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SUPERCONDUCTING TRANSITION TEMPERATURE OF DISORDERED TRANSITION METAL FILMS

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TABLE OF CONTENTS

SUPERCONDUCTING TRANSITION TEMPERATURE OF DISORDERED TRANSITION METAL FILMS

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ABSTRACT

Critical temperatures of superconducting transition metal films prepared by electron beam evaporation onto a helium cooled substrate have been measured. Contrary to recent predictions of increased critical temperatures, no enhancement was observed in Nb, V, Ta, and $Nb_{.85}Zr_{.15}$ films. However, Mo films were found to have the highest T_c(8.3°K) yet observed. Nb, Nb-Zr, and Mo were also codeposited with xenon. In all these films, the T_c was found to be lower than for corresponding films without xenon. The effects of annealing on T_c were also determined.

I. INTRODUCTION

Recent theoretical-empirical developments in superconductivity have indicated the possibility of obtaining higher critical temperatures with films of superconducting materials.[1,2] The research reported herein was conducted with the objective of obtaining higher critical temperatures in superconducting transition elements, particularly Mo, V, Nb, and Ta, via one of the proposed mechanisms.[2] At the beginning of this research no data were available for testing the existing predictions in the superconducting transition metal elements. A brief review of how the theory may be used as a guide to obtain higher T_c materials is presented below.

The superconductivity phenomenon relies upon the so-called "phonon mediated electron-electron interaction". A conducting electron produces a polarization of the ions surrounding it in the lattice; the electron is thereby partially screened. Another electron, sensing the reduced potential field of the screened electron, is attracted and this results in a lowered energy state for the pair of electrons. Superconducting elements in which the distortion of the lattice ions is large are denoted as strong coupling superconductors. The strength of the electron phonon interaction is characterized by an electron-phonon coupling constant, λ, which appears in the theory of superconductivity.

Until recently, the critical temperature of superconductors was given by the relation

$$T_c = 1.14 \langle\omega\rangle \exp\left(-\frac{1}{N(0)V}\right) \qquad (1)$$

from the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity.[3] In Eq. 1, $\langle\omega\rangle$ represents an average frequency of the phonons, $N(0)$ is the density of electron states at the Fermi surface and V is the net

interaction potential between a pair of electrons forming a bound state. While this equation demonstrated the qualitative features of the critical temperature, it does not permit the prediction of actual values.

A more detailed theory, which considers the nature of the electron-phonon interaction (and its retarded nature), is a better representation of the present state of superconductivity theory. It has received experimental confirmation from tunneling experiments.[4,5] The following numerical solution for T_c has been obtained by McMillan[1]:

$$T_c = \frac{\langle\omega\rangle}{1.45} \exp \frac{-1.04\ (1+\lambda)}{\lambda - \mu^*(1+.62\lambda)} \qquad (2)$$

where λ is the electron-phonon coupling constant (which represents the strength of the interaction between electrons and phonons), μ^* is the Coulomb coupling constant, and $\langle\omega\rangle$ is an average phonon frequency. The shape of the phonon spectrum of niobium was assumed in deriving Eq. (2). McMillan was able to determine empirically values of λ, μ^*, and $\langle\omega\rangle$. The Coulomb coupling constant μ^* (determined from the isotope shift coefficient, the Debye temperature θ_D and T_c) was found to be nearly constant (~.13) for transition elements. Using this value of μ^* and the aid of measured critical temperatures λ could then be determined from Eq. (2). Comparing the empirically determined λ with the theoretical value

$$\lambda = \frac{N(0)\ \langle J^2\rangle}{M\ \langle\omega^2\rangle} \qquad (3a)$$

it was noted that the product $N(0)\ \langle J^2\rangle$, given by $\lambda_{emp.} M\ \langle\omega^2\rangle$ was approximately constant for a given class of materials (e.g. the transition elements V, Nb and Ta). $\langle J^2\rangle$ is the average over the Fermi surface of the squared

matrix element of the electron ion deformation potential, M is the mass of the element and $\langle\omega^2\rangle$ is the average square phonon frequency. Thus Eq. (3a) can be rewritten

$$\lambda = \frac{C}{M \langle\omega^2\rangle} \tag{3b}$$

where C is a constant representative of a class of materials. With this simplication in λ, one can avoid calculating $\langle J^2\rangle$ and Eq. (2) takes the form

$$T_c = \langle\omega\rangle \exp \left[\frac{-1.04 \left(1 + \frac{C}{M \langle\omega^2\rangle}\right)}{\frac{C}{M \langle\omega^2\rangle} - \mu^* \left(1. + .62 \frac{C}{M \langle\omega^2\rangle}\right)} \right] \tag{4}$$

The critical temperature thus becomes solely a function of an average phonon frequency for a class of materials. By changing this frequency we can alter the critical temperature of a material. In particular a decrease in $\langle\omega^2\rangle$, corresponding to an increase in λ, leads to an increased T_c. McMillan considers solid solution alloying as a means of changing $\langle\omega^2\rangle$ within a class of materials (e.g. Zr added to Nb where it is apparently assumed that the change in the phonon frequency spectrum is small.)

A more accurate numerical solution, referred to as the generalized McMillan equation was presented by Garland and Allen.[6] They made no assumption regarding the form the phonon density of states; however it must be known for application of the theory. Predictions of maximum critical temperatures have been presented by both authors.[1,6] In general, the values of Garland et al. are lower and more consistent with experimental data. Table I shows values of λ, calculated critical temperatures and

predictions of maximum T_c for ten elements.

Various physical models have been proposed for which the average phonon frequency of a material may be reduced from its bulk value. The models include very thin films,[7] films composed of small metallic crystallites, amorphous metallic granules and homogeneous amorphous alloys.[2] Dickey and Paskin have found theoretically that the McMillan average squared phonon frequency, defined by $\langle\omega^2\rangle = \langle\omega\rangle / \langle 1/\omega\rangle$, decreased for small particles several atom layers thick.[7] This is due to the increased relative contribution of the lower frequency surface phonon modes.

Metallic films produced by deposition on a low temperature substrate have been characterized as amorphous or composed of small metallic crystallites, even for film thicknesses exceeding several thousand angstroms. Such films are also considerably disordered from the presence of large numbers of defects.

In the present research, an attempt was made to test the theoretical predictions of higher critical temperatures in the transition elements (Mo, V, Nb and Ta) using electron beam vapor deposited films (substrate temperature = 4.2°K). In addition, following an idea by Professor Leo Brewer, films were prepared by codepositing elements Nb and Mo with xenon. It was assumed that xenon could contribute to lattice disorder without seriously changing the electronic properties.

TABLE I

The electron-phonon coupling constant λ^{M} (McMillan[1]) and λ^{GM} (Garland et al[6]) as well as maximum predicted T_c's for ten elements

Element	T_c^{bulk}(°K)	λ^{M}	λ^{GM}	Maximum T_c(°K)	
				McMillan	Garland and Allen**
Al	1.16	.38	.39	24	10
In	3.40	.71	.86	8.5	5
Sn	3.72	.60	.77	14	8
Zn	.85	.38	.44	18	3
Pb	7.19	1.12	1.30	10	7.2
V	5.30	.60	~.74	22*	---
Nb	9.22	.82	~.95	22	---
Ta	4.48	.65	~.85	16*	---
Mo	.92	.41	~.50	~23*	---
W	.012	.28	~.29	~ 2*	---

*Estimated from Fig. 11 in Ref. 1.

**Garland and Allen did not calculate maximum T_c's for transition metals.

II. EXPERIMENTAL

A schematic diagram of the experimental set-up is shown in Fig. 1. All films were prepared by electron beam evaporation of transition metal elements onto sapphire substrates maintained at 4.2°, 77°, or 300°K. Xenon was provided through a gas line in the vacuum system. The xenon was dispersed through a multi-hole copper block (denoted as xenon gas source in Fig. 1) below the shutters which shielded the substrate. A more detailed presentation of experimental preparation and apparatus follows.

A. Substrate and Substrate Preparation

Oriented sapphire crystals of dimensions 1/16"×1/2"×1"were used as substrates. The sapphire was cleaned in a Teepol soap solution and boiled for 30 minutes in a 50-50 H_2O_2/H_2O (distilled) solution, followed by boiling in distilled water. Gold electrical contacts were then deposited on the sapphire, maintained at a temperature of 300°C in a vacuum of 10^{-6} torr. Enough contacts were prepared for five metal films on each sapphire. A gold film was also deposited on the back surface of the sapphire substrate to provide better thermal contact with the box maintained at 4.2°, 77°, or 300°K.

B. Vacuum System and Preparation

The vacuum chamber was a large stainless steel cylinder three feet in diameter and three feet long. The outer jacket of the dewar was made of brass; the water cooled plate and the 77°K box were made of copper while the 4°K box, except for the bottom (which is Cu), was made of stainless steel. The entire chamber had water coils around the outside. On the inside water was also used to cool the electron gun hearths.

A 95°C hot water "bake-out" was used to augment evacuation. It was started about an hour before pumping and lasted for 8 to 12 hours. A mechanical roughing pump brought the system pressure down to ~50μ before an oil diffusion pump was started. During bake-out the pressure was lowered to 7-8 10^{-7} torr. After bake-out, with cold water running in the coils, the pressure dropped to 2-4×10^{-7} torr. To assist in trapping gases, a liquid nitrogen cooled plate covered the entire back wall of the chamber (diam. of 3 ft). The chamber had three separate sites for electron beam guns and hearths, so one was used as a titanium sublimation pump. With the LN plate and getter (Ti) functioning, a base pressure of 3 to 6×10^{-8} torr was obtained. A residual gas analyzer indicated that the major impurity was H_2O.

C. Sample Preparation and Control of Deposition Parameters

The metal was evaporated by electron beam bombardment (8 kV) from a water cooled copper crucible. The rate evaporation was controlled by feedback signal from an Evaporation Rate Monitor (Allen Jones Electronic) to an SCR power supply which controlled the current to the tungsten filament. The variation of the rate during deposition was estimated to be less than ±5%. This system was capable of depositing metal films at rates exceeding 200Å/sec.

When the desired rate for a given element was attained, the shutters (one on the water cooled plate, one on the liquid nitrogen cooled box, and one on the liquid helium cooled substrate box) were mechanically open to prescribed positions. In later runs a quartz mirror (Al coated) was installed so that visual checks of the alignment of the shutters could be made.

The flow rate of xenon was controlled with a valve. An exterior flow rate meter and a rate monitor (No. 3 in Fig. 1) were used to indicate the Xe rate. The copper tubing for transport of the xenon into the vacuum system passed through a cold bath at -90°C (composed of approximately 50/50 dry ice and acetone, by volume) as a trap for any water in the gas. The xenon gas was of research grade, with a claimed purity of 99.995%; the major contaminants were krypton and nitrogen.

The sticking coefficient of xenon was unknown, though it was expected to be quite small, so no direct measure of the quantity of xenon in the film was available. The number of xenon atoms impinging upon the substrate surface per unit time were in the range of 0.1 to 10 times the metal atom rates. The metal atoms have heats of condensation (~100-200 kcal/mole) more than ten times that of xenon (3-7 kcal/mole).[8] In addition the metal atoms, evaporated at relatively high temperatures, have larger kinetic energies than the xenon ($k T_{room}$). Consequently any heating at the surface during codeposition was primarily due to the metal atoms.

The deposition times and rates were selected to make films having thicknesses $\gtrsim$ 1000Å. Thickness measurements were made by the Tolansky multiple interferometer method. The measured thicknesses were used to calibrate the rate monitor.

The temperature of the substrate box was monitored during deposition and was found to increase less than 0.2°K. However this is not indicative of the temperature rise at the surface of the substrate where the transition from the vapor to the solid phase occurs. A test of the surface heating due to radiation only was made by exposing a superconducting molybdenum sample, (T_c = 7.2°K) to the radiation from tungsten heated

to the point of vaporization (white hot). The specimen did not become normal during this exposure, indicating that the rise in surface temperature due to radiation was less than 3°K. Consequently, it was assumed that the specimens were not heated significantly during deposition, except at very high deposition rates. (See annealing curves for vanadium prepared at different rates, Fig. 2.).

D. Critical Temperature Measurement

The resistance of the deposited film was measured using two point contacts (supplying the constant current to the sample and measuring the voltage across it). The temperature was monitored with a Ge thermometer (Texas Instrument Co.) calibrated from 1.2 to 40°K. The thermometer was attached to the liquid He cooled box near the substrate (see Fig. 1). The critical temperature of films of Pb, Sn and In made at room temperature were measured to check the thermometer and any possible difference in temperature between the substrate and the thermometer. Agreements within .05°K of the bulk critical temperatures were obtained. No hystersis (< .02°K) in T_c was observed upon passing through a transition by either heating or cooling.

A constant current of either 1 μa or 10 μa (depending on specimen resistance) was sent through the deposited films and the resulting voltage drop across them was measured with an Astrodata Nanovoltmeter (Model 121 RZ), the output of which was fed into the Y-axis of an Electro Instrumets XY Recorder (Model 520). The constant current to the Ge thermometer was 1μa; its resistance (voltage across it) was the input to the X-axis of the recorder. Standard resistors of 10, 100, 1K, 10K, and 100K, ohms were available in the circuit to calibrate the temperature axis.

The critical temperature measurement was made by cooling the specimen to 4.2°K. If $T_c < 4.2°K$, the temperature was reduced by pumping on the helium dewar. Minimum temperatures of about 1.7°K could be obtained in this manner. For $T_c > 4.2°K$, a lower power heater, composed of manganin wire wrapped around a metal extension on the substrate box, was used to increase the temperature of the box. If $T_c \gtrsim 5.5°K$ it was sufficient to allow the substrate box to warm on its own in the absence of liquid helium at a rate of 0.2 to 0.4°K/minute. Often it was possible to heat through the transition after the helium was gone, then turn off the heater to allow the specimen to cool back down through the transition. No hysterisis was found in the measurements reported here. Critical temperature measurements have uncertainties of about ±.05°K, unless otherwise indicated.

E. Annealing of Deposited Films

After T_c measurements were made, many of the films were annealed at rates between 1-3°K/min. by one of two methods: (1) flowing warm He or N_2 gas into the helium dewar or (2) by electron bombardment of the substrate box from a filament located on the liquid nitrogen cooled shield. Specimen resistances were measured as described in Section D. Annealing temperatures never exceeded room temperature.

Often, where the annealing curves showed some interesting changes or where it was thought that the results might be useful, the substrate was again cooled to remeasure critical temperatures. For some specimens this cycle was performed more than once.

F. Microscopy

Upon removal of the specimens from the vacuum chamber at room temperature the films were observed with an optical microscope, an x-ray diffracto-

meter and by electron microscopy. Many of the films had small cracks, some appeared in a flaky plate or layer-like form, and others had fine needles protruding from the film. Photomicrographs were taken of these films.

X-ray diffractometer tracings were taken of the films on the sapphire substrate with a Picker x-ray diffractometer (Model 3488K) set at 40kV using the Cu α line. It was noted that few peaks ever appeared, and when present, they were extremely weak. Consequently, for films of interest Debye-Scherrer powder diffraction patterns were taken to determine the structure of the films.

Electron diffraction and electron microscopy were performed on the 650 kV Hitachi electron microscope. Debye Scherrer x-ray patterns were often taken to be sure that the crystal structure determined by electron diffraction was not the result of heating in the microscope.

III. RESULTS

A. Low Temperature Deposition of Transition Elements

1. Molybdenum

Superconducting films of molybdenum were prepared by deposition on substrate at temperatures of 4.2, 77, and 300°K. The critical temperatures of such films, each deposited at a rate of ~150Å/sec are shown in Fig. 3 as a function of the temperature of the substrate during deposition. The films indicated by circles were shiny and continuous upon observation after removal from the cryogenic apparatus. Other films (prepared at the same rate) having a dull appearance due to many small cracks and some flaking had higher critical temperatures (indicated by squares). The highest critical temperature attained was 8.3°K for a film prepared at a rate of ~600Å/sec which also had many small cracks.

Annealing of the low temperature deposited Mo films resulted in a continuous decrease in T_c after a temperature between 40°-60°K was reached (Fig. 4). This corresponded to the temperature region in which a small decrease in sample resistivity (~5-10%) occurred (see Fig. 2). It is interesting to note that the decrease in critical temperature of annealed Mo films occurred at about the same temperature that the specimens showed a decrease in resistance (compared Figs. 2 and 4).

Upon annealing to room temperature the critical temperature dropped to values between 3 and 5°K, near that for films deposited at room temperature (T_c = 4-5°K). Films removed from the system were found to be nonsuperconducting down to 1.4°K when measured in another apparatus. However, Mo specimens coated with SiO prior to removal had critical temperatures of 2.0 to 2.2°K after exposure to the atmosphere.

Debye-Scherrer powder diffraction patterns as well as electron diffraction patterns at room temperature corresponded to a body centered cubic structure with a lattice parameter of 3.15Å. This is good agreement with the bulk value for molybdenum. Grains covering a broad range of sizes (< 40-200Å) were observed by electron microscopy. The diffuse electron diffraction rings also indicated that the grain sizes of < 100Å were present.

Several Mo films were deposited on a layer of LiF on sapphire in order to facilitate their removal for electron microscopy. These films deposited at 4.2°K, had T_c's of 5.1 and 6.0°K for deposition of ~20 and ~200Å/sec, respectively. Electron diffraction and electron microscopy revealed a bcc structure with grains less than 100Å.

In regard to the cracked films, it was found that by using small magnets to deflect electrons and possibly ions in the incident beam, continuous films having a shiny appearance could be obtained. It was suspected that changing of the films and/or substrate was the cause of the cracked films. Applied electric fields, electrostatically charged substrates, and a charged incident flux are known to have an effect on the structure and growth of films.[9,10]

2. Niobium

Niobium films made at a rate of 250Å/sec in a vacuum of $5\ 10^{-8}$ torr had critical temperatures of 8.3-8.4°K which is less than that of the bulk (9.2°K). These films were made at 4.2°K and subsequently annealed at higher temperatures. Remeasurement of T_c was performed after the 25-30% decrease in specimen resistance that occurred in the temperature interval 50 to 80°K (see Fig. 2); only a slight change in T_c was found

(±0.2°K). No further change in T_c was observed upon annealing to room temperature. Electron diffraction patterns and electron microscopy revealed a bcc structure with grain sizes of $\lesssim$ 30 to 100Å.

3. Niobium-Zirconium

A solid solution alloy of 5% Zr in Nb was prepared by arc melting. The objective of using Zr with Nb was twofold (1) Zr would better oxygen in the sample if that were a problem and (2) the resultant composition of the film placed the alloy at the peak of the density of states curve where any enhancement in T_c would not likely be due to an increase in the density of states. The film formed from this alloy contained ~15% Zr. The critical temperature of the as deposited (at 4.2°K) film was 6°K, considerably less than that of the bulk (10.4°K). Upon annealing very little change in specimen resistance occurred up to 80°K but at that temperature a decrease by a factor of four suddenly occurred. This was followed by a continuous increase to room temperature. Remeasurement of T_c after annealing to room temperature yielded the bulk value of 10.4°K.

4. Vanadium and Tantalum

Vanadium films followed the behavior of niobium films with T_c < bulk T_c, with no change in T_c occurring upon annealing. Critical temperatures of 4.4 to 4.7°K were observed for estimated deposition rates of 50 and 100Å/sec. A factor of three decrease in resistance occurred in a narrow temperature range, 40-60°K, for the specimens prepared at the lower rate. The higher rate (200Å/sec) specimens showed a much smaller decrease in resistance, indicating possible annealing due to heating during deposition.

Preliminary work on tantalum yield a T_c of 2.1°K followed by a rise to 3.4°K after annealing to room temperature. (A fcc phase of Ta has often been reported in the literature and no T_c has been reported for it.) More investigation of the structure of Ta films is necessary.

B. Codeposition of Nb, Mo and Nb-Zr with Zenon

The codeposition of xenon at increasing rates with respect to fixed metal rates (100Å/sec for Nb, 200Å/sec for Mo and ~50Å/sec for Nb-Zr) uniformly decreased the critical temperatures of Nb, Mo, and Nb-Zr, with one exception, a slight increase (~.35°K) for Nb at the lowest xenon rate was observed. T_c values are given in Fig. 5 as a function of the ratio of xenon to metal rates for Nb and Mo, and in Fig. 6 for Nb-Zr. The system pressure increased due to xenon from 5×10^{-8} to as much as 10^{-6} torr for the highest xenon to metal rate ratio. Specimen resistivities increased in general with increasing xenon rate, although some exceptions occurred at low rate ratios which are not at present understood.

Upon annealing to 300°K, and then remeasuring T_c, the codeposited films showed the same behavior in T_c as the pure films: (a) Niobium critical temperatures changed very little (~ + 0.1°K), (b) Nb-Zr films increased in T_c but were still lower for bulk material, and (c) Mo films decreased to about ~3°K except for the pure Mo film (6°K).

The annealing data of Nb-Zr codeposited with xenon showed an additional feature not observed with the other metals or pure Nb-Zr. A gradual decrease in resistivity occurred begining at ~10-20°K which continued to ~100°K where a sharp drop by a factor of 2-3 occurred. The gradual decrease (~30%) was associated with the effect of xenon on the structure, either by its presence in the lattice and/or grain boundaries, or by the nature of defects that it produced.

IV. CONCLUSIONS

The high rates (~200Å/sec) and the relatively high vacuum (~5×10^{-8} torr) condition in these experiments made possible an interpretation of results which is independent of gaseous impurities (which are known to alter T_c values for thin films).[11-14] Even if all of the gases in our system had a sticking coefficient of one, the maximum gas impurity content would only be about .01% atomic percent. Consequently we felt justified in neglecting gas impurity effects on the results.

The processes occurring at low temperatures which results in the resistivity decrease are poorly understood.[15] Similar decreases in the resistivity of Fe films have been observed at ~40°K[16] and at ~10°K.[17] Fijime[18] reported an amorphous structure for iron films made at low temperatures. These films remained amorphous up to 180°K. Amorphous in this instance means that the x-ray diffraction pattern shows few broad halos that could not easily and uniquely be assigned to the diffraction lines of the crystalline structure. Above 180°K the structure became small grained bcc, meaning many rings were observed in the diffraction pattern, the relative spacings of which defined a crystalline structure. It is to be noted that the temperature at which the resistance decreased (10-40°K) and the structure changed were not the same; this may be due to different film deposition conditions. Thin films of Ni made at 4.2°K and annealed to room temperature showed no change in resistivity and were found to be in an amorphous state at 300°K.[17] Similar amorphous diffraction patterns have been observed in the transition elements Cr, Yt, Ti, Co and Pd.[18]

It may not be assumed that the films prepared here were amorphous as deposited for two reasons: (1) the high depositor rates may have caused sufficient heating to anneal the deposited films and (2) the resistance decrease observed in all specimens, including those of other researchers,[17,18] has not been correlated with the amorphous to crystalline transformation. Other possible origins of the decrease in resistance include the annealing of defects (interstitials, grain boundary rearrangements,[15] vacancies), or a metastable to stable phase tranformation. We were not able to determine which of the above possibilities was applicable for each film; such a determination would require in situ diffraction measurements. However, the metastable to stable phase transformation was considered unlikely in those films which had little or no change in T_c before and after annealing.

As a result of the small grain sizes observed ($< 100\text{Å}$) after annealing to 300°K, it is argued that for this reason the average squared phonon frequency $\langle\omega^2\rangle$ was lower than for the bulk metal. As deposited films can be characterized as structures with high defect concentrations. Thus measurements of critical temperatures after annealing to various temperatures provide data for films having varying degrees of disorder.

Applying the above considerations to the results for V, Nb and Ta, it is observed that T_c (film) $< T_c$(bulk) before and after the annealing step. Each of these films had their normal structure (bcc) and small grain sizes at 300°K. These results differ from predictions based on the McMillan theory, which leads to the conclusion that sizeable increases in T_c (~10°K) should have occurred. A similar failure to increase T_c by low temperature deposition of niobium has been reported by Crow et al.[19] We differed from their results in that both as-deposited and annealed Nb

films had $T_c \sim 8.3°K$ while theirs increased from 6°K (as deposited) to ~8°K annealing. It is possible that their as-deposited film was amorphous while ours was not (due to possible heating during deposition at high rates).

The critical temperature and annealing behavior of Nb-Zr films are particularly striking. In the as deposited condition these films had T_c's considerably less than the bulk value, and upon annealing the bulk T_c was regained. Assuming that the large decrease in resistance occurring at ~80°K was not due to a metastable to stable phase transformation, then highly disordered (if not amorphous) Nb-Zr has a significantly reduced critical temperature. In such a film $\langle\omega^2\rangle$ would be reduced relative to the bulk alloy,[2] and T_c should have increased if electronic band structure effects could be ignored as proposed by McMillan.[1] After annealing to 300°K the critical temperature was not enhanced for the small grained bcc structure. Thus the McMillan prediction toward higher T_c was not realized in this alloy.

The highest measured critical temperature for molybdenum, 8.3°K, is reported herein. Crow et al.[19] report a high T_c in Mo films as being due to an edge region having a value of 6.7°K while the film without edges (masked) had a $T_c \sim 4°K$. Others[20,21] have reported the formation of an fcc phase in the early stages of deposition in Mo deposited at room temperature. In these cases a maximum thickness of ~50Å was achieved before the structure was observed to be bcc. In the films we prepared, the decrease in T_c appeared to be correlated with the resistance decrease upon annealing. The decrease in resistance was approximately 10%, much too large to be associated with edge regions. If the edges annealed, it is unlikely that this change would be reflected in the total

resistance of the film because of its extremely small contribution to the total film. Also, no fcc phase was observed in either Debye-Scherrer powder diffraction or electron diffraction patterns. However, this does not exclude the presence of another phase in small quantites, nor does it preclude the possibility of a phase change occurring during annealing.

The interpretation of the xenon-metal codeposited films is complicated by our ignorance regarding the amount and location of xenon in the film. A mass spectroscopic examination of a Nb-Zr film indicated the presence of ~1 at.% xenon.[22] If the xenon were in the lattice, then its effect would be to disorder the film and lower T_c. If the xenon were largely present in the grain boundary regions, then it should have decreased the grain size. Regardless of the location of the xenon, it is felt that it contributed to increased disorder via small grains, defects, or its presence in the lattice. This increased disorder resulted in decreased critical temperatures.

In conclusion, it appears that more than a simple decrese in $\langle\omega^2\rangle$ occurs in small grained transition metal films. Garland et al[2] have argued that band structure effects will be important in transition metals and must also be consiered. Crow et al.[19] have proposed that a smearing out of the band structure may occur in very small grained or disordered films. This would result in a decreased density of electron states, N(0), for elements or alloys having a high N(0) in the bulk form (e.g., Nb, $Nb_{.85}$, $Zr_{.15}$, V, Ta) and visa versa for elements with a low N(0) in the bulk form (e.g. Mo, W). This interpretation is in agreement with the trend of our results (e.g. Mo increases in Ti and Nb-Zr decreases) but it seems surprising that such a large increase in T_c for Mo could be accounted for by this mechanism. These and other considerations will be considered in further work.

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22. This measurement was generously performed by Dr. E. Kay, of IBM, San Jose, California.

FIGURE CAPTIONS

Fig. 1. Schematic diagram of cryogenic, deposition and rate monitoring apparatus.

Fig. 2. Representative annealing curves of films prepared at liquid helium temperature. Arrows indicate reversible ($\rightleftarrows$) and irreversible ($\rightarrow$) temperature paths. Critical temperatures are indicated for as deposited and annealed films.

Fig. 3. Critical temperature, T_c, of molybdenums as a function of substrate temperature for shiny continuous films (O) and cracked (□) films.

Fig. 4. Critical temperature, T_c, of molybdenum films after annealing to temperature T_{anneal}.

Fig. 5. Critical temperatures of niobium and molybdenum codeposited with xenon at liquid helium temperature. The ordinate is the ratio of the relative rates of xenon and metal. T_c for the pure metal films are also presented.

Fig. 6. Critical temperatures of niobium-zirconium codeposited with xenon at liquid helium temperature, both in the as deposited and annealed condition.

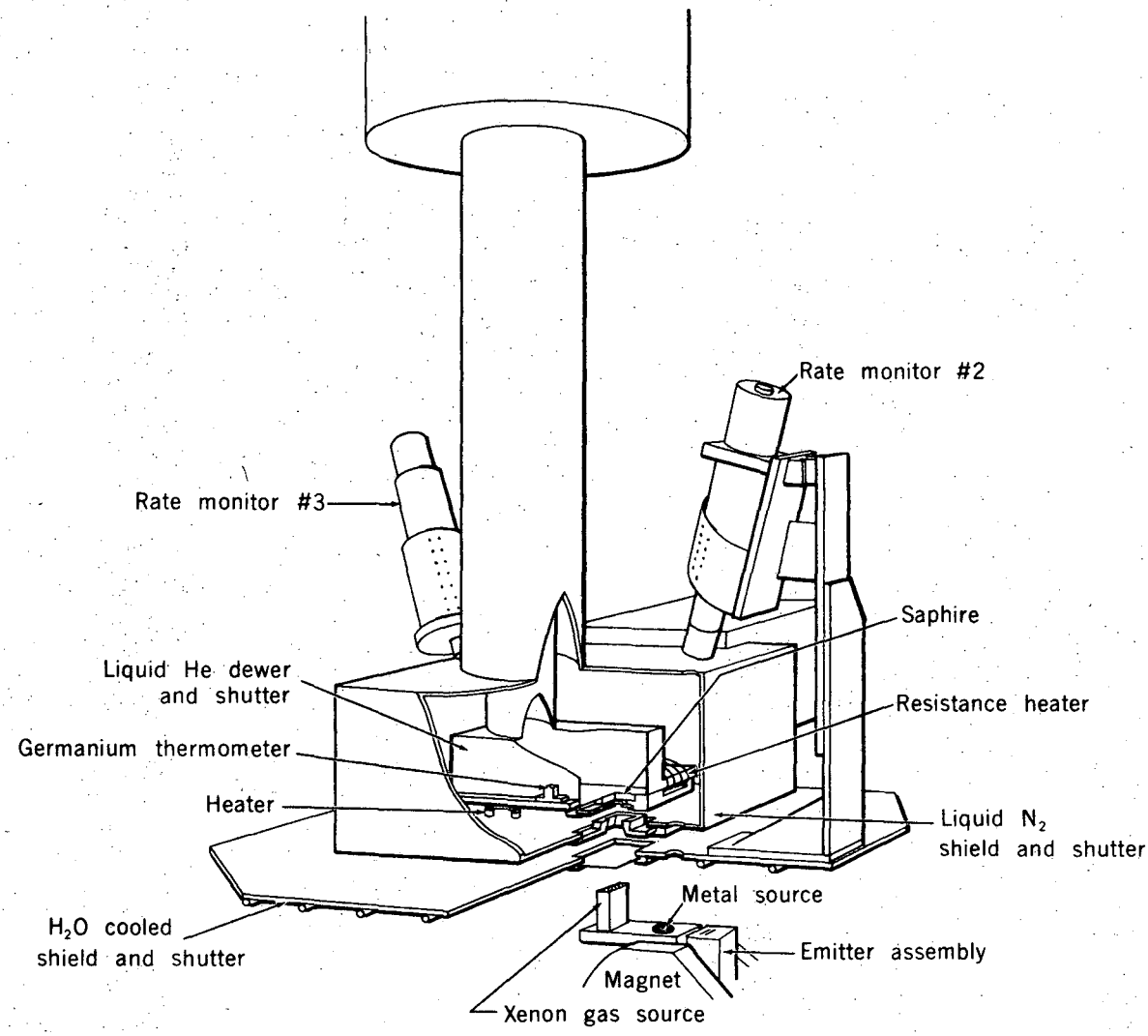
Rate monitor #2
Rate monitor #3
Saphire
Liquid He dewer
and shutter
Resistance heater
Germanium thermometer
Heater
Liquid N_2
shield and shutter
Metal source
H_2O cooled
shield and shutter
Emitter assembly
Magnet
Xenon gas source
XBL698-3448

Fig. 1

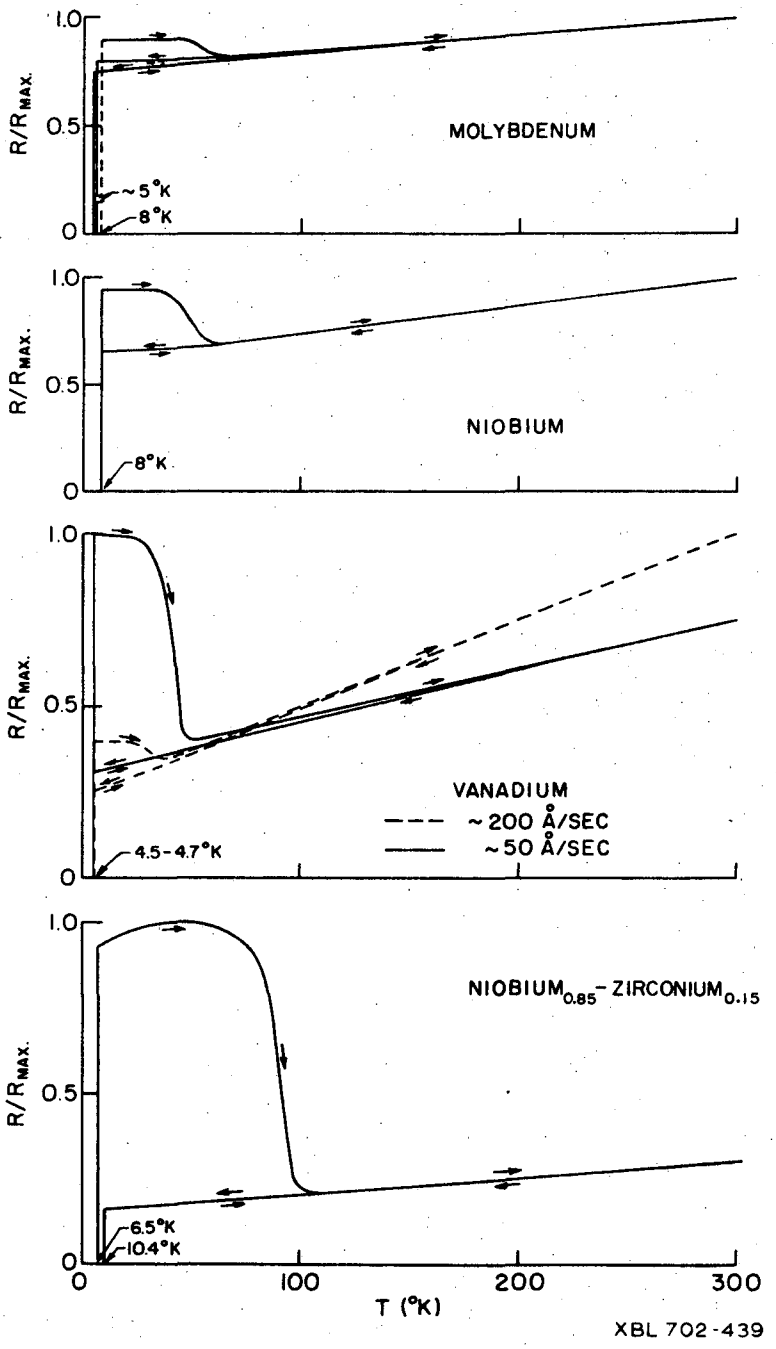
1.0
0.5
0
R/R MAX.
MOLYBDENUM
~5°K
8°K
NIOBIUM
8°K
VANADIUM
~200 Å/SEC
~50 Å/SEC
4.5-4.7°K
NIOBIUM0.85 - ZIRCONIUM0.15
6.5°K
10.4°K
0
100
200
300
T (°K)
XBL 702-439

Fig. 2

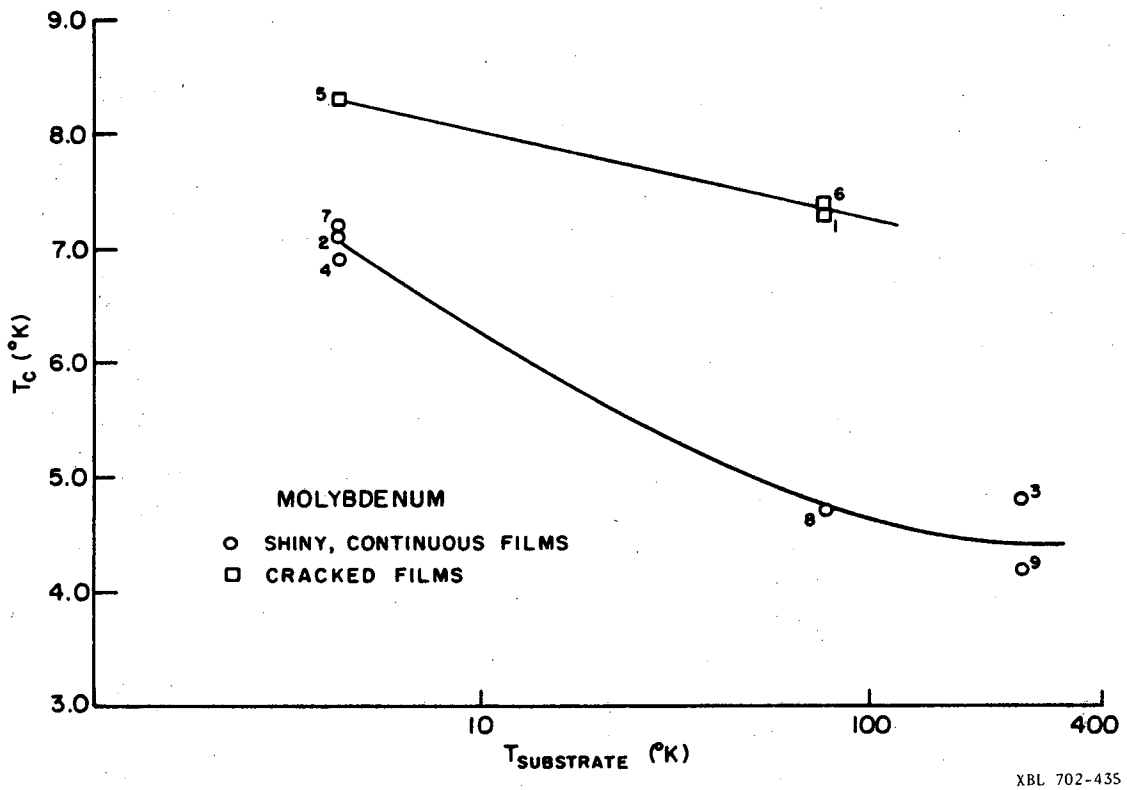
9.0
8.0
7.0
6.0
5.0
4.0
3.0
T_c (°K)
10
100
400
$T_{SUBSTRATE}$ (°K)
MOLYBDENUM
SHINY, CONTINUOUS FILMS
CRACKED FILMS
XBL 702-435

Fig. 3

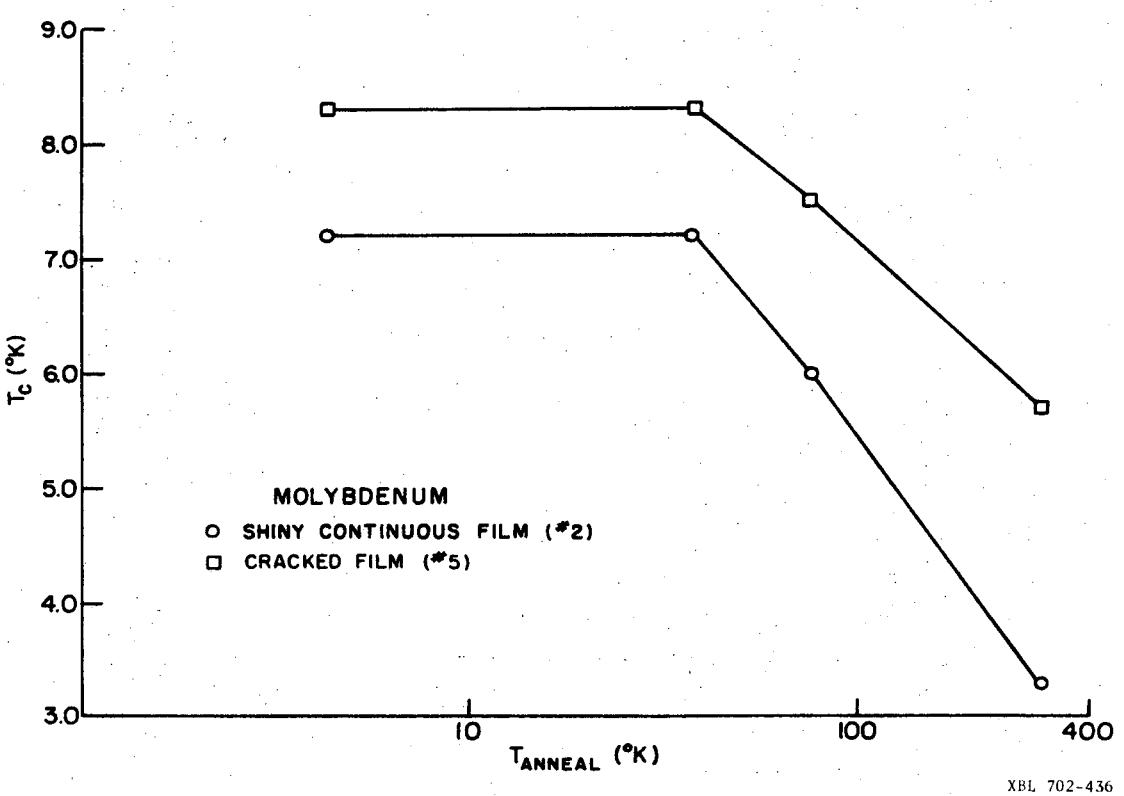
9.0
8.0
7.0
6.0
5.0
4.0
3.0
T_c (°K)
MOLYBDENUM
SHINY CONTINUOUS FILM (#2)
CRACKED FILM (#5)
10
100
400
T_{ANNEAL} (°K)
XBL 702-436

Fig. 4

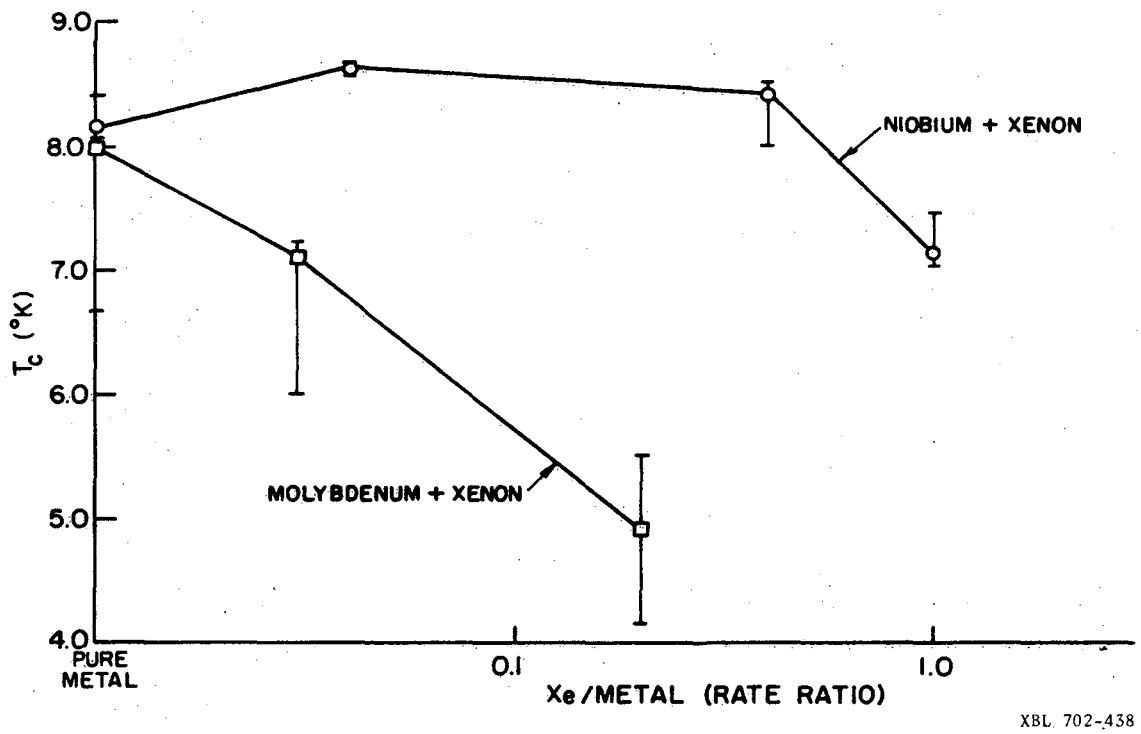
9.0
8.0
7.0
6.0
5.0
4.0
T_c (°K)
NIOBIUM + XENON
MOLYBDENUM + XENON
PURE METAL
0.1
1.0
Xe/METAL (RATE RATIO)
XBL 702-438

Fig. 5

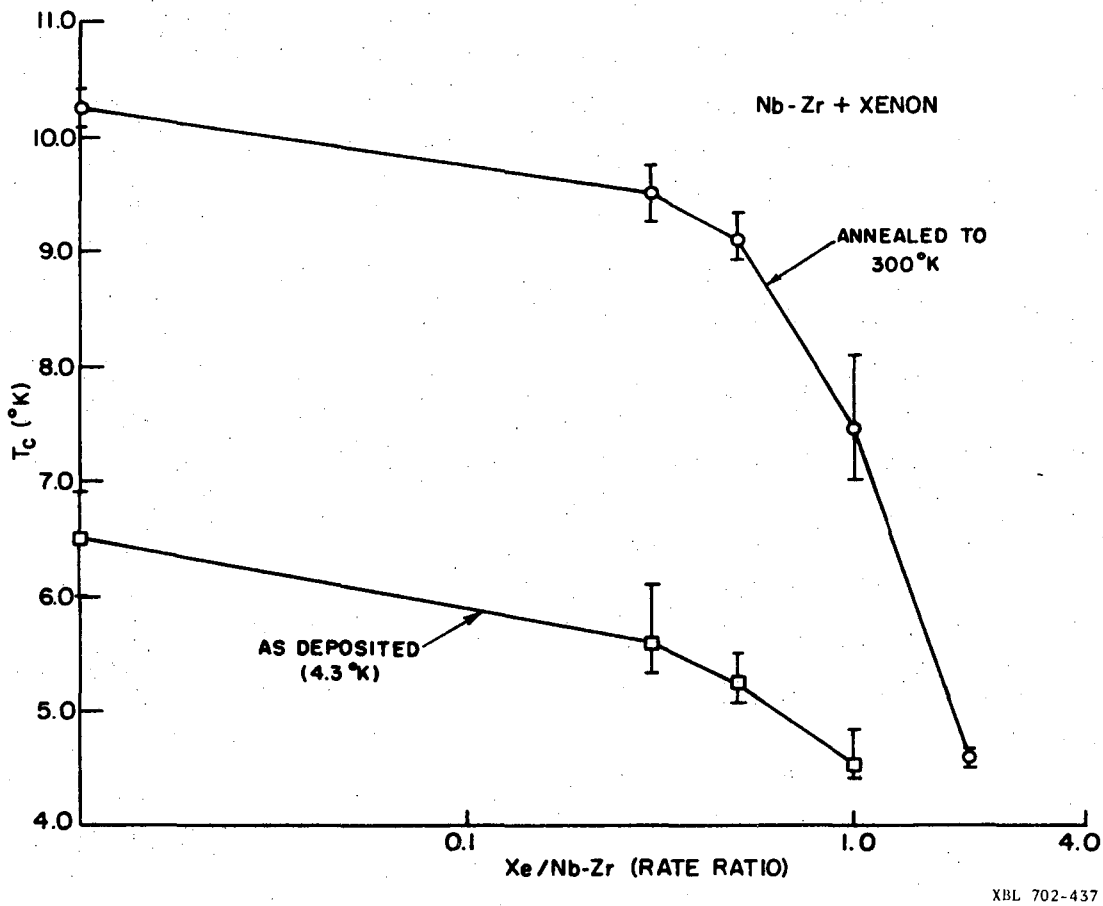
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
T_c (°K)
Nb-Zr + XENON
ANNEALED TO 300°K
AS DEPOSITED (4.3 °K)
0.1
1.0
4.0
Xe/Nb-Zr (RATE RATIO)
XBL 702-437

Fig. 6

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