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Evidence for Filaments in V_3Si

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Thin films of V_3Si were deposited on various substrates such as quartz, sapphire, graphite, but principally on MgO using the hydrogen reduction of the mixed chlorides. The evaporator used for the vapor phase control of the reduction process was designed to take advantage of the principle of steady state and therefore was able to yield films with very accurate chemical compositions. Thin films ranging in thickness from 100 000 Å down to 1000 Å were deposited on MgO at a temperature of approximately 1000°C. The transition temperatures of these films were as high as 16.7°K for the thick films, but as low as 14.85°K for the thin ones. The composition of the films was checked by x-ray diffraction and x-ray fluorescence analysis. The gross composition of the films was found to depend on the composition of the vapor and the substrate temperature.

It is a well-known fact that thin films of soft superconductors smaller than the penetration depth are characterized by a higher critical field than the bulk. In order to check a corresponding size dependence in a hard superconductor such as V_3Si, thin films of various thicknesses were produced with a fixed composition. The transition field of these films was measured at liquid-hydrogen and liquid-helium temperatures by a resistance method. The temperature dependence of the transition field was found to be linear for all films up to 105 kG and to be invariant with film thickness within the limits of experimental error. This behavior, which is very different in nature from that of a soft superconductor, can be interpreted in terms of the filamentary theory of hard superconductivity.

I. INTRODUCTION

It is a very well-known fact that thin films of soft superconductors of thicknesses comparable or smaller than the penetration depth are characterized by critical fields considerably larger than the bulk critical field. The increase in critical field with thickness has been verified by numerous investigators such as Lock[1] who performed experiments on In, Sn, and Pb. The functional dependence of this variation was first calculated by London[2] who found in the case of very thin films

$$H_d/H_c \simeq 2\sqrt{3}\lambda/d \quad \text{for} \quad d \ll \lambda, \tag{1}$$

where H_d is the critical field of a thin film of thickness d, H_c is the thermodynamic critical field, and λ is the London penetration depth. More recently, Hauser and Helfand[3] as well as Toxen[4] have derived with the use of a nonlocal theory the following relation in the case of specular reflexion:

$$H_d/H_c \simeq \frac{2\lambda(\xi_0)^{1/2}}{(d/2)^{3/2}}, \quad d \ll \lambda, \tag{2}$$

where ξ_0 is the coherence distance.

The physical reason for such a behavior can be explained as follows: The critical field of a superconductor is determined by the competition of two effects; (1) the lowering in Gibbs free energy as a result of the electron pairing and (2) the increase in Gibbs free energy which arises from the diamagnetism of the superconducting state and which distorts the magnetic field. Consequently, as the film thickness is reduced below the penetration depth, the latter effect becomes smaller and smaller and consequently the critical field increases. If, however, the high transition field of hard superconductors is the result of embedded filaments[3,5] smaller than the penetration depth, one does not expect a size effect in thin films of hard superconductors, until the thickness of the film becomes smaller than the diameter of a filament. When the thickness of the film is reduced below that of the filament, the transition field may increase. In order to check this prediction, thin films of V_3Si were prepared and the transition field was measured as a function of film thickness.

II. EXPERIMENTAL PROCEDURE

A. Preparation of V_3Si Films

For the purposes of this investigation a series of V_3Si films of uniform composition having thicknesses varying between 1000 and 100 000 Å were required. The films were prepared by the hydrogen reduction of mixtures of the tetrachlorides of vanadium and silicon. The method is an adaptation of that used for the preparation of epitaxial silicon films.[6] With this method the problem of oxygen contamination is virtually eliminated and film growth is linear with time and readily controlled. Silicon tetrachloride purified by standard adsorption procedures[7] was used, and the vanadium tetrachloride was prepared by the chlorination of commercially available 99.8% vanadium. Chlorine was first passed over graphite at 650°C to eliminate traces of water vapor and oxygen by conversion to CO and CO_2. The treated chlorine was then passed over the vanadium in a quartz system heated between 850 and 1000°C. The vanadium tetrachloride was condensed and collected in a glass flask. The resulting VCl_4 contains an excess of chlorine which was eliminated by aspiration with pure dry hydrogen while the VCl_4 was maintained at 0°C in an ice bath. No further purification of the VCl_4 was

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[1] J. M. Lock, Proc. Roy. Soc. (London) **A208**, 391 (1951).

[2] F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950), Vol. 1.

[3] J. J. Hauser and E. Helfand, Phys. Rev. **127**, 386 (1962).

[4] A. M. Toxen, Phys. Rev. **127**, 382 (1962).

[5] K. Mendelssohn, Proc. Roy. Soc. (London) **A152**, 34 (1935).

[6] H. C. Theuerer, J. Electrochem. Soc. **108**, 649 (1961).

[7] H. C. Theuerer, J. Electrochem. Soc. **107**, 29, (1960).

attempted. The apparatus initially used for the reduction of the mixed halides is essentially the same as that used for silicon reduction.[6] It consists of a source of pure dry H_2, a halide saturating system, the reduction chamber and an induction coil for rf heating. With this apparatus it is possible to control the halide composition, the hydrogen-halide ratios, the gas-flow rate, and the reduction temperature which are the parameters controlling the film composition and growth rate. The hydrogen was purified by passing over palladinized alundum for conversion of contained oxygen to water vapor. The gases were then passed through a trap containing Linde No. 5 A Molecular Sieves at liquid N_2 temperature to remove the water vapor and other condensable gases. The hydrogen was saturated with $SiCl_4$ and VCl_4 by bubbling through the saturator usually maintained at 0°C. To obtain a vapor phase halide composition of $3VCl_4$–$1SiCl_4$, the liquid composition in the boiler must of necessity contain a much lower $SiCl_4$ content because of its high vapor pressure relative to VCl_4. At 0°C VCl_4 has a vapor pressure of 1.9 mm compared to 78 mm for $SiCl_4$. Using ideal solution law the mole ratio for the vapor and liquid phases is given by

$$\left(\frac{N_{\mathrm{VCl_4}}}{N_{\mathrm{SiCl_4}}}\right)_V=\frac{(p^0)_{\mathrm{SiCl_4}}}{(p^0)_{\mathrm{VCl_4}}}\left(\frac{N_{\mathrm{VCl_4}}}{N_{\mathrm{SiCl_4}}}\right)_L,$$

where N is the number of moles of the constituents, p^0 is the vapor pressure of the pure constituent, and the symbols V and L are for the vapor and liquid phases, respectively. From this it follows that for a vapor mole ratio of $(3VCl_4/1SiCl_4)_V$ the mole ratio in the liquid must be $123VCl_4$: $1SiCl_4$. Unfortunately, with the above method of saturation because of the exponential depletion of $SiCl_4$ with continued evaporation, the films produced also become progressively low in silicon. To eliminate this difficulty a method involving steady-state evaporation was designed.

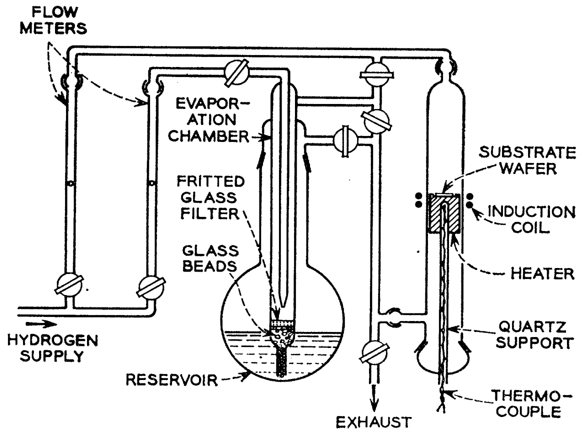

Fig. 1. Steady-state evaporator used for the reduction of mixed chlorides.

If one considers the evaporation of a column of a binary liquid without thermal or mechanical agitation, the initial vapor will be rich in the high-vapor-pressure constituent and the surface liquid will be enriched in the low-vapor-pressure constituent. At steady state, the surface liquid will have the composition required to produce an equilibrium vapor of composition C_0 which is identical to the initial composition of the liquid. Due to liquid diffusion, a concentration gradient will be established from the interface into the solution characterized by the equation[8]:

$$C_L=C_0\left[1+\left(\frac{k}{k-1}\right)e^{-RX/D}\right], \tag{3}$$

where C_L= concentration at X cm in from the interface; C_0= initial concentration; k= relative solubility, for ideal solutions the ratio of the vapor pressures of solute to solvent; R= evaporation in cm/min; D= diffusivity in cm^2/min.

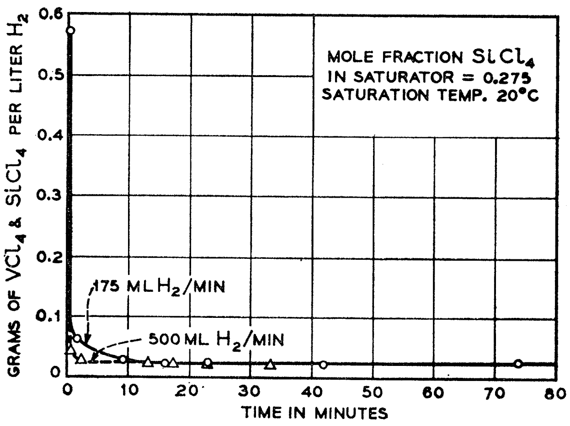

Fig. 2. Determination of the equilibrium time for the saturator.

In the above equation the dimensionless quantity RX/D determines the depth of the concentration gradient. In practice it is desirable to maximize the value of this exponent which means that the evaporation ratio should be made as large as possible. One form of steady-state evaporator and its control equipment are shown in Fig. 1. The apparatus consists of an inner evaporation column and an outer reservoir containing the liquid to be evaporated interconnected by a fritted glass filter and tubulation filled with small glass beads. Due to the capillarity of the frit, its upper surface is continually wetted, even against an appreciable head difference between the frit and the reservoir liquids. Moreover, the frit has large surface area yet contains liquid only in the capillary interstices which maximizes the R in Eq. (3) as is desired. The time required to bring the evap-

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[8] V. G. Smith, W. A. Tiller, and J. W. Rutter, Can. J. Phys. 33, 723 (1955).

orator to steady state is determined by a number of factors chiefly the relative volatility of the constituents and equilibration of the temperature at the evaporating surface. Figure 2 gives the data for the equilibration of the saturator taken from the time of initial evaporation. The total halide content per liter of hydrogen passing through the evaporator at various times was determined by an adsorption method. The data clearly indicate that the saturator reaches steady state within 10 min and as might be expected the equilibration time is shorter when the evaporation rate is increased. With the steady-state evaporation method the gas-phase composition may be precisely controlled and is always that of the reservoir liquid irrespective of the temperature or rate of evaporation.

While maintaining the VCl_4–$SiCl_4$ ratio in the vapor phase is a primary factor in composition control, nevertheless, it has been found that the reduction temperature and hydrogen-halide ratio (ratio of $SiCl_4+VCl_4$ to the hydrogen) can affect the composition over a wide range. Whereas, it has been found that the rate of reduction of VCl_4 is insensitive to temperature in the range between 950–1100°C, the rate of reduction of $SiCl_4$ increases rapidly with temperature. In determining the composition of the V_3Si films, x-ray fluorescence techniques were used. Figure 3 gives a typical plot of film composition vs deposition temperature. The other parameter affecting film composition is the hydrogen-halide ratio. As shown in Fig. 4 decreasing the halide concentration in the hydrogen has the effect of increasing the silicon content of the films. In this work most of the V_3Si films were prepared at 990°C using a VCl_4-SiCl_4 vapor containing 27.5 mole percent silicon and a hydrogen halide ratio of 0.005%. Deposition was carried out for periods ranging from 15 sec to 3 h depending on the thickness of film desired, the growth rate being linear with time. The presence of V_3Si in some of the films was further established by the use of Laue patterns and x-ray powder diffraction techniques.

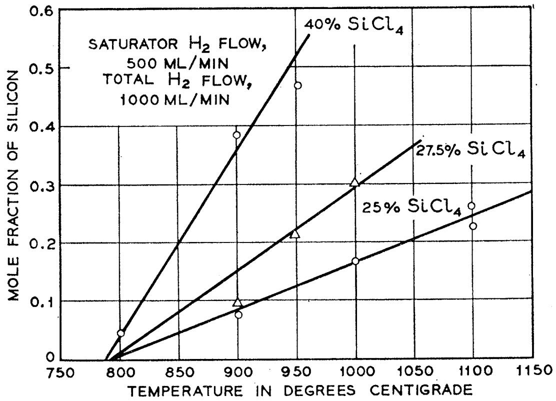

Fig. 3. Composition dependence on temperature of deposition.

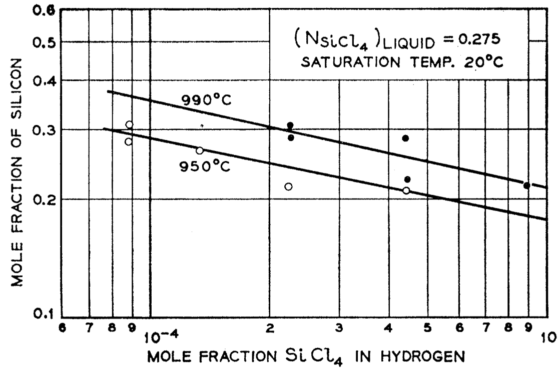

Fig. 4. Composition dependence on the hydrogen-halide ratio.

In general, these films have been prepared on refractory oxide substrates the most satisfactory being crystalline MgO, sapphire or MgO coated with graphitized carbon. For satisfactory results interaction of the substrate and hydrogen must be avoided. It has been found that at 1200°C MgO is reduced to Mg and associated with this a lowering of the critical temperature of the films is observed. Poor results have been obtained with quartz even at 1000°C due to substrate interaction and it has not been used.

B. Measurement of the Thin Films

The thickness of the films was determined by calculating the weight gain obtained after deposition of the V_3Si. The relative thickness of various films obtained by this method is in good agreement with the result that one obtains by a resistivity measurement. The weight loss experienced by heating an MgO wafer at the temperature of deposition for an average deposition time was found to be negligible. Finally, the thinnest film reported in this analysis (1115 Å), was found slightly transparent to visible light ($\simeq 2\%$ transmission) which is another check on the order of magnitude of the thickness estimates. Interferometry could not be used because of the large cleavage steps (a few 1000 Å high) present in the MgO wafers.

The presence of superconductivity was determined by a resistance measurement. Very thin copper leads were attached to the sample with the use of a silver air drying paste. The usual size of the films was 1 cm×0.5 cm. In order to get maximum sensitivity, the current leads were attached to two corners of the sample, while the two potential leads were attached to the two opposite corners. This rather unusual lead configuration gives the same results as the more usual technique which consists in attaching the potential leads between the current leads. The potential drop was measured with a dc amplifier with a sensitivity of 10^{-9} V. The magnetic field was always parallel to the surface of the thin film. The transition field measurements were conducted from the transition temperature down to 14.15°K in liquid hydrogen and in this range the temperature was determined by the measurement of the hydrogen vapor pressure over the boiling liquid. From 14.15°K down, the measurements were performed in liquid helium; the temperature was raised above 4.2°K by a heater and the temperature was determined with a calibrated carbon thermometer. The lowest temperature of measurement is determined by the maximum magnetic field available to us, 105 kOe.

III. EXPERIMENTAL RESULTS

The dependence of the transition field on temperature for the various films ranging in thickness from 100 000 to 1000 Å is reported in Figs. 5 and 6 at a current density of 1/2 A/cm². Two films which were previously discussed by the authors[9] and measured at a current density of 2 A/cm² have been included with the data. The variation of the transition temperature with current density of two of the films is shown in Fig. 7. As is evident from Figs. 5 and 6, the various films have slightly different transition temperatures even when measured at the same current density. Figure 8 shows that the transition temperature is lower for the thinner films. As a matter of fact, films of the order of 1000 Å and below showed pinholes distributed over their entire surface. As films with different transition temperatures, would have a different H_0 (transition field at 0°K) regardless of the absence or presence of a size effect, it is necessary to normalize the films with respect to transition temperatures. This has been done in Fig. 9, in which the results are summarized by plotting the film thickness versus the slope of the transition field dependence on temperature. Two sets of points are shown in Fig. 9: the first set corresponds to dH/dT measured over a 1°K interval below the transition temperature; the second set is the average slope of Fig. 5 and 6 taken over the entire temperature range from T_c to the temperature corresponding to a transition field of 105 kG.

IV. DISCUSSION OF THE RESULTS

In order to study the possibility of a size dependence in thin films of hard superconductors, two requirements must be met. First, the transition field measurements must be made at extremely low current densities, where the transition field is more or less independent of the mechanical state of the material. Indeed, Hauser and Buehler[10] have shown that at the higher current densities, i.e., in the plateau region of the critical current versus magnetic field curve, the transition field depends on the current carrying capacity of the sample which in turn is determined by the mechanical state of the material. Conceivably, thin films of different thickness could be strained by different amounts and consequently, have a different number of filaments and thereby a different current-carrying capacity. For this reason all the films were tested at a low current density of 1/2

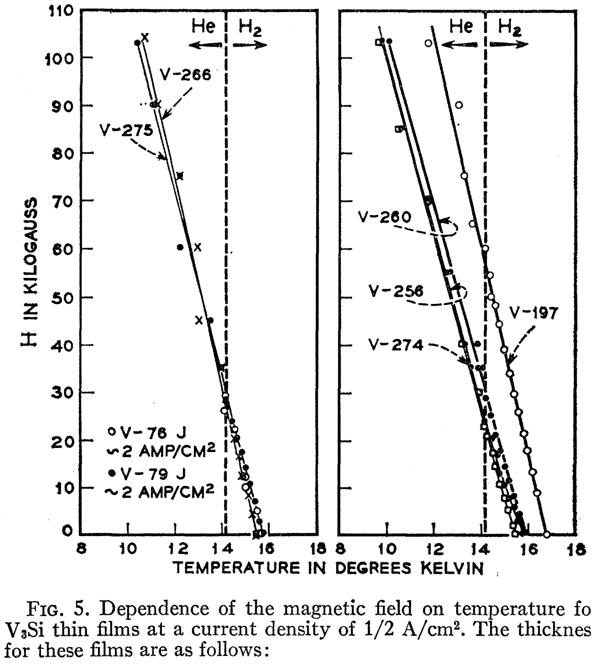

FIG. 5. Dependence of the magnetic field on temperature for V_3Si thin films at a current density of 1/2 A/cm². The thickness for these films are as follows:

v-266	8840 Å	v-260	1.41×10⁻⁴ cm
v-275	2350 Å	v-256	1.12×10⁻³ cm
v-76	9150 Å	v-274	1880 Å
v-79	2320 Å	v-197	7.1×10⁻⁴ cm

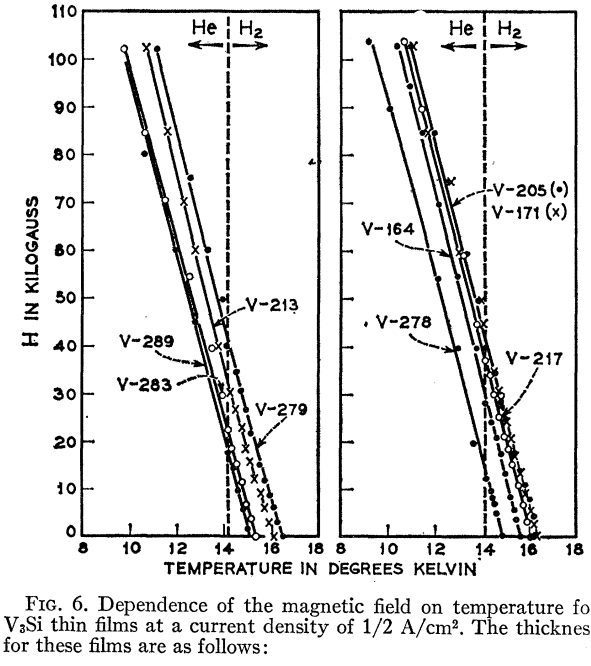

FIG. 6. Dependence of the magnetic field on temperature for V_3Si thin films at a current density of 1/2 A/cm². The thickness for these films are as follows:

v-289	1410 Å	v-164	5840 Å
v-283	2070 Å	v-278	1115 Å
v-213	7900 Å	v-205	4.83×10⁻⁴ cm
v-279	1.11×10⁻³ cm	v-171	1.12×10⁻³ cm
		v-217	1.22×10⁻⁴ cm

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[9] J. J. Hauser and H. C. Theuerer, Bull. Am. Phys. Soc. 7, 189 (1962).

[10] J. J. Hauser and E. Buehler, Phys. Rev. 125, 142 (1962).

A/cm². Because the measured critical temperature depends on the current density as shown in Fig. 7, the films were measured at the same current density.

The second requirement is to compare the transition fields of the various films close to the transition temperature. The justification for this requirement follows from the fact that it has been observed experimentally and justified theoretically[11] that

$$[\lambda(T)/\lambda(0)]^2=1/[1-(T/T_c)^4]. \tag{4}$$

Consequently, close to the transition temperature, the penetration depth gets very large and therefore as evidenced by relation (1) or (2), this will be the region in which a size effect will be most predominant.

It is evident from Fig. 9 that there is no dependence of dH/dT on the thickness of the films in the range investigated. The average dH/dT is 19.1 kG/°K and although the scatter is moderate, the largest dH/dT is exhibited by a thick film (72 000 Å) most probably representative of bulk. Taking a penetration depth of 1000 Å, a film 1000 Å thick should have a critical field 3.4 times as large as the bulk according to relation (1). In other words, if the bulk V_3Si as exemplified by films about 100 000 Å thick has a transition field of about 19.1 kG 1°K below T_c, a thin film 1000 Å thick should have at the same temperature a transition field of approximately 65 kG. The data presented in Fig. 9 shows that this is impossible as the highest transition field reported is 22.5 kG. The absence of a size effect in a film 1115 Å thick measured 1°K below T_c would require a penetration depth of 322 Å according to relation

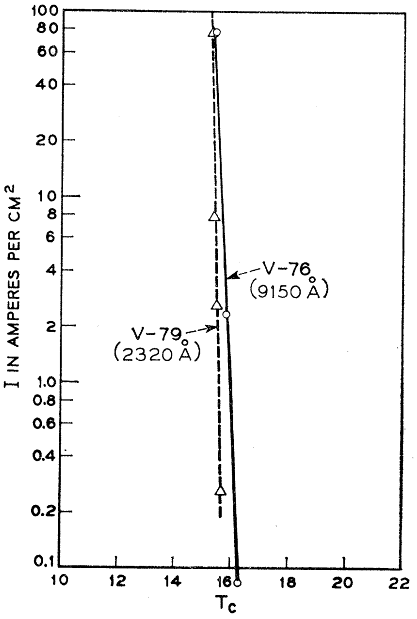

FIG. 7. Change in critical temperature with current density.

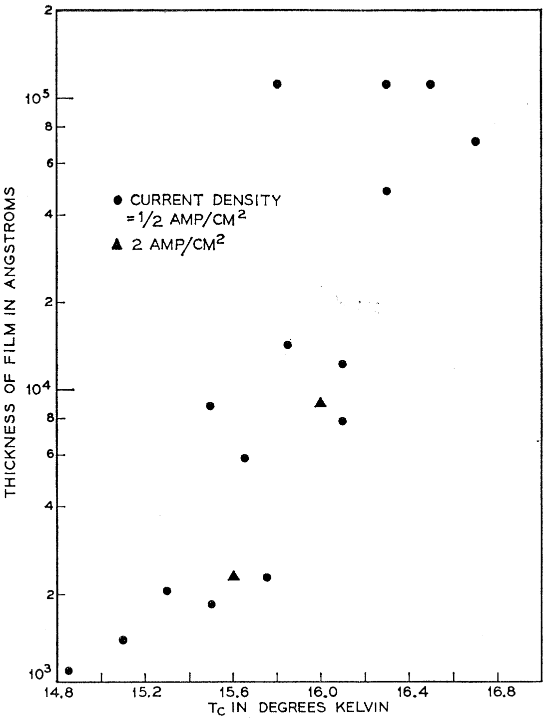

FIG. 8. Change in critical temperature with film thickness.

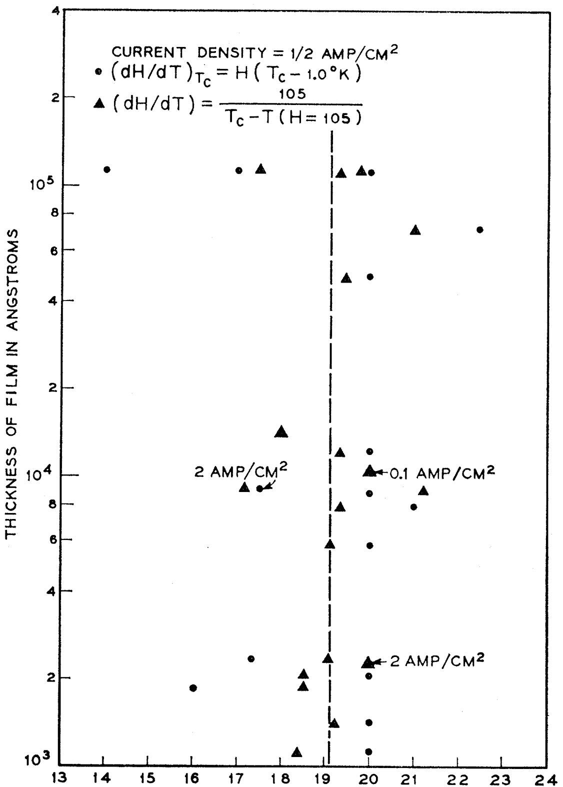

FIG. 9. Summary of the results: dH/dT as a function of thickness.

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[11] D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1960).

(1). This value is much too low for the temperature considered. Actually, it has been suggested by NMR (nuclear magnetic resonance) experiments[12] that the penetration depth in V_3X compounds may be at least an order of magnitude larger than the usually measured values of a few hundred angstroms. This would then make the previous estimate very conservative. This absence of size effect is consistent with the filamentary theory[3,5] which explains the high transition field of hard superconductors in terms of filaments about a few 100 Å in diameter. In such superconductors no size effect is to be expected, unless the size of the film is reduced below that of the filaments.

The average transition temperature of the films reported in Fig. 8 is approximately 15.7°K. For such a film with a transition temperature of 15.7°K the data obtained 1°K below T_c in Fig. 9 correspond to a reduced temperature of $t=0.94$. Even for a very small penetration depth of 500 Å at 0°K, relation (4) predicts for $\lambda(t=0.94)=1070$ Å. Actually Fig. 9 shows that the amount of scatter is slightly greater for the data obtained at 1°K below T_c than for that obtained using the entire curves of Figs. 5 and 6. The explanation for this difference lies in the fact that certain magnetic field versus critical temperature curves display for unknown reasons some curvature in a region close to T_c.

The variation of transition temperature with thickness as shown in Fig. 8 may be thought at first to be caused by an impurity effect in the substrate. However, the same transition temperature was obtained for the same size films on different substrates such as MgO, sapphire, graphitic carbon on MgO and it would be quite coincidental if the same impurity were found in the same amount in all these substrates. The possibility of a gaseous impurity such as oxygen in the reducing atmosphere or in the ambient atmosphere after deposition of the film cannot be ruled out as a plausible explanation for this effect. This does not seem, however, to be the right explanation as some films were annealed in fairly dirty atmospheres without an appreciable effect on the transition temperature. In view of the pinholes which were observed in the very thin films, it seems that at the high temperature of deposition where the films are fairly plastic, the surface energy of the material will tend to promote "balling up" of the film. Consequently, along with the pinholes many areas will be left with a layer much thinner than the average and the very high current density which occurs there will depress the transition temperature. Such an effect could not overcome the expected increase in transition field because, as shown in Fig. 8, films with extremal thickness were compared with a transition temperature very close to 15.6°K.

Although the silver paste technique for fastening leads to a thin film is very satisfactory for a zero current transition field measurement, it is not reliable for determining the current-carrying capacity of such films, because of the very high Ohmic resistance of the contacts. In other words, instead of measuring the true critical current of the film, the measurement is affected by the Joule heating from the leads. In one instance, a current-carrying capacity as high as 20 000 A/cm^2 in zero magnetic field was measured in an 8000 Å film. This is of the same order of magnitude, although lower than the current densities obtained in bulk specimens by Wernick.[13] This estimate of 20 000 A/cm^2 should be taken as a lower limit of the true critical current density of V_3Si, but it is high enough to show that the current densities of 0.5–2 A/cm^2 used in this investigation were in the zero current region.

V. CONCLUSIONS

Films of V_3Si ranging in thickness from 100 000 Å down to 1000 Å were found to possess the same transition field. At 1°K below T_c where a penetration depth of 1000 Å is not unreasonable, a thin film of V_3Si 1000 Å thick should have a critical field 3 times as large as the bulk critical field if it behaved as a soft superconductor. The absence of such a size effect can be taken as evidence of the filamentary structure of hard superconductors. Furthermore, if one could obtain very thin films of hard superconductors, thinner than the filaments, the point at which a size effect appears could then be used to get an experimental estimate of the size of the filaments.

ACKNOWLEDGMENTS

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[12] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y, Yafet, Phys. Rev. Letters 9, 262 (1962).

[13] J. H. Wernick, Proceedings of the AIME Meeting on Superconductivity, New York, 1962 (unpublished).