Size Effects in Thin Films of V_3Ge, Nb, and Ta

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An enhancement of the critical field of V_3Ge, Nb, and Ta has been achieved by reducing the effective coherence length of these materials. This change in the coherence length was obtained in Nb and Ta by changing the grain size and therefore, the mean free path of the bulk material. Such a study yields also an experimental estimate of the coherence length of the bulk material which is in fair agreement with theoretical calculations. Thin films of V_3Ge, Nb, and Ta have been obtained in thicknesses ranging from 200 000 to 100 Å. The V_3Ge films were produced by the hydrogen reduction of the mixed chlorides and by a new method called getter sputtering. The Nb and Ta films were sputtered. In all cases, MgO wafers were used as substrates. The critical temperatures of the films were approximately that of the bulk, although the thinner films always displayed slightly lower critical temperatures. The transition field of the films, measured by a resistance technique, was found to increase as the thickness of the films decreased. In conjunction with the transition field increase, a corresponding increase in the residual resistivity was observed, which implies a reduction in the mean free path. The departure of the transition magnetic field from the bulk value occurred at such large thicknesses (a few 10 000 Å) that such a size effect cannot be explained in terms of the film thickness becoming comparable with the coherence length. This effect can be interpreted in terms of the very small grain size produced by sputtering films which, in turn, leads to a mean free path well below 100 Å. The presence of a sufficiently small grain size provides a means to produce negative surface energy superconductors with decreasing mean free path and consequently increasing κ (the Ginzburg-Landau parameter), without the addition of alloying elements.

I. INTRODUCTION

ONE purpose in studying thin films of hard superconductors is to get an estimate of the coherence length; i.e., the size of the flux vortices responsible for hard superconductivity. As was discussed in a previous paper,[1] while soft superconductors have a critical field which increases when the thickness of the film is decreased below the penetration depth, hard superconductors display a critical field independent of the film thickness, even for films thinner than the penetration depth. In that previous investigation,[1] it was assumed that the high critical field of hard superconductors was caused by the existence of filaments small in size compared with the penetration depth, as postulated by Mendlessohn[2] and Gorter.[3] Consequently, assuming that the radius of the filaments would be of the order of the coherence length, one would not expect size effects, at least as long as the film thickness remains greater than the coherence length. Indeed, the critical field in V_3Si films remained independent of film thickness for films ranging in thickness from 100 000 to 1100 Å. It was therefore concluded from such experiments that the coherence length or the size of the filaments in V_3Si was smaller than 1100 Å. However, in view of the recent calculations of Goodman[4] on a similar material, V_3Ga estimating a coherence length of the order of 50 Å, the previous results are no longer surprising. It therefore became desirable to obtain thinner films and to investigate other materials with a greater coherence length in order to satisfy the criterion for size effect in hard superconductors. The dependence of the critical field of hard superconductors on film thickness has been studied in terms of the negative surface-energy theory by Abrikosov.[5] Although the conclusions of the filamentary model are in qualitative agreement with those of the negative surface energy theory, it has now been recognized that the negative surface is the fundamental cause of high-field superconductivity. As, furthermore, the negative surface energy theory permits a more quantitative treatment of the size effect, it will therefore be used to interpret the data.

II. EXPERIMENTAL PROCEDURE

The preparation of the V_3Ge films by the reduction of the mixed chlorides was identical to the method used in the preparation of the V_3Si films, and has been fully described elsewhere.[1] The getter-sputtering technique was used to obtain the Nb, Ta films and some of the V_3Ge films. This new technique uses the gettering action of part of the sputtered atoms to get an atmosphere very low in the type of interstitials (O_2, N_2, $\cdots$) which are detrimental to superconducting films. This new method will be extensively described in another paper.[6] The substrates used in all experiments were MgO single crystals with a (100) cleaved surface.

The transition fields of the films were obtained using a resistance measuring equipment sensitive to 10^{-9} V. The accuracy in determining temperatures higher than 4.2°K is not greater than ± 0.1°K. In the early experiments the current and potential leads were fine copper wires which were attached to the films with the help of air drying silver paste. Although this technique is entirely satisfactory for the determination of the upper critical field (H_{c_2}) in the limit of zero current ($\simeq$2

[1] J. J. Hauser and H. C. Theuerer, Phys. Rev. **129**, 103 (1963).
[2] K. Mendlessohn, Proc. Roy. Soc. (London) **A152**, 34 (1935).
[3] C. J. Gorter, Physica **2**, 449 (1935).
[4] B. B. Goodman, Phys. Letters **1**, 215 (1962).
[5] A. A. Abrikosov, Dokl. Akad. Nauk SSSR **86**, 489 (1952).
[6] H. C. Theuerer and J. J. Hauser (to be published).

A/cm²), it is not suited for the evaluation of the critical current carrying capacity of the material. The contact resistance of the silver paste is too high and leads to high Joule's heating which reduces considerably the critical current of the material. The copper leads are now attached to the film by ultrasonic soldering with indium solder. This technique may be used for films as thin as 100 Å, and the contact resistance is low enough so that the current carrying capacity of the material may be evaluated.

The composition of the V_3Ge films was established as in the case of the V_3Si films[1] by x-ray fluorescence analysis. One of the 100-Å V_3Ge films was successfully stripped from its substrate, and the grain size was established by electron transmission microscopy. The grain size in the other films was estimated by an electron reflection technique. In certain cases, the grain size estimated by electron reflection was checked by taking replicas of the films.

The thickness of the films was evaluated with the help

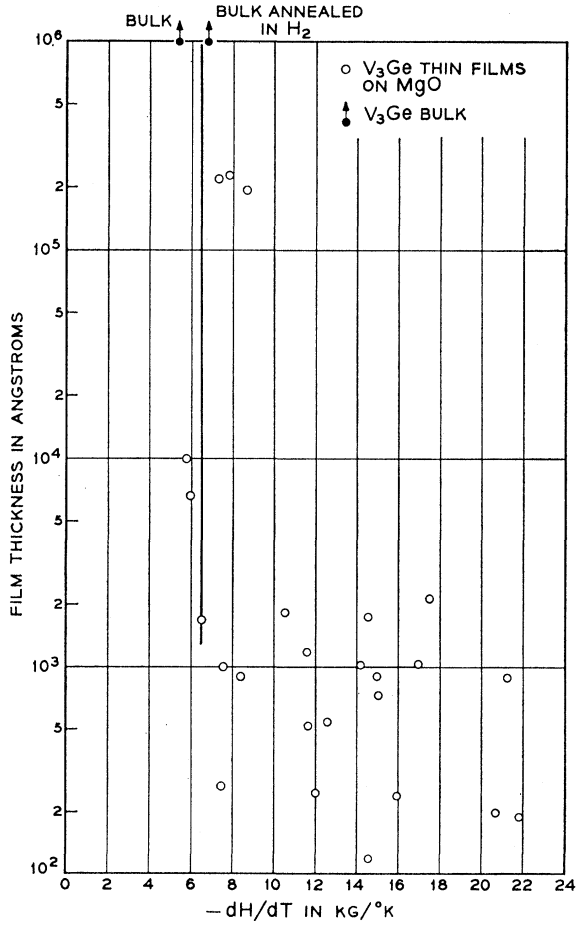

FIG. 1. Slope of the critical field versus temperature curve for V_3Ge films obtained by chloride reduction as a function of film thickness. (The slope was obtained over a range of at least 17.4 kG where the temperature dependence of the critical field is approximately linear.)

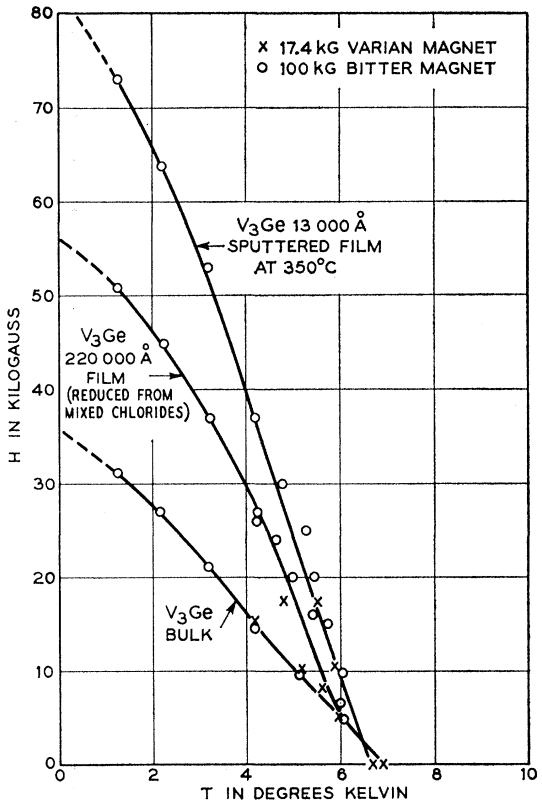

FIG. 2. Critical field as a function of temperature for bulk V_3Ge, for a 220 000-Å chloride reduced film and for a 13 000-Å sputtered film.

of three different techniques depending on the order of magnitude of the film thickness. For thick films, the weight gain is measured by weighing the MgO substrate before and after deposition. From the weight gain and the density of the material, one obtains the film thickness. Such measurements enable one to check that film thickness is a linear function of time deposition. Such a relationship can be used with good accuracy for films thinner than 1000 Å. When films are thinner than 1000 Å, they become translucent, so that one can get correlative film thickness measurements from a linear plot of the logarithm of the percentage transmission measured by a photometer as a function of film thickness.

III. EXPERIMENTAL RESULTS

The dependence of the transition fields of the films on temperature was usually measured up to 17.4 kG. The slopes of these curves which were approximately linear up to this field, are shown in Fig. 1 for V_3Ge films deposited by chloride reduction. In some cases, the critical field was measured from T_c to 1.3°K as shown in Fig. 2 in order to display most of the critical field versus temperature curve. As the films may contain some dissolved hydrogen, a piece of bulk V_3Ge was heat-treated

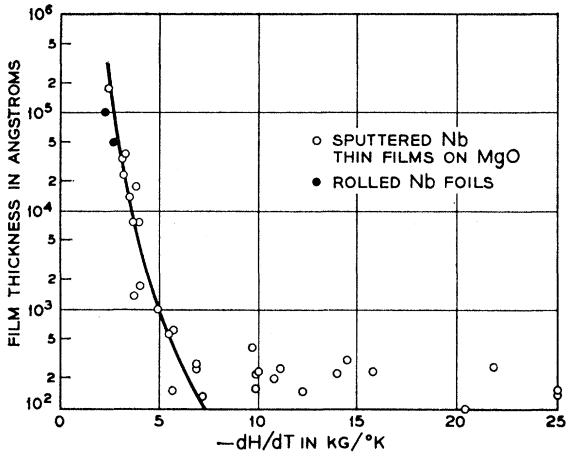

FIG. 3. Slope of the critical field versus temperature curve for sputtered Nb films as a function of film thickness. (The slope was obtained as in Fig. 1.)

in hydrogen and, as shown in Fig. 1, its critical field is not altered very much by the heat treatment. The temperature dependence of the critical field of bulk V_3Ge is shown in Fig. 2, and the slope of this curve is in good agreement with the measurements of Wernick, Hsu, and Kunzler.[7] It is interesting to notice that the bulk curve shown in Fig. 2 is approximately linear. Small pieces of the 120-Å-thick film of V_3Ge were stripped from the MgO substrate. An electron transmission study of these pieces revealed that the material had the β-tungsten structure (A-15) and the grain size was approximately 500 Å. The transition temperature of the films varied between 7°K for the very thick ones and 5.9°K for the 120-Å film. This degradation of the transition temperature with film thickness was also observed in the V_3Si films.[1] The transition temperature for bulk V_3Ge is reported to be 6.01°K.[8] On the other hand, Morin[9] reported 6.1°K as deduced from specific-heat measurements, Wernick *et al.*[7] found 6.5°K resistively and as shown in Fig. 2, 6.95°K was measured resistively in the present investigation. Consequently, the range of critical temperatures of the thin films is close to the spread in critical temperatures of the bulk. It is interesting to point out that a 95-Å film had a transition temperature of 4.6°K, a 45-Å film was not superconducting down to 1.4°K, and a 20-Å film was not conducting. This indicates that the 20-Å film consists of isolated islands, and as the 45-Å film was conducting, the surface roughness of the films is somewhere between 20 and 45 Å.

The sputtered V_3Ge films gave essentially the same kind of data as shown in Fig. 1 for the chloride reduced films. In order to get the superconducting compound V_3Ge, it was found necessary to heat the substrate while sputtering at approximately 1000°C, which is the same temperature as was used for the chemical reduction of the films from the mixed chlorides. The only difference exhibited by sputtered films as compared to chloride reduced films, is that the region of scatter in critical field, which exists up to 2000 Å (see Fig. 1) for the chloride reduced films, persists at higher thicknesses in sputtered films.

The slope of the critical field versus temperature curve of Nb films as a function of thickness is shown in Fig. 3. The data are somewhat similar to that obtained for V_3Ge except that the scatter occurs only up to 400 Å and that a size effect exists at larger thicknesses up to 200 000 Å. A piece of bulk Nb has a $|dH/dT|$ of 1.6 kG/°K. The films described in Fig. 3 were sputtered at approximately 350°C. This is the minimum sputtering temperature without the use of a coolant, as this temperature is created by the power dissipation of the sputtering process. Under these conditions, as shown in Fig. 3, a film 1930 Å thick, has a $|dH/dT|$ of 4.1 kG/°K. A film 1780 Å thick, sputtered at 1000°C has a dH/dT of 1.6 kG/°K and a film 1140 Å thick sputtered at 1000°C has a $|dH/dT|$ of 2.1 kG/°K. Consequently, for fairly constant film thickness and critical temperature $|dH/dT|$ increases with decreasing sputtering temperature. The transition temperatures for the films described in Fig. 3 spread from 10°K for the thicker films to 9°K for the 100-Å film. A 75-Å film of Nb had a transition temperature of 8.1°K and a 50-Å film was not superconducting down to 1.4°K.

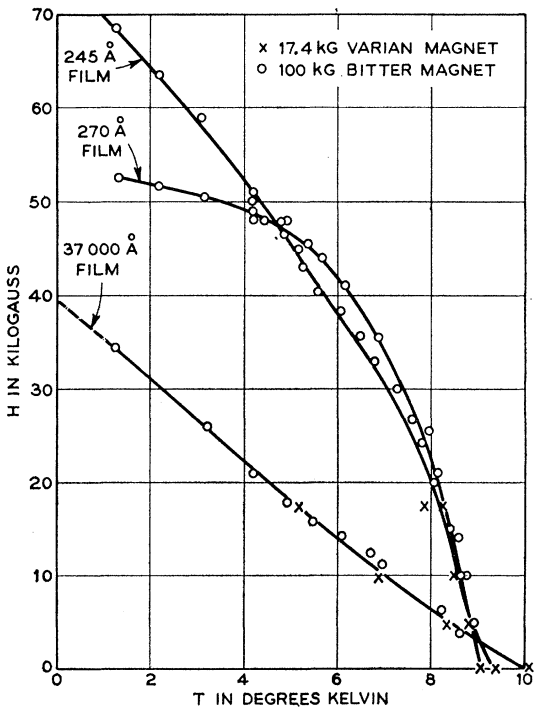

FIG. 4. Critical field as a function of temperature for three sputtered Nb films, respectively, 37 000, 270, and 245 Å thick.

[7] J. H. Wernick, F. S. L. Hsu, and J. E. Kunzler (unpublished).
[8] B. W. Roberts, G. E. Report No. 63-RL-3252M, 1963 (unpublished).
[9] F. J. Morin and J. P. Maita, Phys. Rev. **129**, 1115 (1963).

Some of the Nb films were studied up to higher fields and lower temperatures in a 100-kG solenoidal Bitter magnet, and the results are shown in Fig. 4.

The resistivity at room temperature and 12°K is plotted as a function of film thickness in Fig. 5. The room temperature resistivity is relatively independent of film thickness. The residual resistivity at 12°K on the other hand, increases by a factor of 7 as the film thickness decreases from bulk to 100 Å.

An electron diffraction taken on a Nb film 120 Å thick is shown in Fig. 6. The diffuseness of the pattern and the lack of sharp rings indicate that the grain size is very small, of the order of 20–40 Å. One can notice on this pattern nine wide dots which correspond to the (110) diffraction pattern of Nb. This in turn means that the small Nb grains have a preferred orientation with respect to the MgO substrate. Figure 7 shows an electron diffraction pattern taken on a 37 000-Å Nb film. The grain size is now larger than in the thin film as indicated by the presence of rings, but the rings are not yet very sharp, which means that the grain size is not very much larger than 100 Å. Furthermore, although the strong orientation relationship of Fig. 6 has been reduced, there is still a large amount of preferred orientation with respect to the MgO substrate as indicated by the regions of strong intensity on the diffraction rings.

The experiments on Ta are still of a preliminary nature and will be pursued further at various sputtering temperatures. Bulk tantalum has a transition temperature of 4.4°K and a critical field at 0°K of approximately 1 kG. The following three films have been sputtered so far at 350°C: a 9850-Å film with $T_c=4.15$°K and $|dH/dT|=2.8$ kG/°K, a 1640-Å film with $T_c=4.0$°K and $|dH/dT|=3.7$ kG/°K, and a 300-Å film with $T_c=3.16$°K and $|dH/dT|=13.6$ kG/°K. The dependence of the critical field of the last mentioned film on temperature is shown in Fig. 8. An electron diffraction pattern taken on the 300-Å film revealed again a very small grain size of the order of 30–40 Å.

IV. DISCUSSION OF THE RESULTS

It was already pointed out in the Introduction that, based on a filamentary model, one does not expect a size effect in films of negative surface energy superconductors (also referred to as type II superconductors) until the film thickness is reduced below the coherence distance. It would be helpful at this time to distinguish between three types of coherence distances which are sometimes confused in the literature. The first coherence length as defined by the BCS theory ξ_0, is the distance over which two electrons remain correlated. For impure materials, in which the mean free path l is shorter than ξ_0, one is lead to the concept of an effective coherence distance[10]

$$\xi_{\text{eff}}=(\xi_0 l)^{1/2}. \tag{1}$$

In a study of the dependence of the critical field of superconductors of the second kind on thickness, Abrikosov[5] solved the Ginzburg-Landau equations in the two limits: (1) very thick films and (2) very thin films. In the limit of very thick films, Abrikosov found that

$$H_c=\sqrt{2}\kappa H_{cb}+4\left(\frac{2}{\pi}\right)^{1/2}\kappa^2 H_{cb}\frac{d}{\delta(t)}e^{-[\kappa d/\delta(t)]^2}, \tag{2}$$

where $\delta(t)=\delta_L(t)(\xi_0/l)^{1/2}$ and where H_c is the critical field of a film of thickness $2d$ and H_{cb} is the bulk thermodynamic critical field. For very thick films, one can neglect the second term in Eq. (2) and one finds

$$H_c=H_{c_2}=\sqrt{2}\kappa H_{cb}, \tag{2a}$$

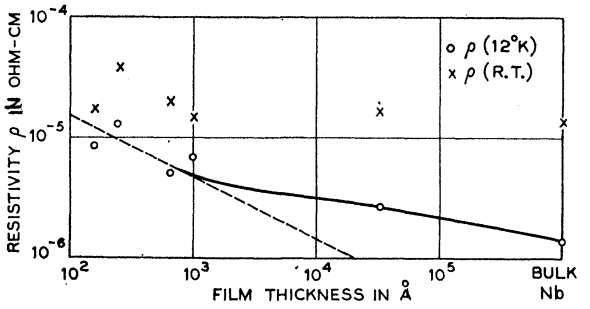

FIG. 5. Resistivity at 300 and 12°K as a function of film thickness.

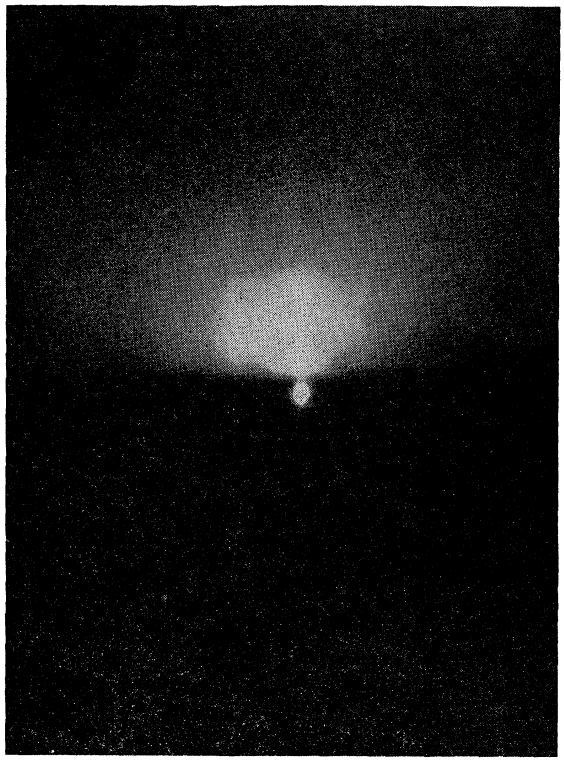

FIG. 6. Electron diffraction of a 120 Å film of Nb.

[10] C. Caroli, P. G. DeGennes, and J. Matricon, Phys. Kondens. Materie 1, 176 (1963).

FIG. 7. Electron diffraction of a 37 000-Å film of Nb.

where H_{c_2} is the upper critical field for a superconductor with $\kappa\sqrt{2}>1$, which arises from negative surface energy.

In the limit of very thin films, Abrikosov found

$$H_c/H_{cb}=(6)^{1/2}\delta(t)/d, \tag{3}$$

which is the well-known high-field expression for the critical field of thin films of soft superconductors. It is important to notice that it is $\delta(t)$, the temperature-dependent penetration depth, which appears in (3) and which is the scaling factor of the dimensionless Ginzburg-Landau theory. Comparison of relations (2) and (3) show that films of superconductors of type II will have a size-independent critical field given by relation (2) until the size effect of the film treated as a homogeneous superconductor [relation (3)] yields a greater critical field. A numerical solution of the Ginzburg-Landau equations for films of intermediate thicknesses shows that the transition between the two behaviors will occur for T close to T_c when

$$d\cong 2.25\delta(t)/\kappa \tag{4}$$

or when the film thickness is

$$\sim 4.5\delta(t)/\kappa. \tag{4a}$$

If one uses the Gor'kov relation $\kappa\simeq\delta_L(0)/l$ and the empirical relation $\delta(t)=\delta(0)(1-t^4)^{-1/2}$, the critical film thickness for a size dependent critical field is:

$$2d_{\rm cr}=\frac{4.5l}{(1-t^4)^{1/2}}\left(\frac{\xi_0}{l}\right)^{1/2}=\frac{4.5}{(1-t^4)^{1/2}}\xi_{\rm eff}. \tag{5}$$

On the other hand, in establishing the magnetic properties of type II superconductors, Abrikosov[11] has shown that once the penetration field H_{c_1} was exceeded, the material was permeated by flux vortices in a square lattice with period $(2\pi)^{1/2}\delta(T)/\kappa$, which is also the distance between two flux vortices.

Comparing the distance between vortices to relation (4a), one comes to the conclusion that a size effect begins in type II superconducting thin films when the thickness of the film becomes smaller than the distance between vortices. At this point, the material cannot break up into a mixed state, and it is energetically more favorable for the film to behave homogeneously. It is apparent from relation (5) that when $T=T_c$, $2d_{\rm cr}$ becomes infinite. This can be explained if one defines a third coherence length $\xi(t)=\delta(t)/\kappa$ and then substitutes in relation (4a); then, $2d_{\rm cr}=4.5\xi(t)$. From the Gor'kov[12] treatment of the Ginzburg-Landau equations, $\xi(t)$ is the length characterizing the spatial variation

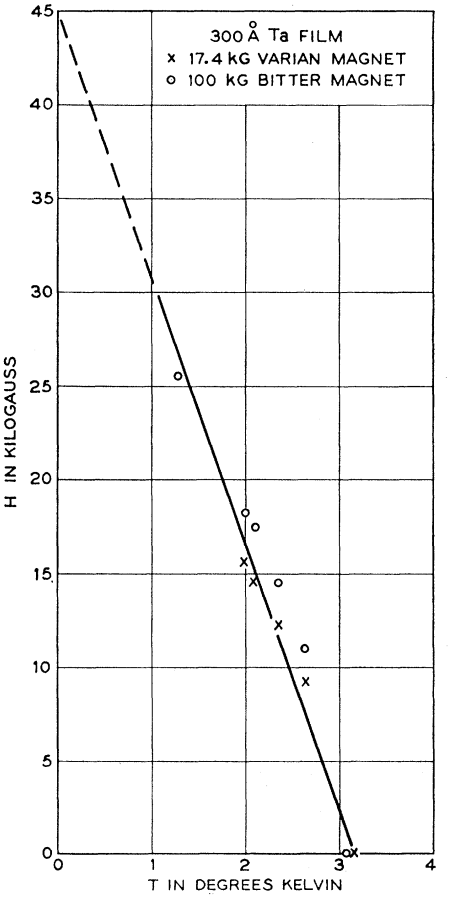

FIG. 8. Critical field as a function of temperature for a 300-Å Ta film.

[11] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **32**, 1442 (1957) [English transl.: Soviet Phys.—JETP **5**, 1174 (1957)].

[12] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **36**, 1918 (1959); **37**, 1407 (1959) [English transls.: Soviet Phys.—JETP **9**, 1364 (1959); **10**, 998 (1960)].

of the energy gap, which certainly becomes infinite at $T=T_c$.

One can now interpret the data in terms of Eq. (5). In the case of the V_3Si thin films,[1] the thinnest film then investigated was 1100 Å, and the highest reliable reduced temperature of measurement was $t=0.94$. Relation (5) then becomes $2d_{cr}=9.5\xi_{eff}$. Using a calculation similar to that used by Goodman[4] on V_3Ga, one finds $\xi_0=50$ Å for V_3Si [this value was obtained from the relation $\xi_0=a\pi kS/3h^2T_c\gamma$ where S is the surface area of the Fermi surface and γ is the coefficient of electronic specific heat per unit volume, assuming that S is the same for V_3Si and V_3Ga and the change in ξ_0 comes predominantly from T_c and γ]. If one assumes that $l>\xi_0$, then ξ_{eff} should be replaced by ξ_0 and $2d_{cr}\simeq 480$ Å and consequently it is not surprising that no size effect was found in Ref. 1 even for films as thin as 1100 Å.

V_3Ge, on the other hand, has a coherence length $\xi_0\simeq 400$ Å. As $H_c=H_0(1-t^2)$ Eq. (2a) can be written as

$$(dH_{c_2}/dt)_{t=1}=-\sqrt{2}\kappa 2H_0. \quad (6)$$

Using the bulk data for H_{c_2} shown in Fig. 2 and $H_0=\gamma T_c^2/0.170$, where γ was obtained from Morin and Maita,[9] one finds $H_0=1.430$ kG and $\kappa=9.4$. As one can see from Fig. 2, the dependence of H_{c_2} on temperature does not have the negative curvature predicted by Shapoval[13]; instead, the dependence is intermediate between a straight line and a parabola and can be best described by the Gor'kov[14] relation:

$$H_{c_2}=H_c[1.77-0.43(T/T_c)^2+0.07(T/T_c)^4]\kappa, \quad (7)$$

which reduces to relation (2a) at $T=T_c$. Assuming that $\delta_L(0)$ can be at most equal to 1000 Å, $l=\delta_L(0)/\kappa\simeq 100$ Å which in turn, by relation (1) means that $\xi_{eff}\simeq 200$ Å. Consequently, it is not the grain size which limits the mean free path in a bulk specimen. The highest reduced temperature at which a reliable estimate of the slope at T_c can be obtained is 0.9, and from relation (5) one obtains $2d_{cr}\simeq 1520$ Å. In other words, one may expect a size effect in the initial portion of the H versus T curve for films thinner than 1520 Å. Actually, it is evident from Fig. 2 that some size effect exists at 220 000 Å and a large size effect exists at 13 000 Å and below. As the grain size in these films is of the order of 500 Å, which is much larger than the bulk mean free path, the enhancement in critical field cannot be explained in terms of a grain size effect. Furthermore, one notices in Fig. 1, below 2000 Å, a large amount of scatter. Some of the scatter is experimental in nature as the high slopes were determined in the Varian magnet over a temperature interval of only 1.1°K. As each point is measured with an accuracy of ±0.1°K, this could lead to an error of 20% in the slope. On the other hand, the initial slope of an H versus T curve shows very often a strange behavior not characteristic of the curve as a whole. The source of the scatter could also be physical in nature: microsegregation on a very fine scale which could vary from sample to sample and would not affect thick films which are necessarily annealed for long times at high temperature. We have also observed a varying degree of preferred orientation in various films, and the resulting strain setup between V_3Ge and the MgO substrate may possibly shorten the mean free path and therefore enhance the critical field. Consequently, it is really incorrect to plot the critical field as a function of film thickness as the film thickness is not the determining the parameter. Increasing the film thickness increases concomitantly the annealing time at 1000°C which may alter such controlling parameters as the degree of preferred orientation or the scale of microsegregation which, in turn, will affect the mean free path. As no size effect, as predicted by relation (5), was observed, it is possible to conclude experimentally that ξ_{eff} in the bulk material is smaller than 200 Å.

Because of the many variables complicating the interpretation of V_3Ge, it is advantageous to study thin films of elemental type II superconductors. The data for Nb shown in Figs. 3 and 4 show again a size effect occurring at very large thicknesses. At $T=0$°K, relation (7) becomes $H_{c_2}=1.77H_c\kappa$ and as relation (2a) must be replaced by this new value, relation (5) will be replaced at $T=0$°K by

$$2d_{cr}=3.3\xi_{eff}. \quad (5a)$$

As mentioned before, a piece of bulk Nb has $|dH/dT|=1.6$ kG/°K and as $H_0=2$ kG, using relation (6) one finds $\kappa=2.65$. Choosing $\delta_L(0)$ to be equal to 500 Å, it follows that $l=190$ Å. As Stromberg and Swenson[15] found that κ_0 in pure Nb was about 1, $\xi_0=\delta_L(0)=500$ Å. Actually, Stromberg and Swenson calculated $\xi_0=\delta_L(0)=250$ Å but the value chosen here seems to better fit the data obtained in this investigation. Using relation (1) with $\xi_0=500$ Å and $l=190$ Å, ξ_{eff} in the bulk material is 310 Å. Consequently, $2d_{cr}\simeq 1000$ Å and as the size effect occurs at thicknesses very much larger than 1000 Å, it must be caused by something other than the film thickness. As from electron diffraction, the grain size in the thinnest films appears to be about 30 Å, the mean free path is therefore about 30 Å. This would mean that there is a change of about a factor of 6 in the residual resistivity from bulk to the thinnest film and this is borne out by the data shown in Fig. 5. Furthermore, as $l=30$ Å in the thinnest film, $\xi_{eff}\simeq 125$ Å and $\kappa\simeq 17$, which yields a zero degree critical field of 60 kG which is again in fair agreement with the data shown in Fig. 4. Consequently, the film thickness represents the wrong parameter, and the proper parameter is the grain size which is related to it. A thicker film only represents

[13] E. A. Shapoval, Zh. Eksperim. i Teor. Fiz. **41**, 877 (1961) [English transl.: Soviet Phys.—JETP **14**, 628 (1962)].

[14] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **37**, 833 (1959) [English transl.: Soviet Phys.—JETP **10**, 593 (1960)].

[15] T. F. Stromberg and C. A. Swenson, Phys. Rev. Letters **9**, 370 (1962).

material which has been annealed at the deposition temperature for a longer time. If one therefore assumes that grain growth occurs by diffusion, the grain size is proportional to (time)$^{1/2}$ and as the film thickness is proportional to time (under the present experimental conditions), and the residual resistivity is inversely proportional to grain size, the logarithm of the residual resistivity should be a linear function of the logarithm of the film thickness with slope $-\frac{1}{2}$. This behavior is shown by the dashed line in Fig. 5. The departure from this line in thick films is due to the fact that as the grain size increases the residual resistivity cannot decrease below that of bulk. As shown in Fig. 3, a film 2000 Å thick has a $|dH/dT|$ of 4.1 kG/°K when sputtered at 350°C. A film of the same thickness, which was sputtered at 1000°C and where the sharp electron diffraction rings indicate a grain size larger than 100 Å, has the $|dH/dT|$ of 1.6 kG/°K of bulk material. On the other hand, an 1100-Å film sputtered at 1000°C has a $|dH/dT|=2.1$ kG/°K, indicating that the grain size dependence on film thickness is still present at 1000°C.

We have used in the preceding analysis values of H_0 and $\delta_L(0)$ characteristic of the pure material, although the enhancement in critical field could be attributed to contamination. However, in the case of V_3Si films[1] where similar techniques were used and where no size effect is expected because of the small bulk coherence length, no effect was observed. In the case of Nb, when the temperature of deposition was high enough to permit grain growth, the same transition temperature and critical field was obtained in the thin films as in bulk material. If any contamination, from the substrate for example, were present, it would be expected to be most severe at the high temperatures of deposition. On the other hand, films of Nb and V_3Ge thinner than 100 Å showed a very low transition temperature and it is conceivable that such films could have been contaminated by the substrate or by exposure to air. However, it is well established that thin films grow from isolated nuclei of crystallographic material and consequently, a critical thickness would be required to observe superconductivity by a resistance measurement. Such an explanation, is just as likely as contamination, and would fit in the general scheme developed to explain the critical field enhancement. Finally, as the grain size estimated from the electron diffraction is sufficient to account for the enhancement in critical field, it is felt that very little contamination if any is present and it is justified to use pure bulk parameters.

The scatter which occurs in Nb films below 400 Å can be explained in very much the same terms as were used for V_3Ge. Because of the error in measuring the temperature, there can be an error of 20% in a $|dH/dT|$ of 20 kG°K. Furthermore, as shown in Fig. 4, a higher initial slope can lead to a lower critical field at 1.3°K. The most probable sources of the scatter are the scatter in the grain size and possibly, the varying amount of preferred orientation found in these very thin films. The orientation relationship is such that the (110) Nb planes are parallel to the (200) MgO planes. Conceivably, as indicated by the wide spots in the electron diffraction pattern (Fig. 6), this mismatch leads to a distortion of the Nb lattice and the strains thus set up, may further enhance the critical field. This would also tend to explain why the scatter in V_3Ge is present at larger thicknesses than in Nb, as the preferred orientation persists in thicker films because of the higher deposition temperature.

As a means of comparison, two rolled Nb foils have been included in the data shown in Fig. 4. Their residual resistivity was comparable to that of films of similar thickness. Such an experiment further supports the grain size explanation proposed to explain the present experiments. In rolling bulk Nb, one certainly does not alter the degree of purity of the material, but the mean free path is reduced by the increasing amount of lattice defects such as dislocations. It is apparent from Fig. 4 that such a decrease in mean free path produces a similar enhancement in critical field as the one found in thin films.

The study of Ta films will be treated very briefly as the conclusions are similar to those reached before. The critical field of bulk Ta at 0°K is about 1 kG and in high purity material $\xi_0=900$ Å [based on $\delta_L(0)=500$ Å and $\kappa_0=0.6$ [16]]. Again the size effect occurs at very large thicknesses, as a 9850-Å film had a $|dH/dT|$ of 2.8 kG/°K as compared to 0.5 for bulk. The critical field dependence on temperature for a 300-Å film is shown in Fig. 8. Taking $|dH/dT|=13.6$ kG/°K implies that l in that film is 27 times smaller than ξ_0 in the bulk Ta used here. Consequently, the grain size in this film is of the order of 30 Å.

V. CONCLUSION

The lack of size depencence found previously in V_3Si thin films,[1] as thin as 1100 Å, indicates that the coherence distance in that material is smaller than 100 Å. This is in good agreement with the theoretical estimate of $\xi_0=50$ Å. In the case of V_3Ge, Nb, and Ta, a size-dependent critical field was found at thicknesses much larger than one would predict from the negative surface energy theory in terms of the effective coherence length in the bulk material. This effect can be explained by the very small grain size produced by sputtering which limits the mean free path. The effect is therefore larger, the larger the initial ξ_{eff} in the starting material. An enhancement in the 0°K critical field by factors of 2, 4, and 27 was found respectively in V_3Ge, Nb, and Ta, where the ξ_{eff} are respectively about 200, 310, and 900 Å. Such experiments also provide an upper limit for the coherence length in the bulk materials which are in good agreement with theoretical expectations. These experiments will be pursued by sputtering some of these materials at lower temperatures to further refine the

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grain size, and the magnetic properties of these films will be investigated as well as the electrical properties.

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Quantum Efficiency of Silicon in the Vacuum Ultraviolet*

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A measurement of the quantum efficiency of silicon has been carried out over the photon energy range from 4.9 to 21.2 eV by measuring the photoresponse of silicon surface-barrier photodiodes. The quantum efficiency increases from 2.0 at $h\nu=4.9$ eV to approximately 3 at $h\nu=6$ eV; between $h\nu=6$ eV and $h\nu\approx10$ eV, the quantum efficiency is approximately constant and beginning at $h\nu\approx10$ eV, increases strongly with increasing photon energy, attaining a value of 15 at 21.2 eV. This observed behavior is consistent with qualitative predictions based upon a model for secondary ionization effects in silicon proposed by Shockley and a simplifying assumption as to how the excess energy available following an ionization event is distributed between the original carrier and generated electron-hole pair.

1. INTRODUCTION

WHEN a high-energy photon is absorbed in the bulk of a semiconductor, the photoelectron and photohole produced by the inner photoelectric effect may be of sufficiently high energy to interact, in turn, with valence-band electrons leading to the generation of new electron-hole pairs. This intrinsic impact ionization was first observed in the breakdown of silicon[1,2] and germanium[1,3] p-n junctions. The quantum efficiency, $\eta(\lambda)$, of the inner photoelectric effect, defined as the number of electron-hole pairs produced as a result of the absorption of one photon of wavelength λ, has been studied in several semiconductors, including germanium,[4,5] silicon,[6,7] indium antimonide,[4] and lead sulfide.[8]

In the case of silicon, the quantum efficiency has been studied for two photon energy ranges: the very-high-energy range in which many generations are involved, and the low-energy range in which the photocarriers just begin to generate additional pairs. A measurement of the quantum efficiency of silicon in the low-energy range (1–5 eV) has been reported by Vavilov,[6] who found that η has a value of unity from 1.5 to 3.4 eV, and beginning at 3.4 eV, η increases rapidly with increasing photon energy to a value of 2.1 at 4.9 eV. Vavilov attributed this increase in η above unity to impact ionization by photoelectrons and photoholes and interpreted the difference between the energy at which η begins to increase (3.4 eV) and the bandgap energy (1.1 eV) as the threshold energy E' for impact ionization in silicon. Assuming that the electron takes all of the excess energy of the photon, Vavilov's photon threshold of 3.4 eV gives $E'=3.4-1.1=2.3$ eV. Shockley[9] has presented a reinterpretation of the energy, 2.3 eV, in which he suggests that when a photoelectron and photohole are created, the residual kinetic energy is shared equally between the two, rather than being given entirely to the electron. As a result, at Vavilov's photon threshold of 3.4 eV, each carrier ends up with an energy of about 1.15 eV, which is taken to be the true threshold energy for pair production.

A determination of η in silicon for the very-high-energy range (γ-ray energies) has been reported,[7] where η was found to be proportional to the energy of the absorbed photon. A mean energy of 3.5 eV was found to be required to produce one electron-hole pair, which is equal to the mean energy required to produce one ion pair by a high-energy charged particle[7] (electron, proton, alpha particle).

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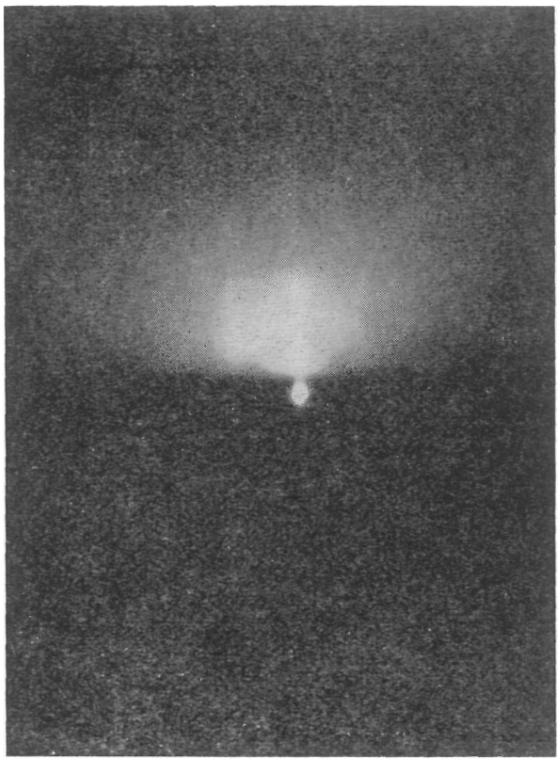

FIG. 6. Electron diffraction of a 120 Å film of Nb.

FIG. 7. Electron diffraction of a 37 000-Å film of Nb.