specimens was estimated to be about ± 1%. The deuterated specimens were prepared in a similar way, using uranium deuteride at *B* as the source of deuterium.

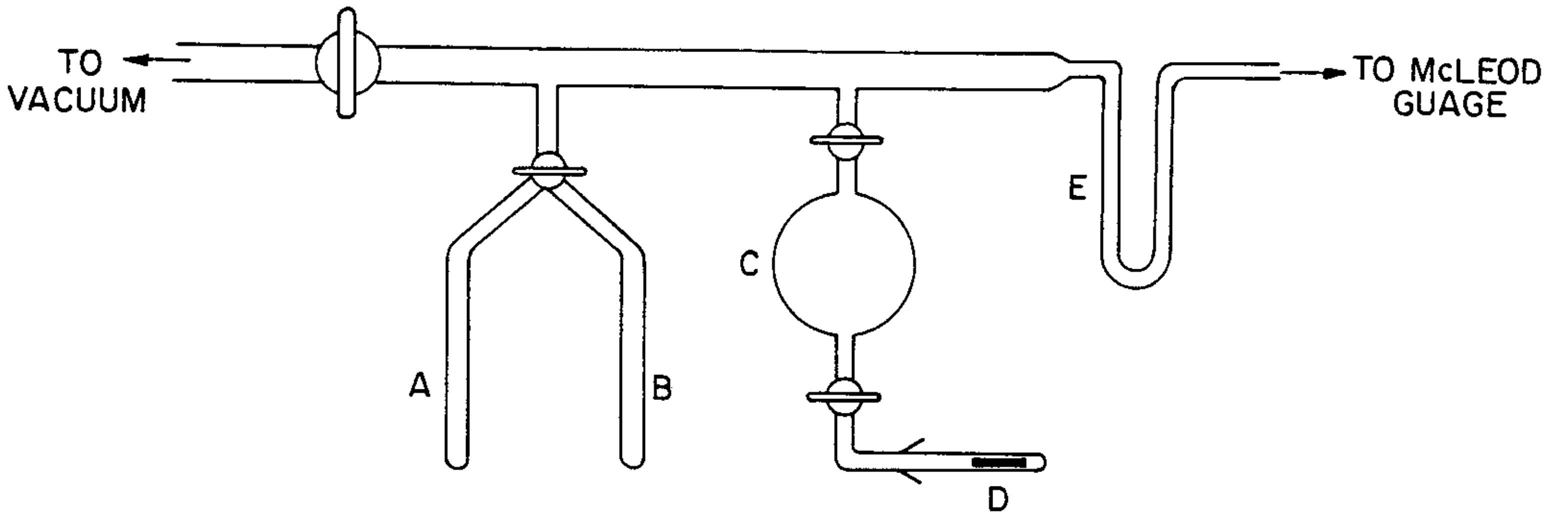

TO VACUUM
TO McLEOD GUAGE
A
B
C
D
E

FIG 8 SCHEMATIC DIAGRAM OF HYDROGENATING APPARATUS

The question that arises is how much hydrogen is present in solution. If the quench were efficient for concentrations up to 8 percent one would expect no precipitation of LaH_2. However, since the encapsulated sample cools gradually, precipitation is likely. Photomicrographs of the specimens indicated signs of precipitation of LaH_2 or LaD_2 even at concentrations of 2 percent of the solute and at 8 percent solute about 2 to 3 percent of the specimen appeared to be precipitated. Residual resistivity data indicated that the presence of the precipitated compound is the main factor determining the residual resistivity ratio. The pure lanthanum had a resistivity ratio $\frac{\rho(300°C)}{\rho(T_c)}$ of about 50; the hydrogenated and deuterated samples had a resistivity ratio of 25 up to concentrations of about 8 percent; the ratio dropped to about 10-13 for solute concentrations around 20 percent. Thus, there is a reason to suppose that there is nearly constant amount of the compound precipitated for solute concentrations up to 8 percent and an increase in the amount precipitated for concentrations beyond this.

The superconducting transition was observed magnetically over the range 1.3°K to 20°K by the usual method of observing the change in coupling between a primary and a secondary coil, the secondary having a lanthanum core. Measurements were made at 20 cps and 50 cps. The ac field on the specimens had an amplitude of 0.08 or 0.8 gauss. Temperatures were determined by a 56-ohm, 0.1-watt carbon resistor in thermal contact with the specimens. In any run, four specimens could be examined. The transition temperatures of the hydrogenated specimens were determined with respect to the pure one. The results of the experiments appear in Table 1, for hydrogen and in Table 2 for deuterium solid solutions.

TABLE 1

CRITICAL TEMPERATURES OF LaH_x SPECIMENS

x $\frac{\text{MOLES H}}{\text{MOLES La}}$	T_c(°K)	WIDTH (°K)	QUENCH
.00	5.96	.10	Water
.01	5.95	.09	Water
.02	5.83	.05	Oil*
.02	5.61	.28	Water
.03	5.59	.13	Water*
.04	5.30	.25	Water
.04	5.23	.24	Oil
.06	5.23	.24	Water
.08	5.10	.22	Water
.10	5.13	.25	Water
.12	5.15	.21	Water
.16	5.22	.26	Water
.20	5.37	.20	Water
.05	5.23	.50	Oil*
.05	5.15	.28	Water

*Samples prepared from a new batch of lanthanum.

The data are also shown in Fig. 9 and Fig. 10 respectively. Three characteristic regions are noted in these results: (1) for solute concentrations below 1 percent a small decrease in transition temperature; (2) for concentrations between 1 and 8 percent a sharp decrease in transition temperature; (3) for concentrations above 8% a gradual increase or no change in transition temperature. The effects (1) and (2)

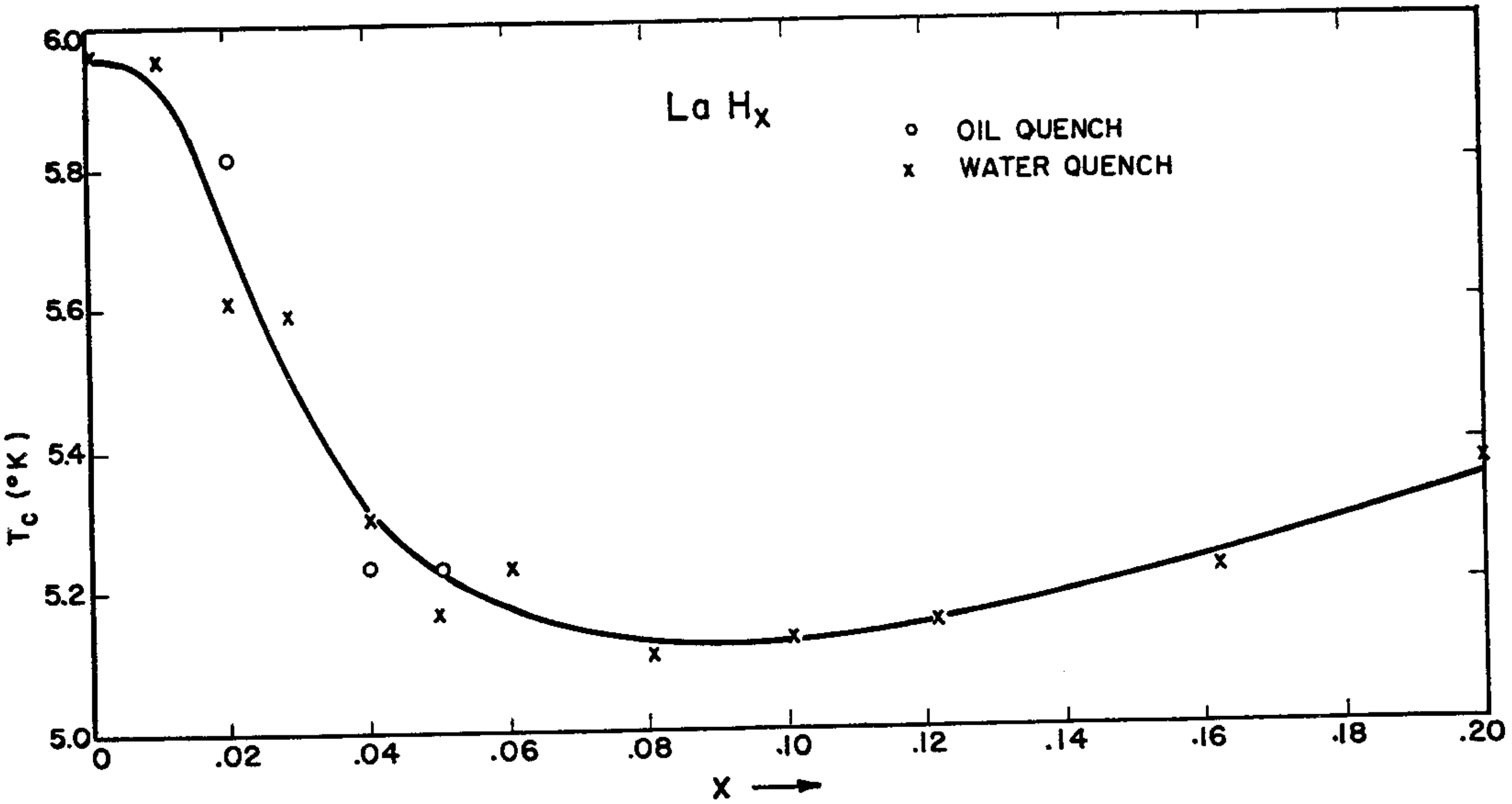


FIG. 9 TRANSITION TEMPERATURE VS CONCENTRATION FOR La H_x

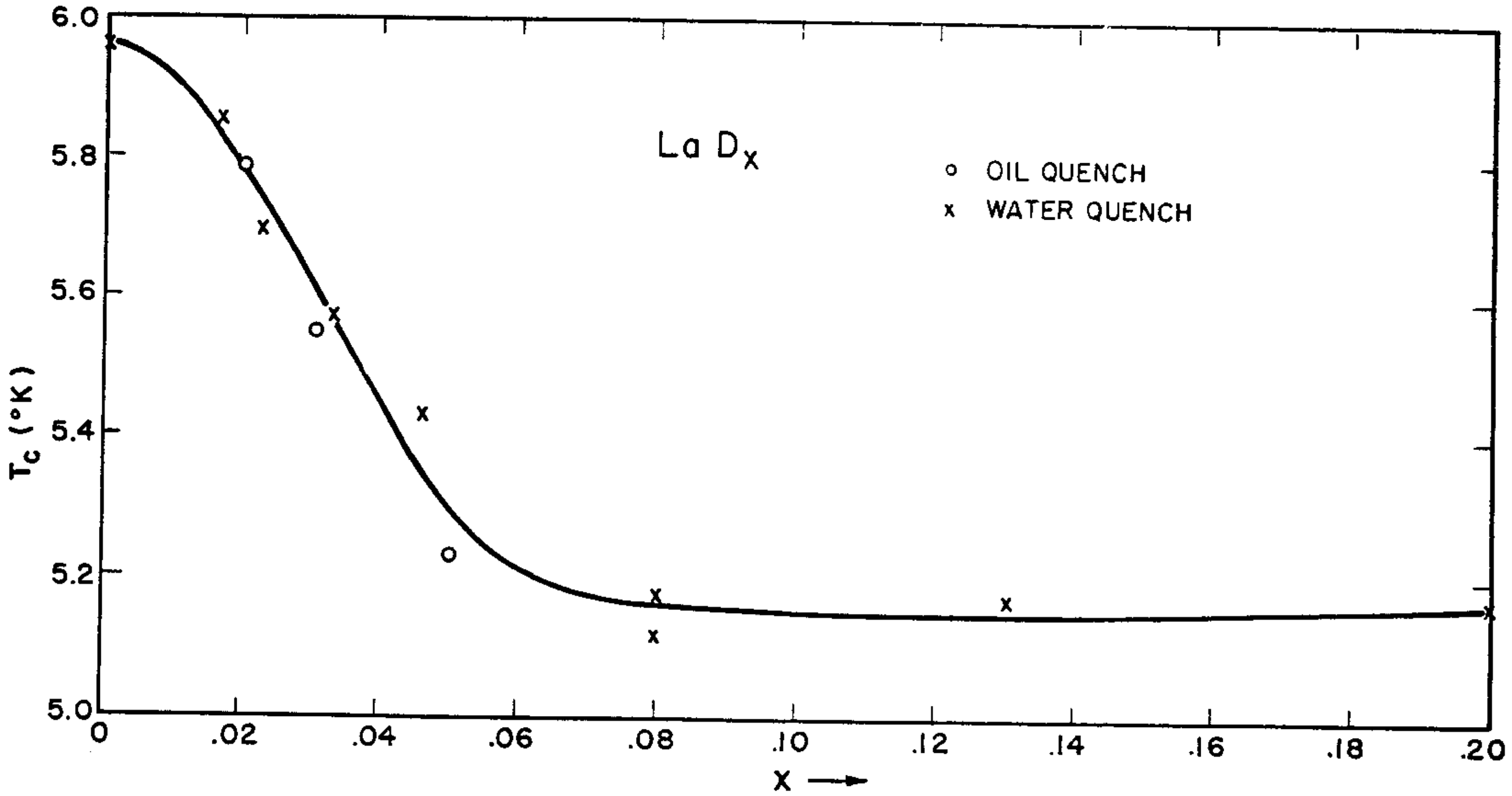


FIG. 10 TRANSITION TEMPERATURE VS CONCENTRATION FOR LaD_x

are qualitatively similar to the behavior of impurities in tin, indium, and aluminum observed by Lynton *et al.*(32) However, both the decrease in T_c and the impurity concentrations are greater than those obtained by Lynton *et al.*(32)

TABLE 2

CRITICAL TEMPERATURES OF LaD_x *SPECIMENS*

x MOLES D / MOLES La	T_c(°K)	WIDTH (°K)	QUENCH
.017	5.85	.15	Water
.02	5.81	.11	Oil*
.024	5.70	.30	Water
.030	5.55	.28	Oil
.033	5.53	.29	Water
.046	5.37	.28	Water
.050	5.23	.40	Oil
.080	5.17	.28	Water
.080	5.12	.2	Water
.13	5.17	.32	Water
.20	5.17	.35	Water

*Sample prepared from a new batch of lanthanum.

As noted previously, measurements of the residual resistance ratio made in order to find a correlation with the transition temperatures failed to show any correlation due to the precipitation. Nevertheless, it appears safe to conclude from the low temperature measurements, resistivity ratio measurements and from metallographic investigation that up to 8 percent of the solute the concentration of the dissolved solute increases although there is some precipitation of LaH_2 and LaD_2. At present it is uncertain whether in the range of 1 to 8 percent the lowering of T_c by the dissolved hydrogen or deuterium is due to the change of e/a ratio of the alloys, electronic spin interaction, or to impurity scattering.

The third effect observed above 8 percent of the solute is consistent with an increasing amount of precipitated LaH_2 or LaD_2 as predicted from the phase diagram. In the case of lanthanum-hydrogen solution an anomalous rise in T_c is observed above 8 percent which is probably due to an enhanced rate of precipitation of LaH_2 (and, hence, lowering of concentration of dissolved hydrogen) caused by nuclei of LaH_2 present in the sample prior to quenching. The lanthanum-deuterium system showed a leveling in the transition shift beyond $LaD_{.1}$ but this difference can be ascribed to the fact that for these concentrations the specimens were annealed at 700°C where the formation of LaD_2 nuclei would not occur at the concentration investigated.

The region of interest in these two systems proved to be between 1 and 8 percent of the solute. The transition temperature drops almost linearly and there seems to be a possible difference between the results for hydrogen and deuterium. In order to avoid bias in evaluating the results portions of the curves which appeared to be straight lines (between 2 and 5 percent) were fitted by the least squares method to the following linear equations:

(1) for La-H system $$T_c = 6.10 - 0.19\,x \qquad (6)$$

(2) for La-D system $$T_c = 6.11 - 0.17\,x \qquad (7)$$

where x is the concentration of the solute in atomic percent. It is noteworthy that both the hydrogen data and the deuterium data extrapolate to about the same temperature (6.10°K) for zero solute concentration. The difference between this temperature and the transition observed for pure lanthanum (5.95°K) could be associated with a small amount of the hexagonal phase in the "pure" specimen. There is a difference in the slopes (~ 10 percent) in (6) and (7) which might be due to the difference in isotopic mass. However, as noted previously, even in the range of concentrations of up to 8 percent an undertermined amount of LaH_2 (LaD_2) has precipitated. Therefore, the significance of these results must await improved quenching of the specimens.

Since evidence was obtained for a partial precipitation of LaH_2 (LaD_2) during the quenching of the specimens having relatively low concentrations, a new method has been developed for rapid quenching of the specimens. This method involves the sealing-off of the hydrogenated specimen in a quartz ampule with a thin-walled bubble on one end. The specimen is then annealed in an evacuated vertical quartz tube situated in a furnace. After the annealing a suspended metal weight is released on the ampule which breaks and allows the bare specimen to fall into degassed, cold silicone oil. Several specimens have been prepared by this method and await experimental examination.

B. (Nb, Ta, V)$_3$ Sn System

1. PREPARATION AND TRANSITION TEMPERATURES OF SINTERED SPECIMENS

The compound Nb_3Sn(33) has one of the highest transition temperatures known (18.05°K), hence, it seemed to be of interest to relate this temperature to material parameters of the compound. One way of approaching this problem is to examine materials which: (1) have similar crystal structures as Nb_3Sn (β-tungsten); (2) maintain the same electron-to-atom ratio (4.75); and (3) permit the possibility of alloying with Nb_3Sn. The system selected for this study was the ternary system (Nb, Ta, V)$_3$Sn since it seems to have these prerequisites and yet it possesses widely differing molecular weights and atomic volumes. Moreover, the published values of the transition temperatures cover the range 6°K to 18°K(34).

The synthesis of these compound alloys was accomplished by power-metallurgical techniques. Powders of the component elements were thoroughly mixed and heated to ≈650°C to effect a partial reaction. The mixtures were pulverized, pressed, and finally sintered at 1200°C in vacuum for times varying from two hours to two days.

X-ray analysis of the compounds prepared indicated predominant β-tungsten structure. For a few of the compounds unidentified lines were present, and for one, NbV_2Sn, an excess of one of the components (Sn) was noted. Table 3 gives the results of the X-ray measurements. In this table comparisons are made to literature values, and to lattice constants obtained by Vegard's Law.

Transition temperatures of the materials were measured by a mutual inductance method. The transitions were determined in zero field and the temperatures were measured by a carbon resistor calibrated with respect to helium vapor pressure. It is estimated that the maximum temperature uncertainty was about one percent. For all samples except TaV_2Sn and $V_{1.5}$ $Ta_{1.5}$ Sn only one transition was noted; for TaV_2Sn the transition corresponding to pure tantalum was also observed; for $V_{1.5}Ta_{1.5}Sn$ the transition corresponding to pure tin was also observed. Transition temperatures and transition widths are given in Table 4.

A convenient way of plotting the data in Table 4 is shown by the ternary diagram of Fig. 11. In this diagram the binary alloys are plotted along the sides of an equilateral triangle and the lengths of the projection from any point to a side is a measure of the ternary components present. The transition

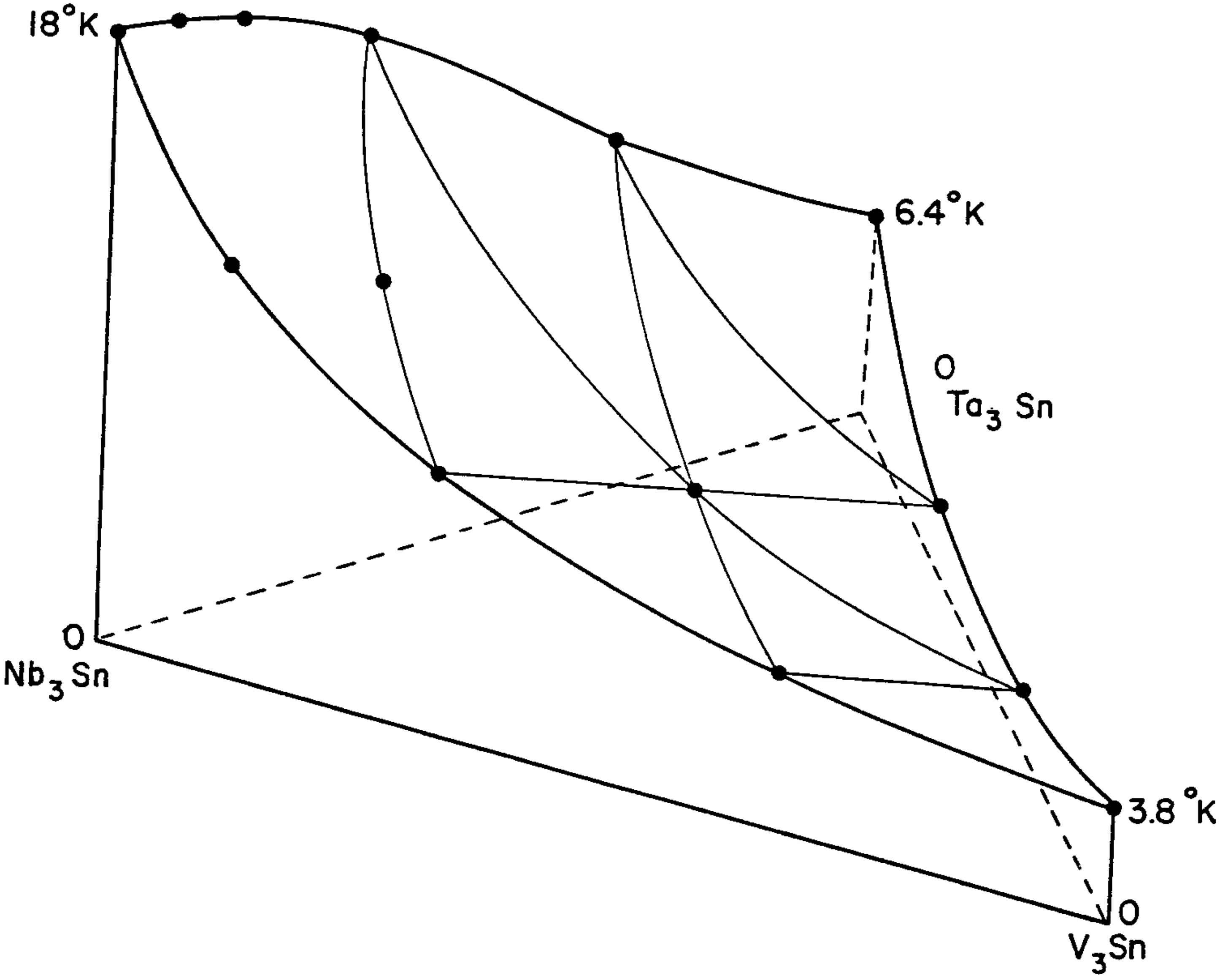


FIG. II SUPERCONDUCTING TRANSITION TEMPERATURE FOR THE SYSTEM $(Nb,Ta,V)_3Sn$ IN PSEUDO TERNARY REPRESENTATION

temperature furnishes a third dimension Table 4 thus represents a surface. A projection of this surface on the V-Ta plane is given in Fig. 12. The surface in Fig. 12 is such that this projection can be used for interpolation of transition temperatures.

TABLE 3

LATTICE CONSTANTS (Nb, Ta, V)$_3$Sn SYSTEM

COMPOUND	LITERATURE (Å)	OBSERVED (Å)	VEGARD'S LAW (Å)
Nb_3Sn	5.289(34)	5.289 ± .001	–
Nb_2TaSn	–	5.287 ± .001	5.285
$NbTa_2Sn$	–	5.280 ± .001	5.282
Ta_3Sn	5.276(34)	5.278 ± .002	–
Ta_2VSn	–	5.174 ± .001	5.172
TaV_2Sn	–	5.041 ± .001	5.066
V_3Sn	4.94(34)	4.96 ± .02	–
V_2NbSn	–	5.115 ± .004	5.070
VNb_2Sn	–	5.171 ± .003	5.179
NbTaSnV	–	5.175 ± .001	5.176
$Nb_2Ta_{.5}V_{.5}Sn$	–	5.237 ± .001	5.228
$Nb_{2.5}V_{.5}Sn$	–	5.249 ± .001	5.229
$Nb_{2.75}Ta_{.25}Sn$	–	5.291 ± .001	5.288
$Nb_{2.5}Ta_{.5}Sn$	–	5.289 ± .001	5.286
$V_{1.5}Ta_{1.5}Sn$	–	5.144 ± .001	5.108

It is to be noted that the transition temperature obtained for V_3Sn is much lower than that reported in the literature. At present there is no explanation for this fact. A possible explanation is non-stoichiometry of the compound. Furthermore, it is noteworthy that this system permits the choice of a material having any transition temperature between 2.8°K and 18°K.

Using the diagram of Fig. 12 it is possible to determine the variation of transition temperature along curves of constant atomic volume, and constant mass. Analysis of the data in this manner leads to an expression

$$T_c(M,V) = T_o(M_o, V_o)(M_o/M)^3 \; e^{.12(V-V_o)} \qquad (8)$$

Using for T_o the transition temperature corresponding to NbTaVSn (6.2°K) one obtains:

$$T_c(M,V) = (6.2)(453/m)^3 \; e^{.12(V-137.4)} \qquad (9)$$

where M is in grams, and V is in cubic angstrom units.

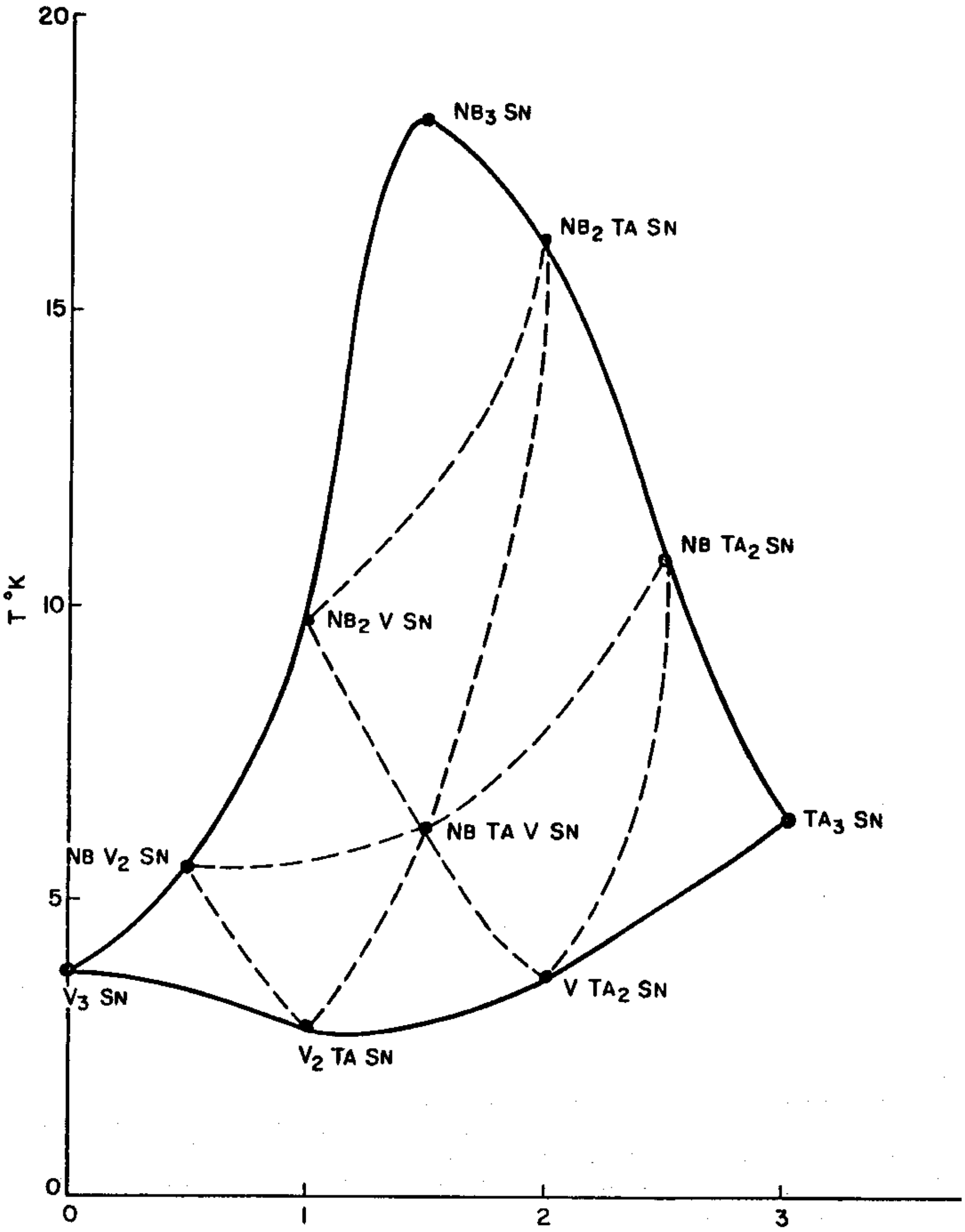


FIG. 12 PROJECTION ON V-TA PLANE OF TRANSITION TEMPERATURE VS ATOMIC CONCENTRATION OF PSEUDO-TERNARY SYSTEM $(Nb,Ta,V)_3Sn$ SYSTEM

The column, T_c (calculated), in Table 4 gives transition temperatures obtained from Eq. (9). Over this series of alloys the exponential varies from 0.13 to 3.4, the mass term from 0.32 to 4.6 and the transition from 2.8°K to 18°K. Except for Nb_3Sn this expression gives the transition temperatures within 40 percent. Moreover if we exclude all compounds of the form (Nb > 2, V, Ta)Sn the agreement between calculated and experimental values is better than ten percent.

TABLE 4

TRANSITION TEMPERATURES FOR (Nb, V, Ta)$_3$Sn SYSTEM

COMPOUND	LITERATURE T_c	T_c(°K)	T_c(°K)	T_c (CALCULATED) (°K)
Nb_3Sn	18.1(34)	18.0	0.1	31
$Nb_{2.75}Ta_{.25}Sn$	–	17.8	0.5	–
$Nb_{2.5}Ta_{.5}Sn$	–	17.6	0.7	24.8
Nb_2TaSn	–	16.4	3.2	16.5
$NbTa_2Sn$	–	10.8	3.0	9.9
Ta_3Sn	6.0(34)	6.4	0.2	6.2
Ta_2VSn	–	3.7	0.3	3.8
TaV_2Sn	–	2.8	0.3	3.2
V_3Sn	7.0(34)	3.3	0.1	3.8
V_2NbSn	–	5.5	1.4	7.0
VNb_2Sn	–	9.8	1.0	14.3
$V_{.5}Nb_{2.5}Sn$	–	14.2	.5	19.9
NbVTaSn	–	6.2	1.3	–
$Nb_2Ta_{.5}V_{.5}Sn$	–	12.2	.6	14.5
$V_{1.5}Ta_{1.5}Sn$	–	3.10	.3	3.3

The crystal structure of these compounds is the β-tungsten type shown in Fig. 13. It is to be noted that the transition elements are in close-packed array in each of the faces of the cube. For transition elements in such a structure, one expects rather strong D-D exchange interactions competing with S-D interactions. Recent work has shown magnetic interactions to have a strong effect on the transition temperature.(35) It is interesting to speculate that one source of the rapid variation in transition temperature is the magnetic interaction.

2. CRITICAL FIELD MEASUREMENTS

Critical field measurements were made on several samples of Nb_3Sn, V_3Sn, and Ta_3Sn, both to determine the critical temperature magnetically and to determine if the critical field values obtained follow an expression similar to Eq. (9). Measurements were made in the usual manner using two coils connected in series opposition. The superconductor to be examined is placed in the center of one of the coils. A niobium solenoid surrounds both coils and the magnetic field is increased in uniform steps

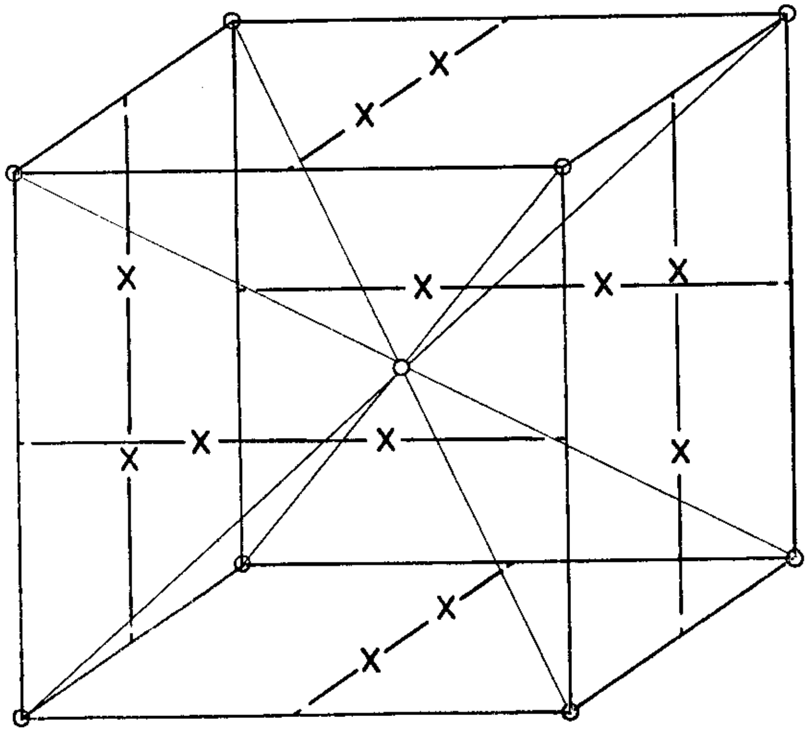


FIG. 13 STRUCTURE OF $(Nb,Ta,V)_3$ Sn COMPOUNDS
○ Sn × TRANSITION METALS

through the transition. The coils are connected to a flux meter and the total amount of flux change noted at any setting of the external field. Since the two coils balance in the normal state of the material, one expects to see deflections up to the point where the specimen goes normal.

Representative curves are shown in Figs. 14, 15, and 16. In these figures the ordinate is proportional to the negative magnetic moment per unit volume (I) in the sample, and the abscissa is proportional to the magnetic field (H). In Fig. 17, a curve of B against H is shown derived from the data in Fig. 14. One notes that the transition starts gradually, that it is linear over a fairly large region and that appreciably large fields, for this sample, are required before the sample goes completely normal. One can analyze the data in terms of two critical fields, the intersection of the linear region with the line $B = 0$ at H' and the intersection with the line $B = H$ at H''. If the linear region is a real intermediate state, H'' is the true critical field and H' is then proportional to the demagnetizing factor of the sample.(36) For these three samples H' is about ⅓ to ¼ H''. In all these measurements appreciable frozen-in moments were present after any one measurement and it was necessary to warm the sample above the zero field transition temperature before each measurement. In Figs. 18, 19, and 20, the data obtained for the three samples first examined are given. In Table 5 the critical field data obtained for these samples are summarized.

TABLE 5

CRITICAL FIELD DATA FOR Nb_3Sn, V_3Sn AND Ta_3Sn

SAMPLE	dH_c''/dT (oersted/°K)	dH'/dT (oersted/°K)	$T_c(H=0)$ (°K)	$T_c(H\to 0)$ °K
Nb_3Sn #1-a	1240	440	17.9	17.5
V_3Sn #1	605	207	3.8	3.8
Ta_3Sn #1	1420	396	6.4	6.5
Nb_3Sn #1-g	230	74	18.0	17.3
Nb_3Sn #2	303	41	18.0	17.9
Nb_3Sn #F-1	≈1600	≈270	17.9	≈17.3

In Figs. 21, 22, and 23, the data obtained for additional samples of Nb_3Sn are given. The results of these measurements are also summarized in Table 5.

The first specimen, Nb_3Sn #1-a, was prepared in the following manner. The constituents were reacted at 600°C, ground so as to pass through a 40 mesh sieve, pressed and sintered at 1200°C. Nb_3Sn #1-g was a portion of #1-a which was ground to pass through 240 mesh and simply pressed together. Later examination showed the particle size to range from 750°A to 20,000°A. Nb_3Sn #2 was prepared by reacting the constituents at 600°C, grinding the product to pass through 240 mesh, and then pressed and sintered at 1200°C. This sample appeared to be particularly porous. Nb_3Sn #F-1 was a film specimen whose preparation is described in a subsequent section of this report.

The results of the magnetic measurements to date can be summarized as follows:

1. Within the accuracy of the experimental data the extrapolation of the magnetic data for the transition temperature to zero magnetic field agrees with the zero field ac data.
2. An extrapolation of the results obtained from Nb_3Sn #1-a to 4.2°K is in fair agreement with the results obtained by Bozorth *et al.*(37)

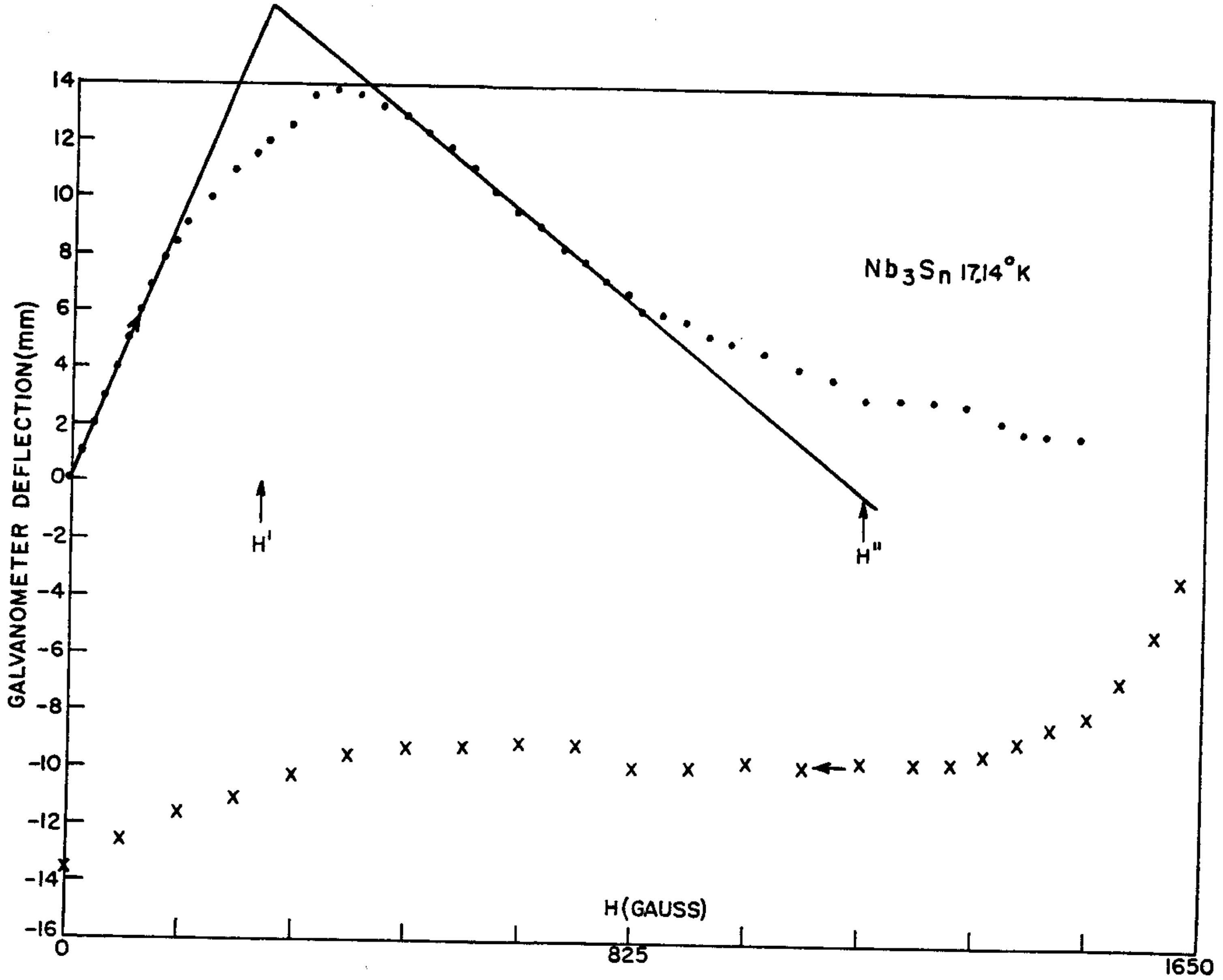


FIG. 14 GALVANOMETER DEFLECTION AGAINST FIELD FOR Nb_3Sn

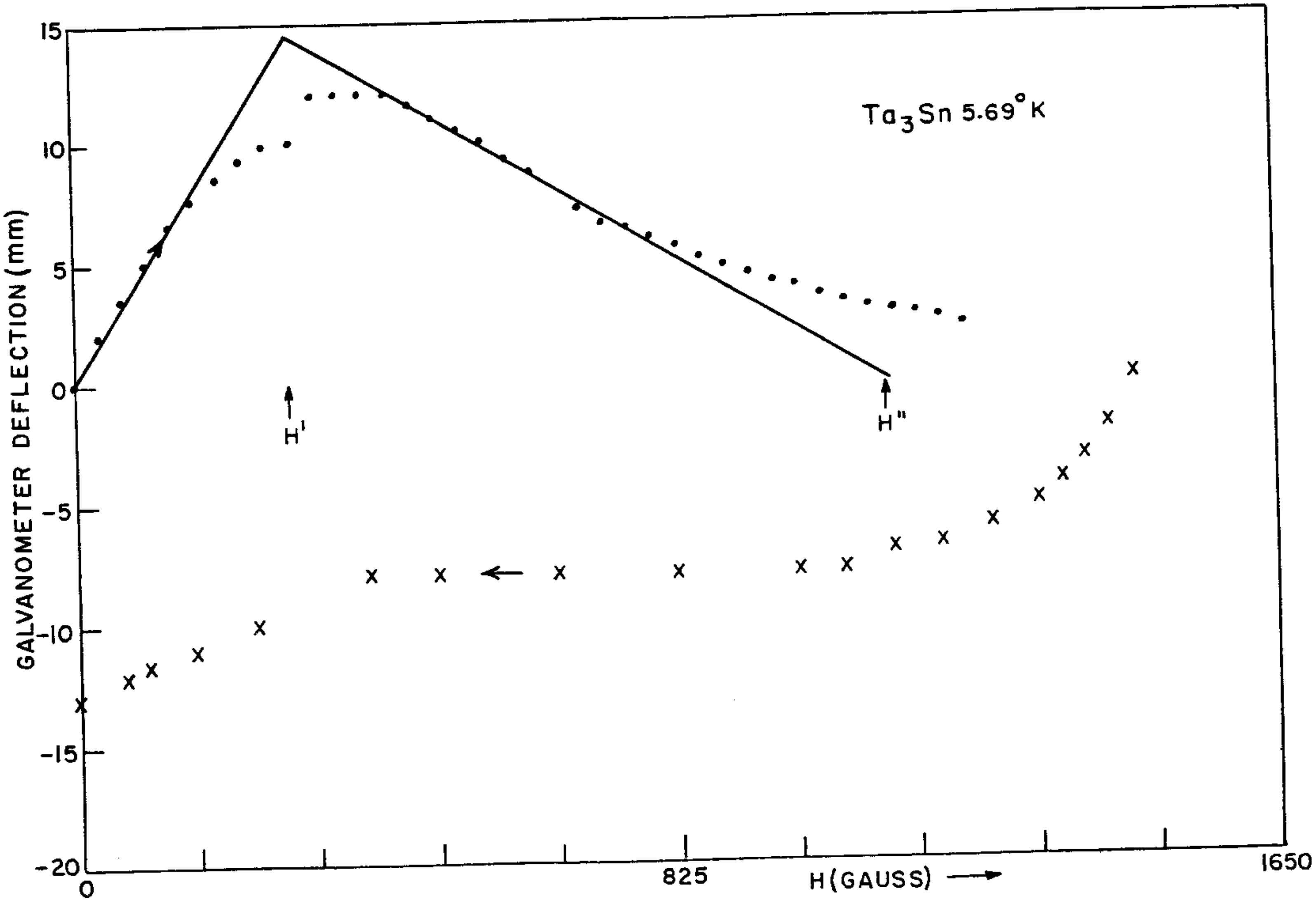


FIG. 15 GALVANOMETER DEFLECTION AGAINST FIELD FOR Ta_3Sn

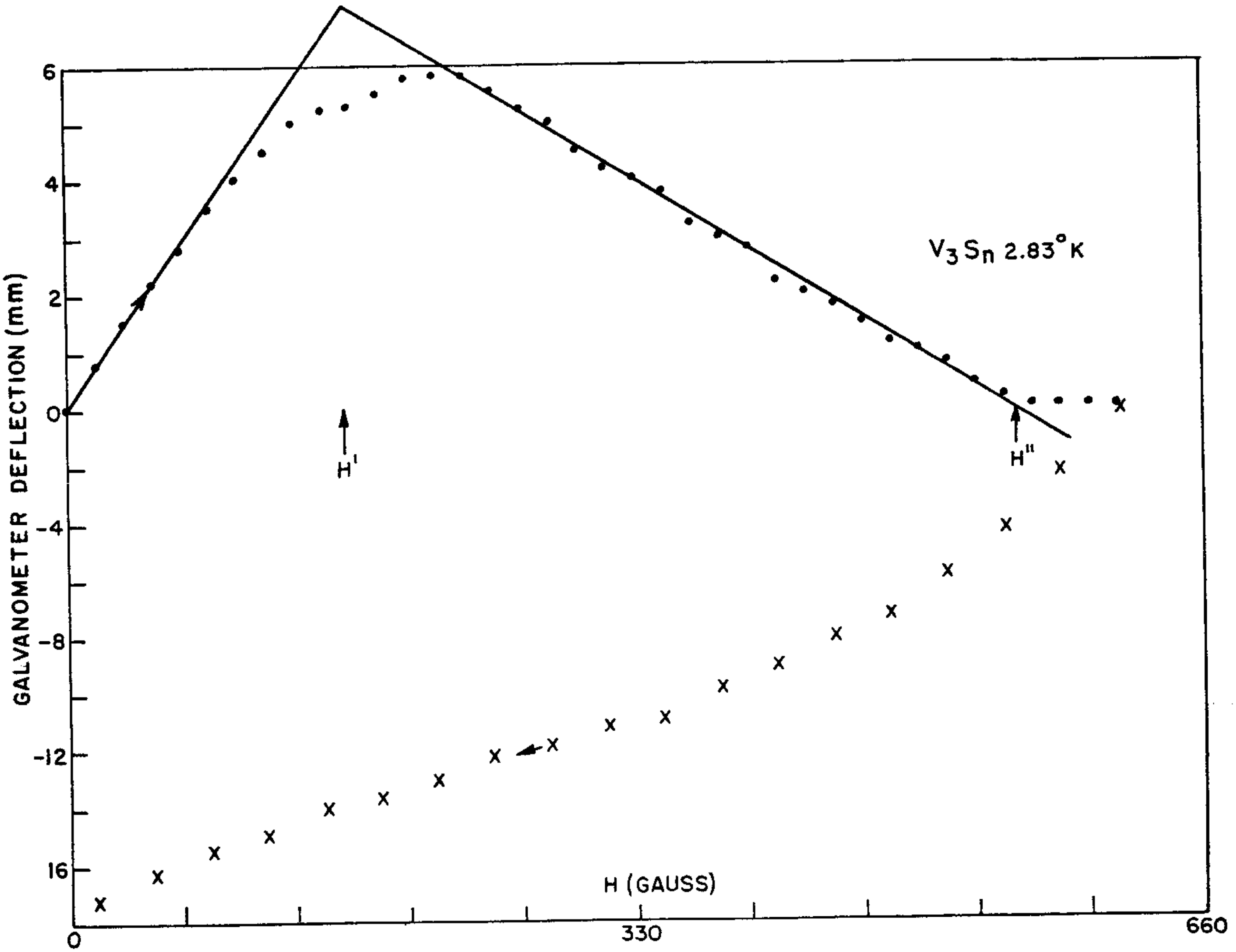


FIG. 16 GALVANOMETER DEFLECTION AGAINST FIELD FOR V_3S_n

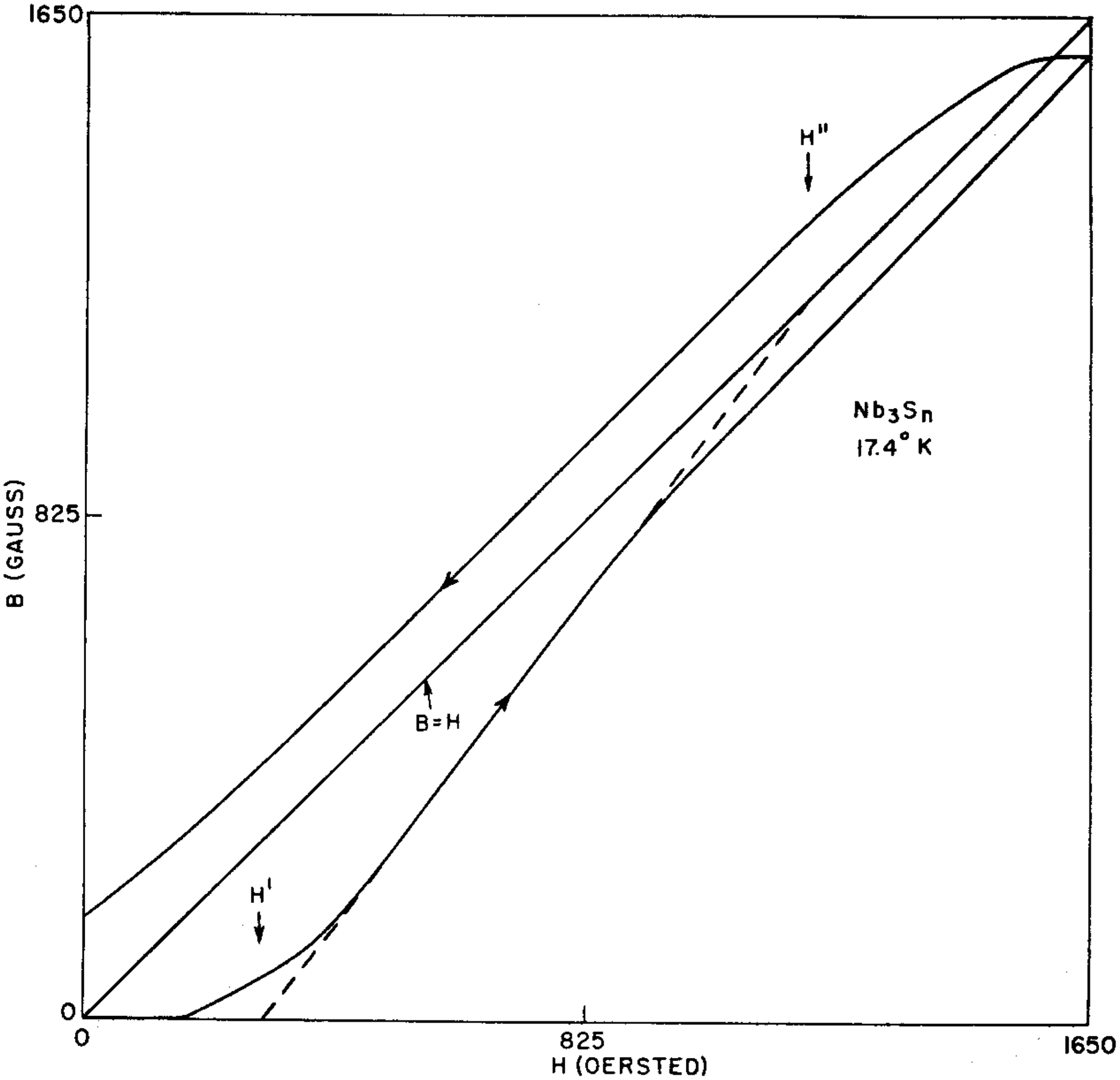


FIG. 17 B AGAINST H FOR Nb_3Sn AT T=17.4°K

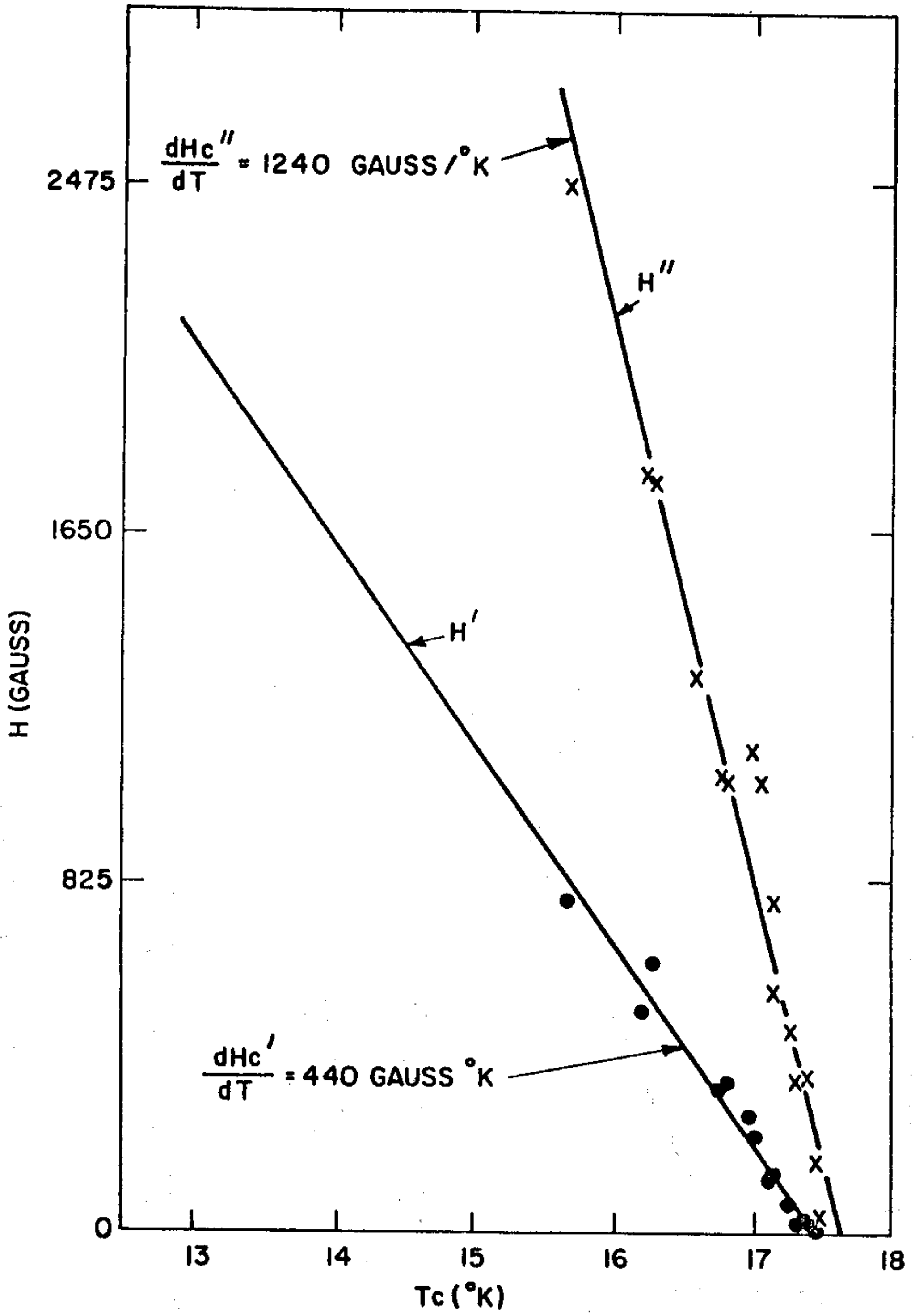


FIG. 18 CRITICAL FIELDS FOR Nb_3Sn #1a

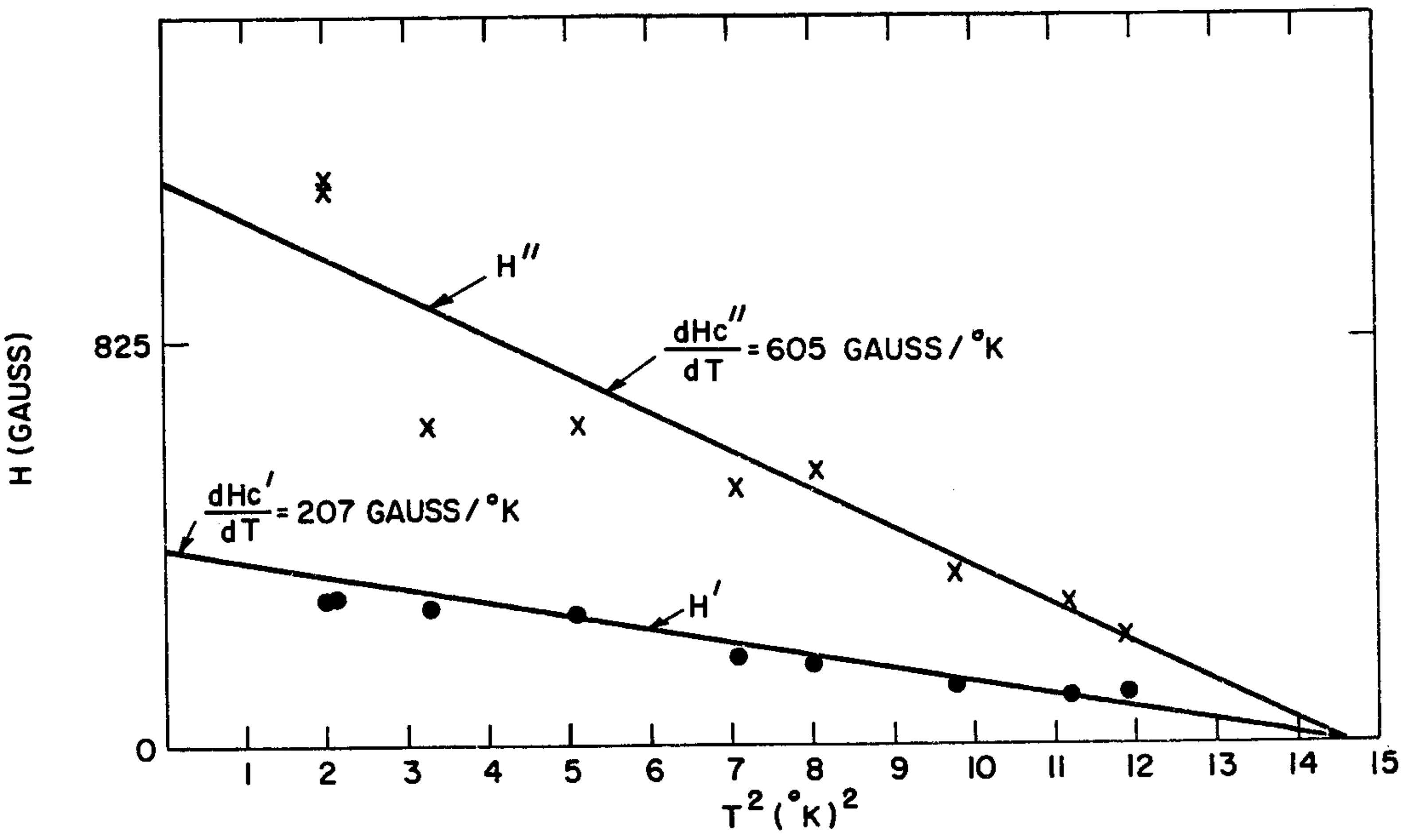


FIG. 19 CRITICAL FIELD FOR V_3Sn #1

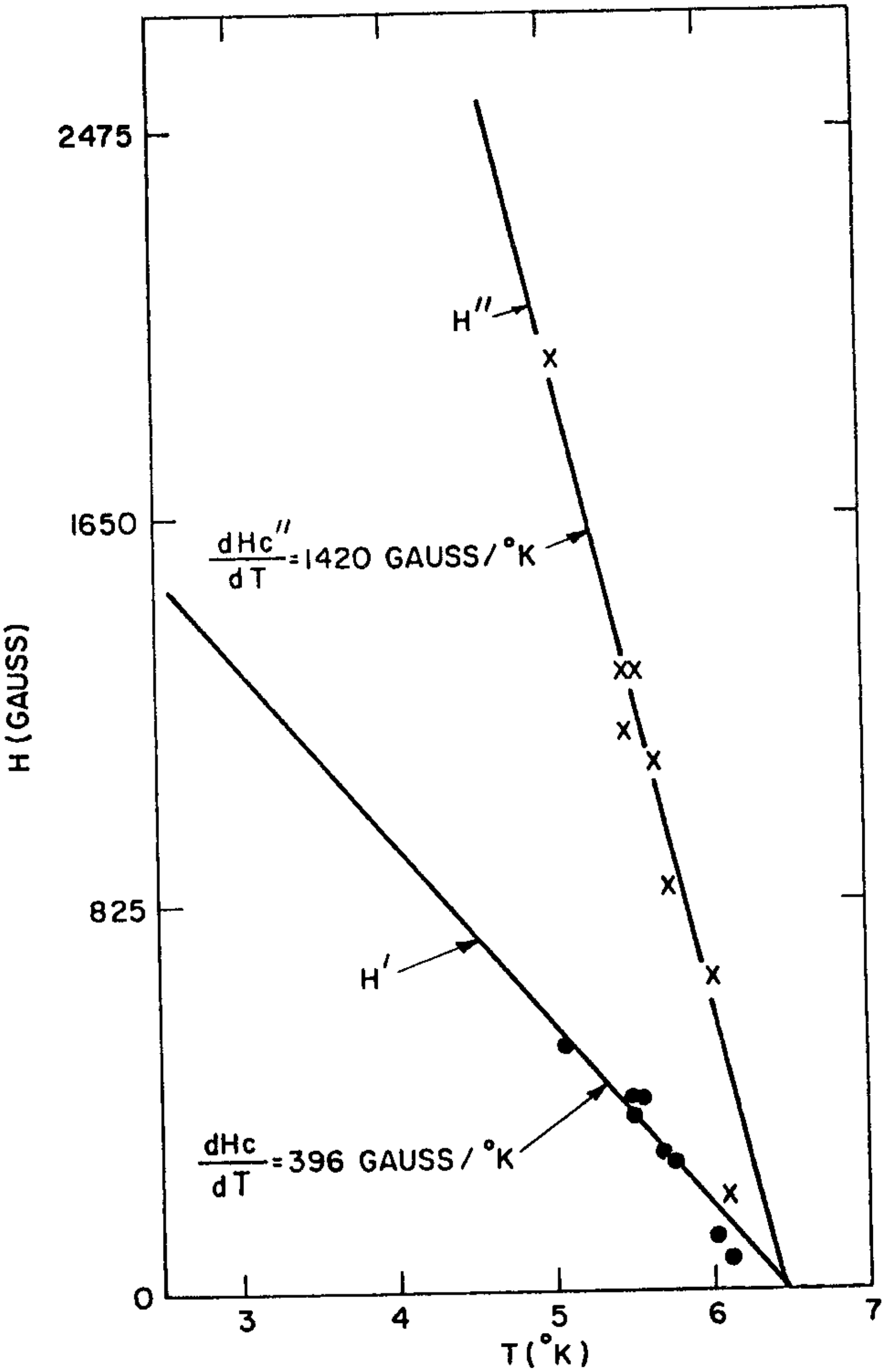


FIG. 20 CRITICAL FIELD FOR $Ta_3Sn^{\#}1$

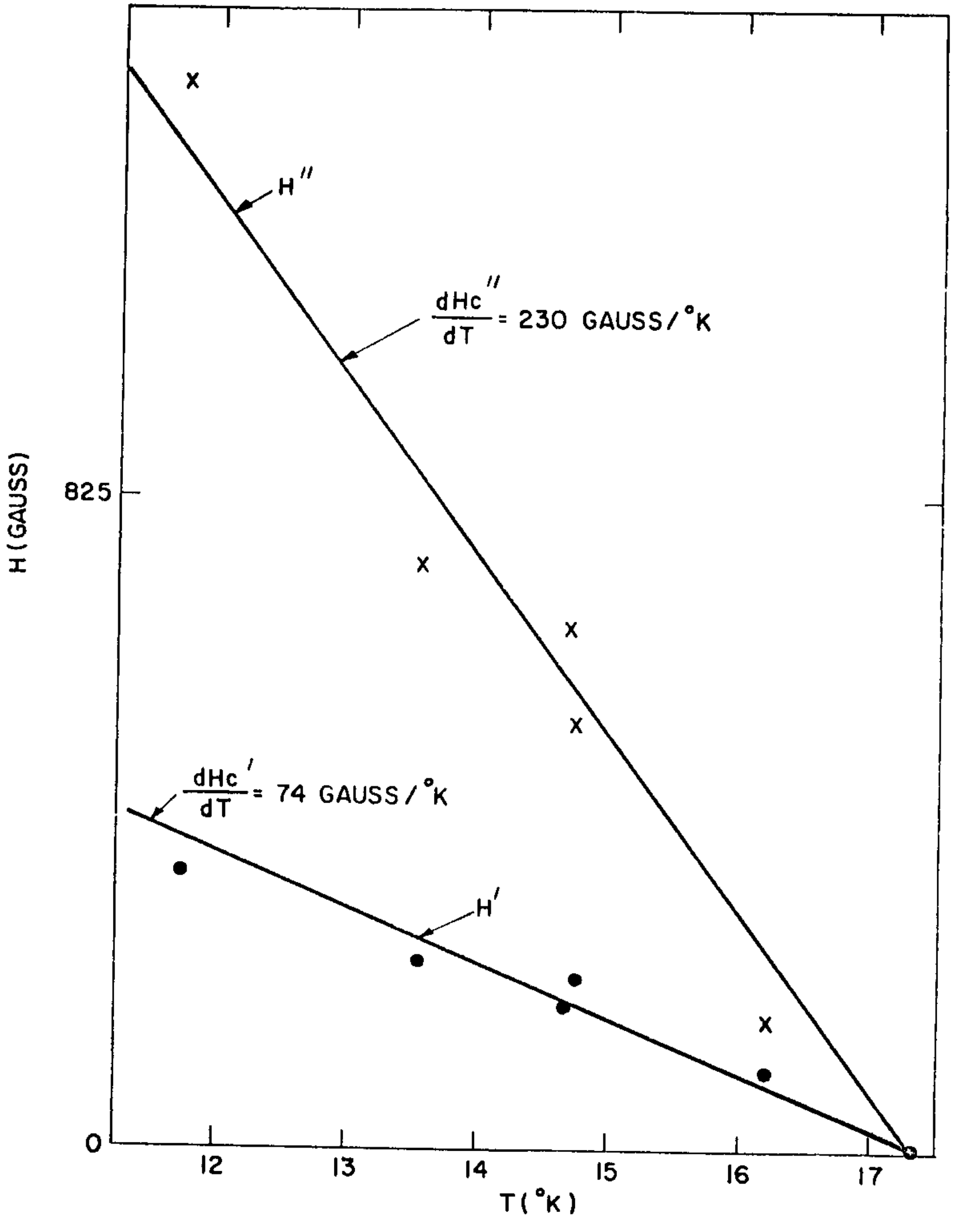


FIG. 21 CRITICAL FIELDS FOR Nb_3Sn #1g

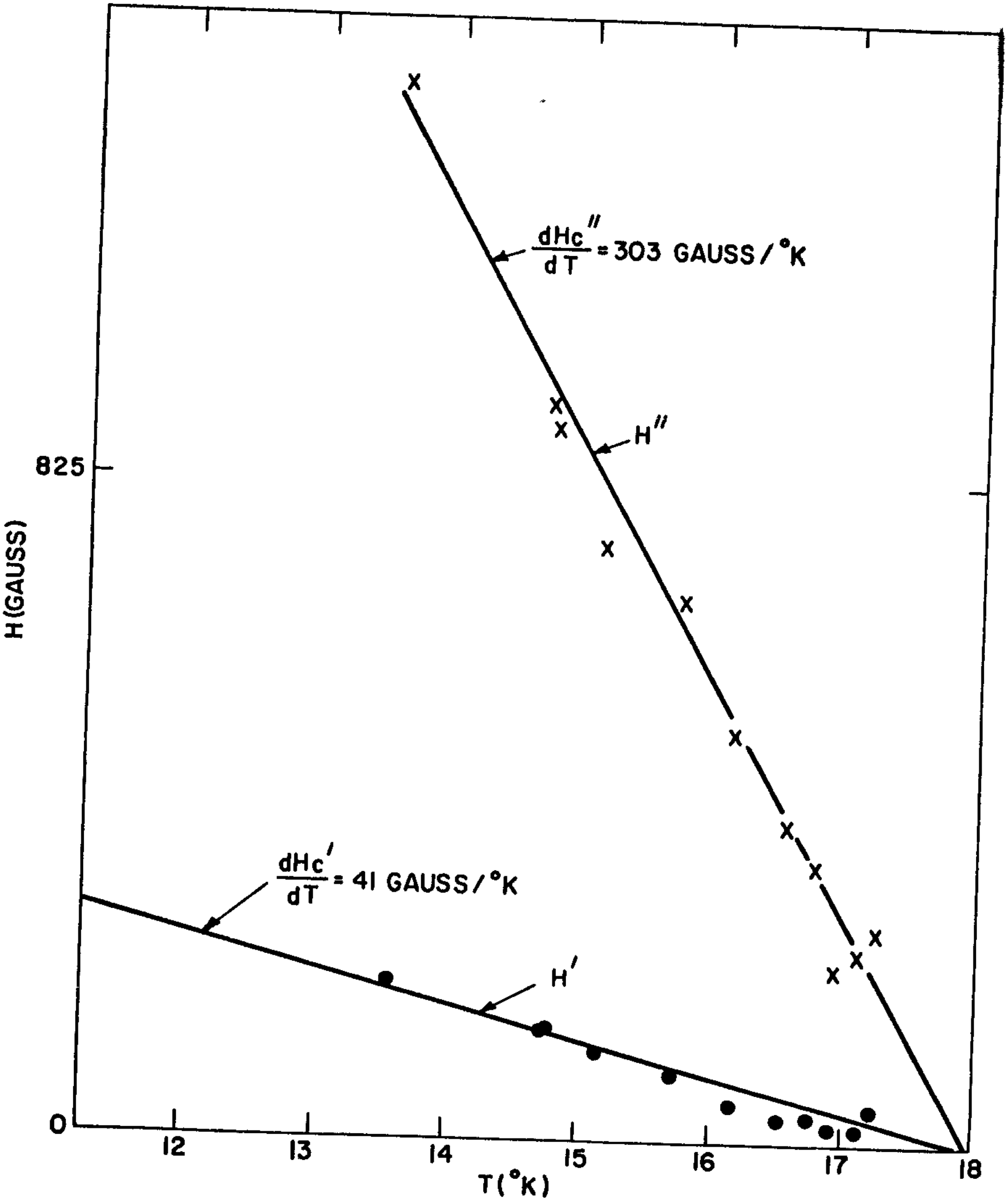


FIG. 22 CRITICAL FIELD FOR Nb_3Sn #2

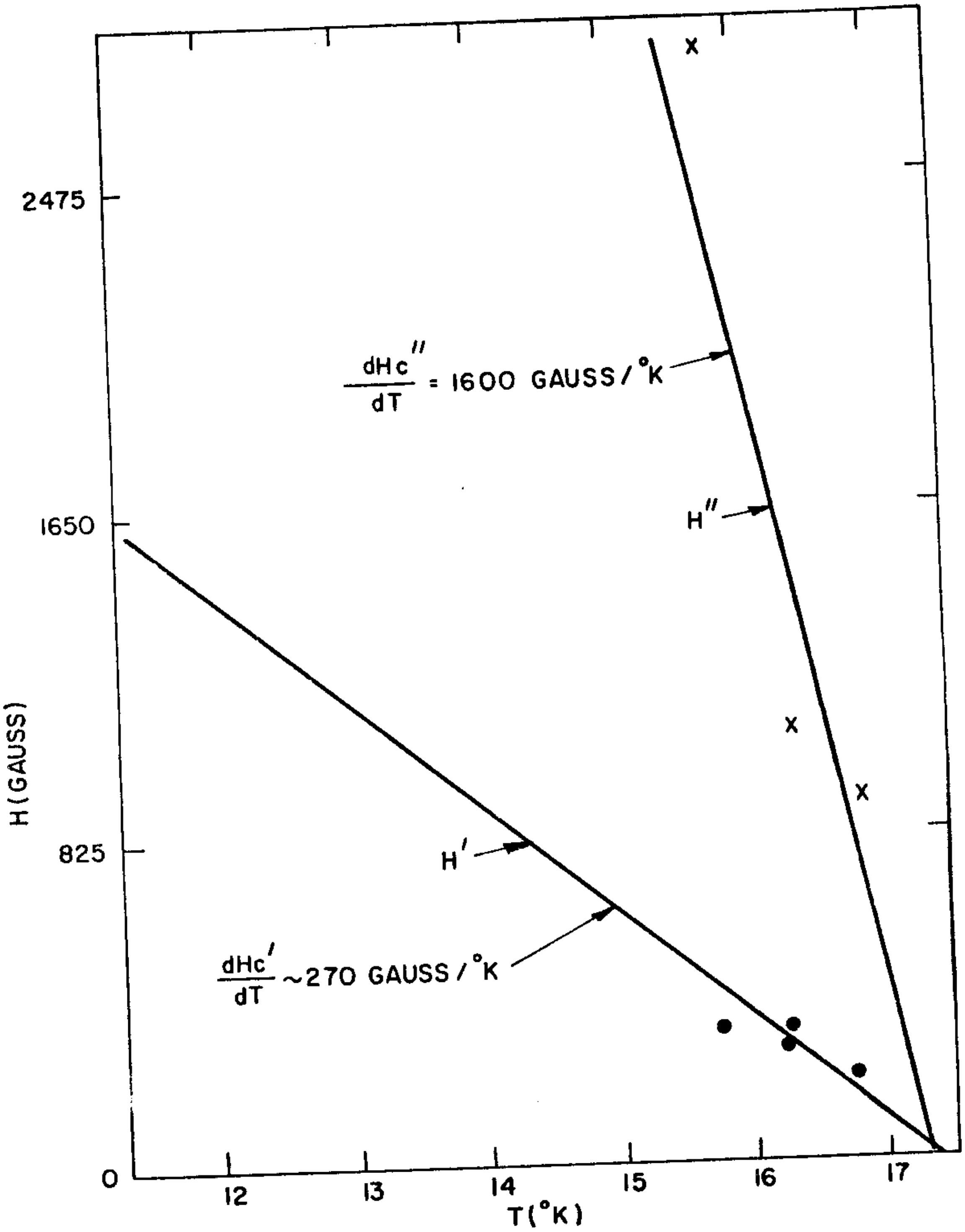


FIG. 23 CRITICAL FIELD FOR Nb_3Sn # F-1

3. The critical fields measured in these experiments appear to depend on the particle size of the materials, their geometrical shape, and their degree of porosity. This dependence would imply that the critical fields depend on macroscopic currents through superconducting regions that are not simply connected.
4. At present it is not clear how significant a role is played by particle size and/or shape. Fortunately, unlike many superconducting materials, Nb_3Sn can be ground to extremely fine particle size. The magnetic behavior of a suspension of such fine particles will be examined in the near future.

Research will continue on the magnetic behavior in an attempt to understand the transition itself, and in an attempt to obtain behavior characteristic of bulk material.

3. RESISTIVITY MEASUREMENTS $(Nb,TaV)_3Sn$ SYSTEM

To complement the critical temperature measurements described in the previous sections, resistivity measurements were made on several specimens of Nb_3Sn, V_3Sn, and Ta_3Sn. With the exception of Nb_3Sn, up to the time of this report, all the specimens were prepared by sintering. For Nb_3Sn, in addition to the sintered specimens, a sample was examined which had been prepared by the reaction of niobium with excess tin. In contrast to the sintered specimens, this sample was non-porous. In Fig. 24 and Fig. 25, the results of the resistivity measurements are shown. It should be emphasized that the absolute magnitudes of the resistivities for the various samples differ considerably due to porosity. All data has been normalized to give the same absolute value as sample #1-a at 300°K.

The results for all samples are qualitatively similar. As the temperature is lowered, the resistance departs from a linear dependence on T, dropping rapidly to a constant value until, finally, the superconducting transition is reached. Since a large variety of specimens have been examined, it would appear that the results obtained are characteristic of the materials, and not of their form. Further samples will be examined to confirm this hypothesis, but in the following discussion it will be assumed that the resistivity data of Figs. 24 and 25 is characteristic of the bulk material.

One can represent the data for all specimens examined by an expression of the form

$$\rho = \rho_o + \rho_1 (T - T^*) + \rho_{ext} 4 \frac{e^{-T_o/T}}{(1 + e^{-T_o/T})^2} \qquad (10)$$

The first and second terms in Eq. (10) are what one would expect for an ideal metal. The first term corresponds to the residual resistance, the second to the ideal temperature dependent resistivity,(38) giving a straight line intersecting the temperature axis at about .15 θ where θ is the Debye temperature. The third term in Eq. (10) is of the form suggested by Elliott(39) for the elastic scattering of electrons by the unfilled F-shells of the rare earth metals. He assumes that the degeneracy of the f-electrons is removed by the crystalline field and that the thermal distribution of the f-electrons among the resultant levels resulted in an additional thermal resistance. An alternative way of deriving the form of the resistivity is given by Ziman(40) for a crystalline field splitting of the f-electrons into two levels. One considers a Nordheim type disorder resistance of the form

$$\rho = 4 \rho_{ext}(x)\ (1 - x) \qquad (11)$$

where ρ_{ext} is a function of the s-f-interaction, x is the probability of finding the f-electrons in the lower state, i.e.,

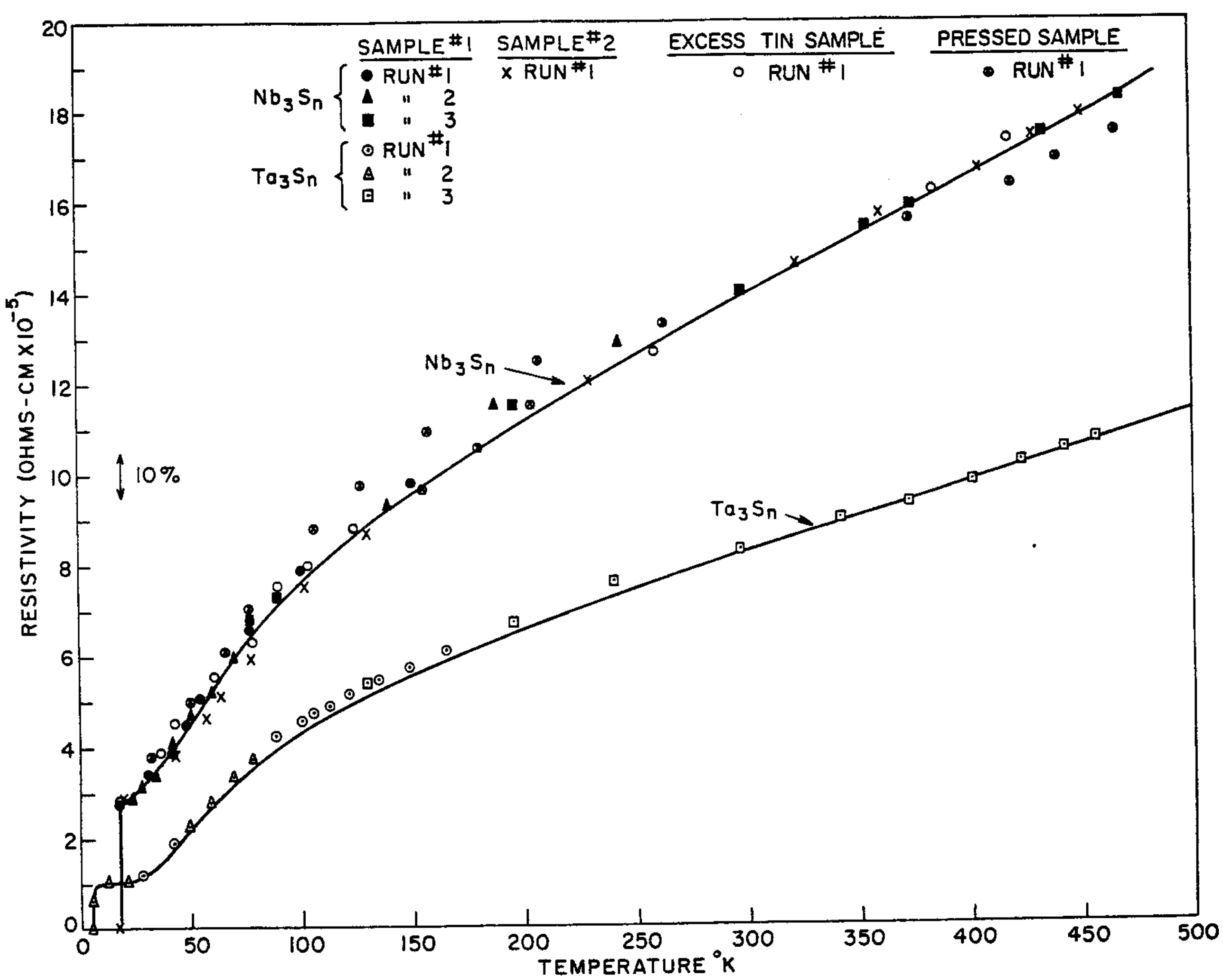


FIG. 24 RESISTIVITY Nb_3Sn AND Ta_3Sn AGAINST TEMPERATURE

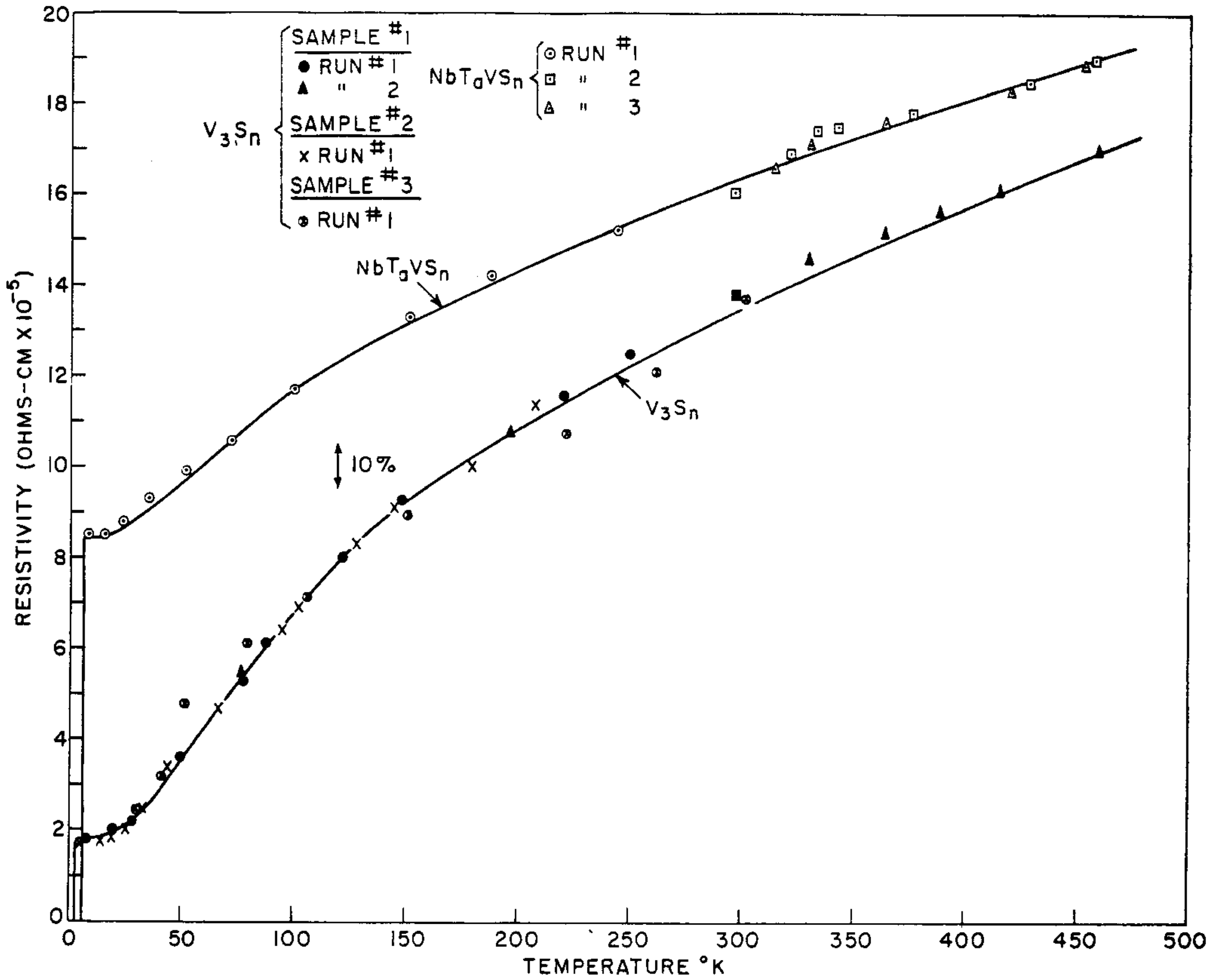


FIG. 25 RESISTIVITY V_3S_n AND NbT_aVS_n AGAINST TEMPERATURE

$$x = \frac{1}{1 + e^{-T_o/T}} \tag{12}$$

where kT_o is the energy separation of the states.

In Figs. 24 and 25 the solid lines are drawn on the basis of Eq. (10) using the data shown in Table 6.

TABLE 6

RESISTIVITY DATA (Nb, Ta, V)$_3$ SYSTEM

COMPOUND	$\rho_o \times 10^5 (\Omega)$	$\rho_1 \times 10^5 (\Omega/^\circ K)$	T*(°K)	$\rho_{ext} \times 10^5 (\Omega)$	$T_o (^\circ K)$
Nb_3Sn	2.9	2.5×10^{-2}	28	4.5	137
Ta_3Sn	1.1	1.5×10^{-2}	24	3.0	114
V_3Sn	1.9	2×10^{-2}	14	6.0	174
NbTaVSn	8.5	1.8×10^{-2}	18	2.8	144

As can be seen from the figures the fit of Eq. (10) to the data is quite good. It is somewhat surprising that a theory constructed to describe the scattering of conduction electrons by localized electrons should fit these compounds so well. In the present system one is not dealing with well shielded f-electrons, but with d-electrons. In this connection it is pertinent to note the speculation of Zener(41) that transition metals in the β-tungsten structure maintain their electronic configuration in the d-shell from the gaseous to the solid state – $4d^45s^1$ for Nb, $3d^34s^2$ for V, and $5d^36s^2$ for Ta. Recent work would appear to indicate considerable localization of the d-electrons in transition metals such as iron.(42) Moreover, the cubic field splitting predicted for transition metals is of the order of 100°K,(43) i.e., the same order as the T_o found experimentally. Unfortunately, the width of the d-band is much larger than this number for the elemental transition metals, a fact which might imply that neither the localization nor the cubic field splitting of the d-electrons has much meaning. Measurements of specific heats, susceptibilities, and/or magnetoresistance should help to clear up this difficulty. Correlations between the anomalous resistivity of these samples and their superconducting behavior are presently being sought.

4. PREPARATION OF Nb_3Sn BY GAS-PHASE REACTIONS

Measurements of critical magnetic fields on Nb_3Sn specimens prepared by powder metallurgical methods revealed that particle size has an effect on the results. Therefore, it was decided to attempt to prepare Nb_3Sn from the gas phase in order to avoid porosity and also to obtain larger crystals. Some success has been achieved in this direction (see section III.B.2). The results are too fragmentary to be discussed at this time, but they will be described in detail in subsequent reports.

C. STUDIES RELATED TO THE (Nb, Ta, V)$_3$Sn SYSTEM

1. Nb_3Sn-Ti_3Sn ALLOYS

In the (Nb, Ta, V)$_3$Sn system a strong dependence of T_c on molecular weight was found. In order to test this dependence on other systems binary alloys in the system Nb_3Sn-Ti_3Sn were made by the usual powder-metallurgical methods. The compound Ti_3Sn has a molar volume only 2 percent smaller than that of Nb_3Sn, but its molecular weight is 11 percent smaller. According to the empirical equations obtained for the $(Nb, Ta, V)_3Sn$ system these alloys should have a higher T_c than Nb_3Sn. It should be noted, however, that with increasing concentration of Ti_3Sn the electron-to-atom ratio decreases. Since Ti_3Sn has a hexagonal structure only a partial solubility could be expected; hence, alloys with a maximum of 33 percent Ti_3Sn were made.

The results for three such alloys appear in Table 7. The x-ray results indicate that the lattice constants of the alloys are very similar to Nb_3Sn and yet the transition temperature decreases. The solubility of Ti_3Sn was found to terminate at $Nb_{2.5}Ti_{0.5}Sn$. The results indicate that the decrease in the electron-to-atom ratio or increased disorder dominated over any decrease in the mass.

TABLE 7

TRANSITION TEMPERATURE AND LATTICE CONSTANT OF Nb_3Sn, Ti_3Sn ALLOYS

MATERIAL	T_c(°K)	ΔT(°K)	M.W. (GMS)	LATTICE CONSTANT (Å)		R (Electron/Atom)
				From Vegard's Law	Observed	
Nb_3Sn	18.0	0.1	397.4	5.289	5.289	4.75
$Nb_{2.8}Ti_{0.2}Sn$	17.0	0.1	388.3	5.286	5.290	4.70
$Nb_{2.5}Ti_{0.5}Sn$	17.2	0.3	374.2	5.282	5.287	4.63
Nb_2TiSn	13.6	0.5	352.5	5.276	5.287	4.50

2. $(Nb, Ti, Cr)_3Sn$ ALLOY

Following the preceding observation concerning the electron-to-atom ratio, a single-phased alloy of the composition $Nb_{2.5}Ti_{0.25}Cr_{0.25}Sn$ was made in which the e/a ratio was the same as that of Nb_3Sn. This alloy should closely resemble $Nb_{2.5}V_{0.5}Sn$ since titanium and chromium are neighboring elements to vanadium. For this alloy both the lattice constant and the molecular weight changed in the direction favorable to increasing T_c, yet its T_c was lower than for $Nb_{2.5}V_{0.5}Sn$ indicating that some other variable, possibly disorder, has had an effect. For this sample $T_c = 13.6$°K with a transition width of 1.2°K.

D. Zr-Au-Rh ALLOYS

The effect of alloying of small amounts of gold or rhodium with zirconium was studied by Matthias(5), who showed an increase in T_c in these alloys with increasing concentration of either metal. Since gold is believed to have one electron per atom and rhodium eight, these binary alloys had less than four or more than four electrons per atom respectively. Since the minimum in T_c occurred with pure zirconium which has an electron-per-atom (e/a) ratio of four, ternary alloys made of these three elements (Zr-Au-Rh) with an electron-per-atom ratio of four should have essentially the same T_c as pure zirconium (0.6°K).

Several specimens of such ternary alloys have been made ranging in nominal e/a ratio from 3.95 to 4.11 depending on the concentrations of Au and Rh in Zr (taking e/a of Zr = 4, of Rh = 9 and of Au = 1). Preliminary low temperature measurements on these samples at 4.2°K indicate that the addition of Au into Rh-Zr alloys or of Rh into Au-Zr alloys does not lower the T_c as would be expected, but rather increases it. For some of these alloys the increase in T_c is larger than the combined increase in T_c produced in the binary alloys of zirconium by gold and rhodium separately.

Although final conclusion cannot be made before the T_c of each of the specimens is determined it can be stated that in the ternary alloys Au-Rh-Zr the effects of gold and rhodium on the T_c is additive rather than compensating. In view of Matthias' rules relating T_c and the electron-per-atom ratio one would conclude that the e/a ratio of gold or rhodium or both is incorrect. If gold were assigned e/a of 11(44) instead of one, the e/a ratio of the alloys in the system Au-Rh-Zr would be always greater than four and the expected effect of addition of Au and Rh would be consistent with the observed results.

E. SUPERCONDUCTOR IN A NON-SUPERCONDUCTING MATRIX

Superconducting materials with high T_c usually have inferior mechanical properties and, cannot be easily fabricated. Therefore, an attempt was made to embed such material into a soft metal with a hope that such a two-phased mixture would have the desirable superconducting and mechanical properties.

The pair of substances selected for investigation were Nb_3Sn and copper metal. Powder of particle size to pass 260 mesh screen were used in making three mixtures of variable composition which were then compressed and annealed for two hours at 700°C. These mixtures contained 25% (weight or volume) copper, 50% copper, and 75% copper respectively. All three mixtures were found to be superconducting, having transition temperatures 16.7, 15.3, and 11°K, respectively, and the transition widths were 0.5, 0.7, and 8°K, respectively. X-ray analysis of the annealed and specimens showed no variation on the lattice constant of Nb_3Sn and gave evidence that copper and tin reacted with each other to only a slight extent.

The fact that all three mixtures are superconducting can be explained on the basis of formation of a network of superconducting paths. What remains unexplained is the decrease in T_c although the X-ray results show no change in the Nb_3Sn component in the mixture. Strain is one possible explanation, but except for the 75% copper specimen, the transition widths are of the same order as for unstrained material.

The annealed mixtures were subjected to rolling to produce sheets of these materials. It was found, however, that these samples were about as brittle as Nb_3Sn which cannot be rolled. A somewhat similar attempt was therefore made by substituting lead for copper. An attempt was made to make a molten slurry of Nb_3Sn powder and molten lead, and then freeze the slurry and roll it into sheets. It was found, however, that the powder was not wetted by lead and only floated on its surface. Nevertheless, during the heating of the mixture at 1000-1100°C some lead was evaporated onto the powder and adhered to it. The resulting powder, slightly coated with lead would sinter when pressure was applied, and it was possible to roll this sintered mass into sheets as thin as 3 mil. Low temperature measurements will be performed on these sheets.

F. GENERAL MATERIALS PREPARATION

A number of alloys and metallic compounds have been prepared in a search for new superconducting materials. These materials are listed below with the reasoning that led to their preparation. Most of these alloys and compounds are still awaiting low temperature measurements the results of which will be given in future reports.

A. Attempts to prepare the materials Nb_3In, Ta_3In, V_3Tl, Nb_3Tl, and Ta_3Tl by powder metallurgical methods were not successful; only mixtures of the pairs of metals were obtained.

B. Six compounds with the formula YbM_2 were prepared where M represents the noble metals. These compounds were prepared with the hope of obtaining compounds in which ytterbium would have variable valence. It is hoped that the superconducting properties and the crystal structures of these compounds can be explained on the basis of the electronic structure which ytterbium assumes in these compounds.

C. Samples of niobium hydride and niobium deuteride were made to study the effect of isotropic substitution on the transition temperature. This was done in conjunction with the study of the superconducting properties of the La-H (La-D) solid solutions. Several specimens of La-H (La-D) solutions were also made using a new method of annealing and quenching.

D. More than 300 grams of $Gd_{0.08}Ce_{0.92}Ru_2$ were made by arc-melting of the constituents. This compound is said to be ferromagnetic and superconducting at low temperatures. Neutron diffraction studies will be performed on it to investigate whether superconductivity and ferromagnetism coexist at the same temperature.

E. Sixteen binary alloys of tin with small amounts of Hg, Bi, Cd, and Hg were made for studying the surface energy in the intermediate state.

F. The following compounds were prepared to search for superconductors among the rare-earth compounds: Y_3C, Y_3Ni, YCu, YCu_2, $LaSn_3$, La_3Co, La_3Ni, LaCu, Ce_3Co, Ce_3Ni, La_3Al, La_3Ga, La_3In, YRh_3, YRu_3, and YPd_3.

G. About a dozen of additional zirconium and titanium alloys with various solutes have been prepared to aid in the studies of the Zr-Au-Rh alloy system.

H. Finally, the preparations of Nb_3Ag and of Nb_3Sn with Sn partially substituted by Pb were attempted without success. In the case of the silver compound a solid solution of silver in Nb was obtained.

G. GROWTH OF METALLIC WHISKERS AND THIN WIRES

A program of preparation of metallic whiskers and thin wires was initiated as a first step in studying their superconducting properties. Although metallic whiskers are relatively easily prepared, it is difficult to obtain them in desirable physical dimensions, namely, several millimeters long and less than 0.1 microns thick.

Work has been started on copper in order to obtain experience in the field of whiskers and their behavior at low temperatures. Whiskers of copper can be readily prepared by the reduction of cuprous iodide with hydrogen at elevated temperatures. The first few reductions at 650°C yielded several dozens of whiskers 5 to 30 mm long and 10 to 20 microns thick. Attempts to decrease the diameter of a 10-micron whisker by electrolytic etching were not successful because of heavy pitting which was probably due to the presence of many dislocations in this relatively thick whisker. Attempts were therefore made to grow thinner whiskers directly by reducing cuprous iodide at low temperature. To date, the best results were obtained at 580°C, where whiskers one to three microns thick were produced with lengths only slightly less than those obtained previously.

Although more work is planned in growing of metallic whiskers a more direct approach was taken to obtain thin, long wires, namely by drawing them out of molten metal contained in a thick-walled glass capillary. In this manner it was possible to obtain thin wires of lead several centimeters long with thickness ranging from 0.5 mm to 0.2 microns as estimated under a microscope. Accurate determinations of the thickness of these wires will be made by electrical resistance measurements once the problem of making electrical contacts is solved.

IV. SUMMARY AND FUTURE WORK

A. TRANSITION STUDIES

1. INTERPHASE SURFACE ENERGY

The superconducting transition is known to take place via nucleation and growth processes. Our attention has been concentrated on determining the surface energy of a boundary between the normal and superconducting phases and the factors which control this energy. The importance of this surface energy to this program is that surface energy is the dominant factor in determining the nucleation of the superconducting state and a major factor in the growth process.

Our work, to date, indicates that studies of the effect of the surface energy on the intermediate state would best satisfy our objectives. The intermediate state of a superconductor is that state in which, because of its shape and magnetic environment, the specimen is composed of a mixture of normal and superconducting regions. The values of the magnetic field for which specimens enter the intermediate state from the superconducting state and from the normal state can be related to the surface energy.

The experimental method to be used is a modification of one due to Davies(17). Specimens in the form of foils and evaporated films will be placed between two spiral coils. In one of the coils a small ac current will be present; the signal in the second coil, due to this current, will be observed. When the specimen is subjected to a dc magnetic field which is perpendicular to its surface, the signal will be zero when the specimen is wholly superconducting, increase with increasing magnetic field as the specimen passes through the intermediate state, and reach a maximum value when the specimen becomes wholly normal. In this way the magnetic field, H_t, at which the specimen goes from the intermediate state to the normal state can be determined. The ratio of H_t to H_c, the critical value, gives a measure of the surface energy.

The specimens will be prepared from tin containing from 0 to 1 atomic percent of selected solid solution impurities which will be annealed for long periods to insure homogeneity and minimum strain.

The electronic mean free path is proportional to the residual resistance ratio, $R_o/R\ (0°\mathrm{C}) - R_o$, where R_o = the low temperature residual resistance and $R(0°\mathrm{C})$ = the resistance at 0°C. The final data will be displayed as a plot of the surface energy vs. the residual resistance ratio.

2. THERMAL CONDUCTANCE MEASUREMENTS

Little(20) has calculated the thermal conductance of an interface between two dissimilar solids. In his dissertation he points out that although his calculations, which are based on the scattering of phonons at the interface because of the discontinuity of the elastic constant, agree well with experimental data obtained for metal to metal interfaces; they cannot account for data obtained at copper to liquid helium interfaces. The explanation he offers for this case predicts that there should be "an appreciable difference between the thermal contact resistance of a metal in the normal state and in the superconducting state." It is our intention to measure the thermal conductance of the interface between a metal in the normal and superconducting state and liquid helium.

It should, perhaps, be added that in addition to the obvious interest in proving (or disproving) a hitherto untested theoretical prediction, our interest in the surface thermal conductance also arises because of its role in the transition kinetics. Whenever a transition takes place (except at T_c), particularly a current-induced transition, heat is evolved. The rate at which this heat is transferred to the bath, which is in part determined by this surface conductance, is related to the speed of transition.

For the measurement, a specimen in the form of a tin rod will be placed in a vacuum with one end in contact with a column of liquid helium. A thin-walled stainless steel tube will confine the liquid. Carbon resistance thermometers will be attached to the rod and to the helium column for measuring the temperature gradients in the two media when heat is caused to flow by means of a heater mounted at the isolated end of the rod. From these data the temperature discontinuity at the solid-liquid interface can be computed and, knowing the power input, the thermal conductance of the interface can be calculated.

Because of the very poor heat conductivity of He I, the initial measurements will be made at temperatures below the λ-point (2.19°K). In this temperature range He II is the stable phase of the liquid, a superfluid having a very high effective thermal conductivity as one of its outstanding properties. It is expected that these measurements will, later on, be extended to the higher temperature range after making suitable modifications to the apparatus.

B. MATERIALS RESEARCH

1. HYDROGENIC IMPURITIES IN TRANSITION METALS

Much of the work on superconducting alloys is obscured by the inability to attach a definite valency to the solute atom. Hydrogen, as a solute in transition metals, is thought to be completely ionized, and thus offers no ambiguity as to its valence in such systems. The system hydrogen plus lanthanum is a particularly convenient one for studying the effects of alloying on the superconducting transition. One can insert relatively large amounts of hydrogen in lanthanum as a single phase alloy, and moreover lanthanum is a superconductor of particularly convenient transition temperature (~ 6°K). Finally, the availability of deuterium permits one to determine if other parameters than the electron to atom ratio are effecting the transition temperature.

The results obtained indicate that hydrogen and deuterium up to concentration of about 6% reduce the transition temperature of pure lanthanum by about 1°K. There appears to be significant differences between the effects of hydrogen and deuterium, but nonuniformity of the concentration makes it difficult to determine this difference quantitatively. The source of the difficulty, and the limitation to concentrations less than 6% are due to the inefficient quench presently used. In the coming year research will continue on this system utilizing a more efficient quench. From this research the mechanism responsible for the decrease in the transition temperature of lanthanum will be determined, and the difference between the effects of hydrogen and deuterium analyzed.

The experience with lanthanum-hydrogen-deuterium system has led to other transition metal-hydrogen-deuterium systems. The solubility of hydrogen in the β-phase of such a metal, as niobium, is much greater than in lanthanum and, besides, the compound formed in the β-phase (NbH) has been reported to be superconducting. With higher T_c and greater hydrogen concentration the absolute magnitude of the effects observed should be larger and differences between hydrogen and deuterium should be more easily determined. Finally, the comparison with the lanthanum results should be illuminating. Other transition metal-hydrogen-deuterium systems will also be studied.

2. TRANSITION METAL ALLOYS OF THE β-TUNGSTEN STRUCTURE

In the past year methods have been developed for the formation of transition metal alloys in stoichiometric proportions. For example, the system (Nb, Ta, V)$_3$Sn has been prepared for varying compositions and determined to be single phase. This system is a particularly interesting one since one of its compounds (Nb_3Sn) has the highest transition temperature presently known, and moreover several superconductors of particularly high transition temperatures share its crystal structure (β-tungsten).

The transition temperatures of 15 alloys of the form $(Nb, V, Ta)_3Sn$ have been determined and range from, 2.8°K to 18.0°K. In this alloy system the electron to atom ratio is constant but the mass and volume vary considerably. It is noteworthy that the transition temperatures of all the alloys follow a curve of the form:

$$T_c = T_o(M_o, V_o)(M_o/M)^3 \, e^{-12(V-V_o)}$$

where M is the molecular weight, V the unit cell volume in cubic angstroms, and T_o is the transition temperature of a particular alloy of weight M_o, volume V_o. Work will continue on these alloys to determine the implications of this empirical formula and to relate it to other parameters of the system. For example, an attempt will be made to obtain the variation of Debye temperature and density of states for these alloys in hope of relating the above formula to the theory of Bardeen, Cooper and Schrieffer. Research will also be directed to the source of the resistance anomaly found in this system and attempts made to relate it to their superconducting properties.

Finally, other compounds and alloys crystallizing in this structure will be examined in order to find out if similar relations apply, examples being such pairs of compounds as Nb_3Au, Nb_3Ag and Nb_3Ru, Nb_3Ir and their alloys. Through a more complete understanding of the role of mass volume, spin and electron atom ratio in the β-tungsten structure, it is hoped to obtain superconducting materials of appreciably higher transition temperature than the present limit of 18°K. Research will also be directed toward obtaining these materials in single crystal or thin film form. At present some success in this direction has been obtained for Nb_3Sn utilizing a gas-phase reaction.

3. NEW SUPERCONDUCTORS

Research will be directed toward rare earth intermetallic compounds and alloys as several of these compounds have electron-atom ratios and crystal structures favorable for the occurrence of superconductivity. Moreover, it is possible to effect variations in the lattice constant, mass, and inner-electronic structure (spin) by appropriate intra-rare earth substitutions and thus to study the effect of such variations on the superconducting transition temperatures. Research will continue on alloy systems selected to elucidate the concept of electron to atom ratio.

4. SUPERCONDUCTOR IN NON-SUPERCONDUCTING MATRIX

In some of our work it has become apparent that the presence of a non-superconducting material as a second crystalline phase within the bulk of a superconductor has a definite effect on the superconducting transition temperature. Such an effect varies directly with the amount of the non-superconducting phase. Moreover, it has been observed that the concentration of the second phase can be as much as 75 weight % for the material to remain superconducting. The latter observation is of a particular interest since it offers possible means of obtaining materials with high T_c that could easily be fabricated if proper choice of the non-superconducting matrix is made. It is, therefore, proposed to make a study of these phenomena with special emphasis on the microstructure of such mixtures, i.e., the size and the distribution of the two phases, the strain due to different thermal expansion coefficients and the solubility of one material in another.

5. WHISKER STUDIES

In addition to the above work on bulk materials it is proposed to examine films and whiskers of known superconductors for the measurements proposed in Section II and also to investigate the formation of these structures for some of the new materials obtained. Thin films appear to be the natural form of superconducting computer element, from the point of view of size. Whiskers, however, are of interest not only for their small dimensions but also because of their high degree of structural perfection. The current quenching characteristics of whiskers are thus expected to be markedly different from either films or bulk superconductors and will be examined. Moreover basic studies on the superconducting properties of whiskers have yet to be made. The technology of whiskers growth from the point of view of low temperature applications, however, is difficult, and will require extensive research.

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APPENDIX I

LOW TEMPERATURE TECHNIQUES

Low temperature physics has reached a point where its techniques are rather well known, and do not require detailed descriptions. However, it is sometimes helpful to group in one place a description of experimental methods, either because they have proven particularly effective, or because a proper appreciation of some of the results require a description of how they were obtained.

1. LOW TEMPERATURE CRYOSTATS

The usual double dewar systems were used for the maintenance of the samples at low temperatures. Temperatures above that of the bath are attained through vacuum isolation of the sample from the bath, and electrical heating.

It is often convenient to utilize the storage dewar itself, for measurements, rather than to transfer helium to a separate cryostat. However, for measurements above the temperature of liquid helium it is again necessary to isolate the sample from the bath. In the course of the program described in Section III a very convenient "dip-stick" has been developed for this purpose. Rather than use a separate pumping system, it has been found sufficient to use a closed tube enclosing the sample holder, with provision for a rough pump down with a fore pump. The tube is subsequently sealed off with a vacuum valve. When this "dip-stick" is inserted in the helium storage vessel, a high vacuum is attained through the pumping action of the liquid helium. Initial thermal contact with the bath is accomplished by pressing the sample holder against the end of the closed tube. An indium disk is used to reduce the thermal contact resistance. The pressure required for thermal contact (≈ 25 lb/cm^2) is produced in one model by a threaded rod, in another by a spring. Thermal isolation is then achieved by lifting the sample holder away from the end of the tube. Routine transition temperature and resistance measurement have been made in this apparatus from helium temperatures to about 40°K. Since all demountable joints are woods-metal soldered, transfer of specimens can be made quite easily and rapidly. The loss of helium from the storage dewar is quite small – about 0.1 liter per dip.

2. SUPERCONDUCTING SOLENOID

A solenoid fabricated from annealed niobium wire has been used for critical field measurements. The solenoid supplies 554 gauss per amp and is wound with 7450 turns of 5-mil niobium wire. The maximum current is about 4 amps at 4.2°K, above this current the wire goes normal. A transistorized current regulator regulates the current to $1/10^5$ with the provision of increasing or decreasing the current in equal steps. The solenoid gives a maximum field of 2200 oersted, and is wound to give a field uniform to better than 0.1% over the total length of the solenoid (6") – with zero power dissipation!

3. TRANSITION TEMPERATURE AND TRANSITION FIELD MEASUREMENTS

One can simply determine the onset of perfect (infinite) conductivity in either of two ways: dc measurements, or low frequency ac measurements. Perfect conductivity would manifest itself in the first case as vanishing dc potential drop, in the second case, as either a vanishing ac potential drop or a rapid change in the ac skin depth. Magnetically the perfect conductor would maintain any flux originally present inside its boundaries.

The superconductor exhibits many of the characteristics of a perfect conductor, but with the additional property that a simply connected superconductor expels any magnetic field inside its boundaries. Empirically it is found that low frequency or dc magnetic field penetrate a slight distance into the superconductor; a distance of the order of 10^{-6} cm. Of course, a non-simply connected superconductor would behave identically to a perfect conductor.

The distinction between perfect conductivity and superconductivity becomes less obvious for hard superconducting materials. These materials enter the intermediate state at very low critical fields, and maintain small regions of superconductivity material to very high fields. Moreover, the width of the temperature transition is quite wide. Both these effects are probably due to the presence of internal strains, strains which are quite difficult to remove. Whatever the cause it is important to note that superconducting materials as prepared can be quite inhomogeneous due to the presence of strains. The surface of the material can be different than the central portion, and can act as a superconducting shield. Regions of superconducting materials can short out any resistance in the material. Moreover, such small regions can have low critical currents (quenching currents) and fields and hence lead to a current dependence of the transition. All these phenomena should be taken into account in examining the data.

Three techniques have been used to determine the zero field transition temperature: dc resistance measurements, a mutual inductance method, and a self inductance method. The resistance method needs little description. It suffers the disadvantage that the sensitivity is low, and rather large measuring currents are required. Poor contacts then lead to the generation of heat, and introduce temperature instabilities. It is of interest, however, to determine the temperature variation of the resistivity prior to the transition, and these measurements give the most direct method of determining the resistivity.

Susceptibility measurements do not require contacts to the sample, can be quite sensitive, and do give a measure of bulk properties. Unfortunately, surface phenomena can obscure measurements through shielding of the interior. There are two important methods for determining the susceptibility, mutual inductance and self inductance.

To determine just the transition temperature a mutual inductance method is quite satisfactory. The sample forms the core of the secondary of a mutual inductance; changes in the susceptibility of the sample effect the coupling of primary and secondary. It is possible to balance out the signal when the sample is in the superconducting state, and thus detect only changes in the susceptibility of the sample. The apparatus used in this manner had four secondaries coupled to the same primary.

A more sensitive method is to measure the self-inductance of a coil containing the superconducting material as a core. An Anderson bridge(45,46) appears to be particularly appropriate means of measuring self-inductance. With this bridge one can measure, in addition to self-inductance, the resistivity of the specimen. With the bridge in use one can detect the superconducting transition in a volume of 1 mm^3 with a field as low as 0.02 oersted at 300 cps.

Measurements of the magnetization of the specimen were made using two coils connected in series opposition. The sample was placed at the center of one of the coils, and the turns ratios were such that there was zero deflection when the specimen was in the normal state. A heavily over-damped galvanometer was used as a flux meter and the deflection was noted for equal increment changes in the main solenoid current. The galvanometer was used as an integrator, and hence the galvanometer deflection was proportional to the magnetic moment per unit volume of the specimen. Calibrations were made using rods of high purity lead. By a judicious choice of primary and secondary coils it was possible to make zero field transition temperature measurements on four samples, and then make critical field measurements on the same samples without removing the samples from helium temperatures. Since appreciable frozen-in moments were observed after a magnetic transition, it was necessary to heat the sample, in zero field, above the transition temperature, prior to each magnetic transition.

4. TEMPERATURE MEASUREMENTS

Two secondary thermometers were used over the range 1.2°K-400°K for all measurements. A 0.1-watt, 56-ohm carbon resistor calibrated against the vapor pressure of liquid helium, the superconducting transition temperature of pure lead, and the boiling point of oxygen, served as one thermometer. The other secondary thermometer was a copper-constantan thermocouple calibrated against a gas thermometer. In resistance measurements the temperature measurements with the two secondary thermometers overlapped. Over the whole range it is thought that the maximum temperature uncertainty was about 1% for the measurements described in Section III.

APPENDIX II

APPARATUS FOR MATERIAL PREPARATION

1. ELECTRON-BEAM FURNACE

An electron-beam furnace was constructed from existing unused equipment for the purpose of purification and growth of single crystals of superconducting materials.

The apparatus is equipped with a four-inch diameter oil diffusion pump and a 3000 V dc supply. The emission current is stabilized by means of a saturable-core reactor which controls the temperature of the furnace filament.

To date, specimens of iron, niobium, and tungsten were melted in this apparatus, but not zone-refined, since arcing occurs when melting begins. To maintain an electron beam on a molten specimen a more efficient vacuum system is necessary than used so far.

2. ARC FURNACE

In connection with that phase of program concerned with the exploration of new superconductors, an arc-melting furnace was constructed for operation up to 3500°C under an atmosphere of argon. This furnace is useful for melting, alloying, synthesizing and, at times, purifying various metallic materials. Specimens can be melted in it rapidly and without crucible contamination. Specimens up to 20 cubic centimeters in size can be melted readily and only a minor modification in the present design is needed to melt larger specimens.

The power supply is a variable silicon rectifier with 500 amp capacity. The power supply is equipped with a remote control to enable the operator to observe the specimen continuously during melting.

An arc furnace was designed and constructed for the purpose of melting small specimens, for sealing specimens in reactive metallic crucibles, and for fabricating such crucibles. This furnace consists of a 24-inch long brass tube 8 inches in diameter. It has two movable electrodes which can be manipulated from the outside. One of these electrodes is used for mounting the specimen (or the crucible) and the other is used for moving the arc to a desirable position. The furnace can be evacuated prior to introducing an inert atmosphere.

3. TANTALUM-TUBE FURNACE

A resistance heated furnace designed for operation under vacuum or under an inert atmosphere was constructed. This furnace uses a cylindrical tantalum foil heating element the inner dimensions of which are 2 inches in diameter and 10 inches in length. The furnace is designed to be able to handle various high temperature measurements as well as preparations and heat treatments. It is expected to attain working temperatures of up to 2200°C. A more detailed description of this furnace will be given when its performance data become available.