

## Effect of Plastic Deformation and Annealing Temperature on Superconducting Properties

J. J. HAUSER AND E. BUEHLER

*Bell Telephone Laboratories, Murray Hill, New Jersey*

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Single crystals and polycrystals of Nb and Re were deformed in tension at room temperature. The critical field was found in both cases to increase with deformation and in the case of Nb the increase was as large as 150%. The change in critical field is related to the increase in plastic deformation. Annealing the plastically deformed sample restored the original critical field. The transition temperature in Nb was not affected either by the deformation or the annealing treatment. These experimental results can be explained theoretically if one assumes that in a hard superconductor the current is carried by filaments. The filaments may be identified with dislocations.

The transition temperature of Re was found to depend on the annealing temperature and in some cases on plastic deformation. The transition temperature is higher, the higher the annealing temperature before plastic deformation. Plastic deformation does not affect the transition temperature in the cases where the transition is sharp. However, when the transition is broad, plastic deformation raises the transition temperature and sharpens the transition region. These results can be interpreted in terms of the equilibrium number of vacancies at the annealing temperature.

### I. INTRODUCTION

THE effect of elastic and plastic deformation on superconducting properties has been studied by numerous investigators. The studies were usually conducted on soft superconductors in polycrystalline form. Lasarew and Galkin<sup>1</sup> reported that inhomogeneous stresses applied on Sn at helium temperatures raised the transition temperature from 3.72°K to 9.0°K and increased the critical field from 210 to 15 000 oe. Chotkevich and Golik<sup>2</sup> increased the transition temperature of Sn and In by compression. Grenier<sup>3</sup> studied the effects of elastic deformation on the superconducting properties of Sn. Most recently, Shaw and Mapother<sup>4</sup> deformed Pb wires in tension at liquid helium temperatures. They reported a small increase in critical field with increasing strain and suggested that their results could be explained in terms of interconnected filaments such as dislocations.

DeSorbo<sup>5</sup> studied the effects of quenched-in defects in tin and showed that vacancies were responsible for a change of a few millidegrees in the transition temperature.

However, except for Shaw and Mapother<sup>4</sup> who in one case used a nearly single crystalline sample of Pb, all other studies were always performed on polycrystalline material where the deformation process is very difficult to interpret. Furthermore, the deformation had to be carried out at liquid helium temperatures to produce a permanent effect. If the change in superconducting properties with plastic deformation is produced by a change in the dislocation content, it should be possible to obtain this effect by deforming at room temperature any hard superconductor which does not recrystallize at room temperature. This is what prompted the choice of Re and Nb for this experimental study. The purpose

of the experiment was to gain a better understanding of the phenomenon of hard superconductivity and to study the nature of the filaments.

### II. EXPERIMENTAL PROCEDURE

Single crystals of Re and Nb were grown under vacuum by the floating-zone technique using induction heating for Nb and electron-beam melting in the case of Re. The Nb single crystals were grown with one pass and their resistivity ratios  $(\rho_{300^\circ\text{K}})/(\rho_{4.2^\circ\text{K}})$  varied between 125 and 500. Re single crystals grown with one pass had a resistivity ratio of 1500; other single crystals subjected to six passes had a resistivity ratio of 4000 which is higher than any other value reported for this material in the literature.<sup>6,7</sup> The single crystals were grown without seeding and their orientation was determined by the Laue back-reflection technique.

It is noteworthy to point out that all the Re single crystals grown by the floating-zone technique were oriented in such a way that their growth axes lie in the basal plane. This can be explained by the fact that in hexagonal metals the  $c$  axis is a slow direction of growth as compared to any direction lying in the basal plane. The crystals were deformed in tension using an Instron tensile machine. The rate of elongation was 0.02 in./min and the samples were deformed until necking occurred which corresponds to a strain of about 20%. The state of deformation of the sample was inferred from the resulting stress-strain curve.

The annealing treatments were performed in vacuum by heating the Re single crystals in an rf field to the desired temperature for the prescribed length of time, and quenching by shutting off the power supply.

The transition temperature and the critical field were determined using facilities which are sensitive to about  $\pm 10^{-9}$  v. Nickel lead wires were attached to the samples by spot welding prior to deformation and were soldered to copper wires. Four wires were used on each

<sup>1</sup> B. Lasarew and A. Galkin, *J. Phys. U.S.S.R.* **8**, 371 (1944).

<sup>2</sup> V. I. Chotkevich and V. R. Golik, *JETP* **20**, 427 (1950).

<sup>3</sup> C. Grenier, *Compt. rend.* **240**, 2302 (1955).

<sup>4</sup> R. Shaw and D. E. Mapother, *Phys. Rev.* **118**, 1474 (1960).

<sup>5</sup> W. DeSorbo, *J. Phys. Chem. Solids* **15**, 7 (1960).

<sup>6</sup> J. G. Daunt and T. S. Smith, *Phys. Rev.* **88**, 309 (1952).

<sup>7</sup> J. K. Hulm and B. B. Goodman, *Phys. Rev.* **106**, 659 (1957).

sample and the center pair served as potential leads which were used to determine the existence of superconductivity. The critical field was always measured with the magnetic field perpendicular to the axis of the sample which had the shape of a circular cylinder. The transition temperature is defined as the foot of the curve of resistance vs temperature. The critical field is defined similarly as the magnetic field which restores the smallest measurable resistance. The temperature was determined through the combined use of helium vapor pressure and a calibrated carbon thermometer.

### III. EXPERIMENTAL RESULTS

A Nb single crystal with an axial orientation  $3^\circ$  off the  $[4\bar{1}0]$  was extended in tension. The crystal was annealed for 15 hr at  $2100^\circ\text{C}$  and slowly cooled before deformation yielding a resistivity ratio of 125. The yield stress was  $4.76 \text{ kg/mm}^2$  and the critical field as a function of current density and strain is shown in Fig. 1. The strain of  $2.6\%$  corresponds to a stress of  $4.94 \text{ kg/mm}^2$ , i.e., to the early stage of plastic deformation, and one can observe that the corresponding increase in critical field is very small. In a single tension experiment the critical field increases with plastic strain until a strain of  $20\%$  is reached which corresponds to a true stress of  $12 \text{ kg/mm}^2$  and to the onset of necking. The slope of the curves increases with increasing strain over the whole range of current densities investigated. All the curves tend to level off at the lower current densities. The transition temperature remained fixed at  $9.8^\circ\text{K}$  for the entire range of deformation.

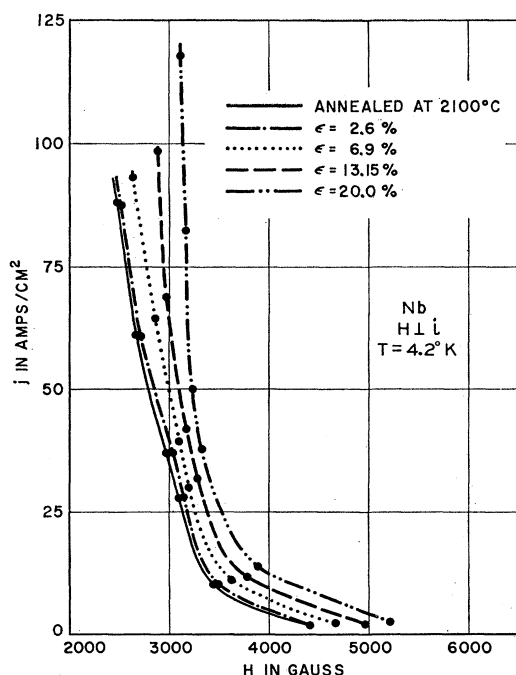


FIG. 1. Effect of increasing tensile strain on the critical field at  $4.2^\circ\text{K}$  of a Nb single crystal.

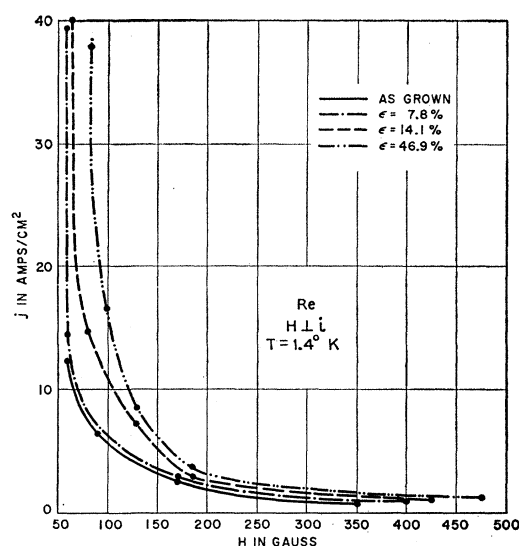


FIG. 2. Effect of increasing tensile strain on the critical field at  $1.4^\circ\text{K}$  of a Re single crystal.

An as-grown Re single crystal with a resistivity ratio of 1500 and an axis  $5^\circ$  off the  $[\bar{3}210]$  pulled in tension yields qualitatively the same results as those found in Nb. These results are shown in Fig. 2. The yield stress of this crystal was  $1.48 \text{ kg/mm}^2$  and the first critical field measurement after a strain of  $7.8\%$  corresponds to a stress of  $10.2 \text{ kg/mm}^2$ . The as-grown single crystal had a transition temperature of  $1.8^\circ\text{K}$  and the critical field measurement was performed at  $1.4^\circ\text{K}$ . The final extension of  $46.9\%$  corresponds to a true stress of  $73 \text{ kg/mm}^2$ . However, in this case the transition temperature rises from  $1.8^\circ\text{K}$  to  $2.1^\circ\text{K}$  with increasing strain.

A single crystal of Nb annealed for one hour at  $2350^\circ\text{C}$  and quenched in vacuum with a resulting resistivity ratio of 500 was extended and then subjected to the initial annealing treatment. After annealing, the single crystal became a coarse-grained polycrystal. The axis of the single crystal was  $[0\bar{3}2]$  and the results are summarized in Fig. 3. One can notice that the annealed crystal described in Fig. 3 has a much lower critical field than the one described in Fig. 1. This can be explained by the higher resistivity ratio of the crystal, which in turn may be due to the higher annealing temperature which led to a more complete degassing. The increase in critical field with plastic strain is of the same nature as that described in connection with Fig. 1 but is more pronounced. The yield stress of this crystal was  $2.76 \text{ kg/mm}^2$  and the final extension of  $26.8\%$  was produced by a stress of  $14.5 \text{ kg/mm}^2$ . Figure 3 shows that except for a small divergence at low current densities, the annealing treatment after deformation restores the initial critical field dependence on current density.

The Nb single crystal described in Fig. 1 was annealed for 16 hr at  $1850^\circ\text{C}$  after the  $20\%$  extension and the resulting critical field versus current density curve for the recrystallized single crystal is shown in

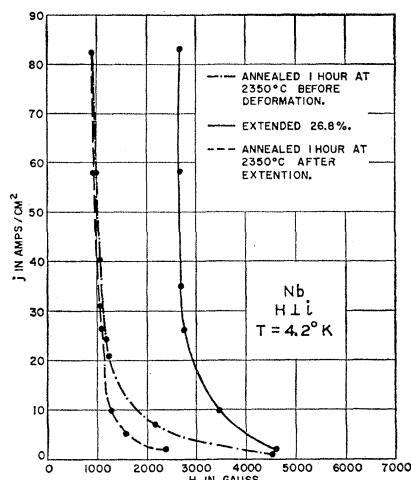


FIG. 3. Change in critical field of a Nb single crystal due to plastic deformation and annealing.

Fig. 4. A polycrystalline rod with a resistivity ratio of 30 subjected to the same annealing treatment has approximately the same critical field. This polycrystalline rod had a yield stress of 9.5 kg/mm<sup>2</sup> and a stress of 19.5 kg/mm<sup>2</sup> was required to produce the elongation of 10.3%. Figure 4 reveals that the effects of plastic deformation on a polycrystal are of the same nature as those exhibited by the single crystals.

Within the limits of accuracy of the experiment, Fig. 5 shows that when plotted against current density a polycrystalline rod  $\frac{1}{4}$  in. in diameter and one  $\frac{1}{8}$  in. in

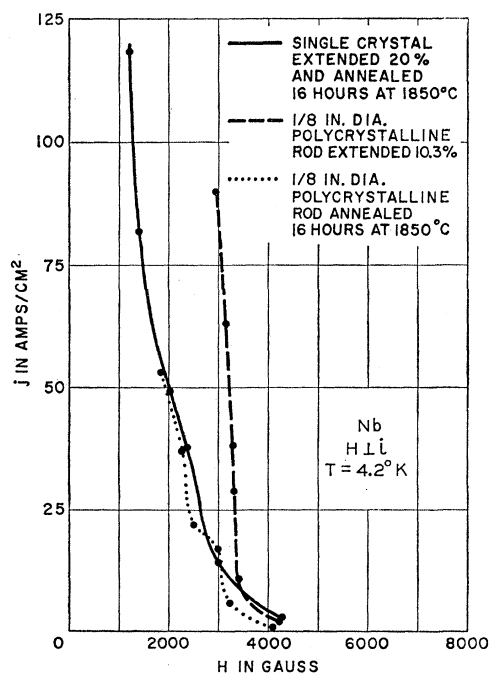


FIG. 4. Effect of deformation on the critical field of a polycrystalline Nb rod.

diameter have the same critical field. Consequently, for the range of sizes investigated, the critical field dependence on current density is independent of the dimensions of the sample. The curve shown in Fig. 5 for a polycrystalline tube 0.25-in. o.d. and 0.15-in. i.d. superimposes approximately on the other curves, demonstrating the independence of the critical field on the shape of the sample as long as the shape does not drastically alter the intermediate state. The conclusion to be drawn from Fig. 5 is that for a given annealing treatment, the critical field versus current curve depends only on the cross-sectional area of the sample.

The effect of plastic deformation on the critical temperature of a Re single crystal is revealed in Fig. 6.

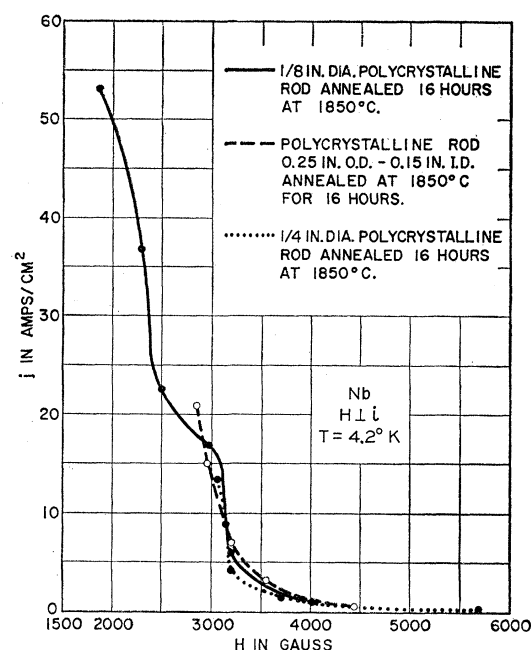


FIG. 5. Size and shape dependence of the critical field of polycrystalline Nb.

The as-grown single crystal described in Fig. 6 is the same as the one shown in Fig. 2. Increasing plastic deformation raises the transition temperature from 1.8° to 2.1°K. The transition  $R/R_0$  vs  $T$  (where  $R_0$  is the resistance at room temperature) which is very wide in this case, sharpens with increasing strain. This is in qualitative agreement with the experiment performed by Alekseyevski<sup>8</sup> on Ta wires. The transition temperature of 2.1°K after 46.9% extension is approximately the middle of the transition range in the original as-grown crystal. Another crystal oriented 5° off the [0110] axis and annealed for 16 hr at 2400°C exhibits a very sharp transition. The transition temperature for this sample which had a resistivity ratio of 1560 remains constant at 1.450°K up to a strain of 39%. It is also

<sup>8</sup> N. E. Alekseyevski, J. Phys. U.S.S.R. 3, 443 (1940).

shown in Fig. 6 that if the as-grown sample is annealed for 16 hr at 2400°C after deformation, the transition is sharpened and the transition temperature is lowered from 2.1° to 1.37°K. Figure 7 shows that the transition temperature of a polycrystalline Re sample is higher, the higher the annealing temperature.

A series of Re single crystals were annealed for different times and at different temperatures under vacuum. The single crystals were quenched in vacuum after annealing by shutting off the power supply. The results are shown in Table I, and it is evident from this table that the higher the annealing temperature, the higher the transition temperature. However, there is no correlation with the resistance ratios. On the other hand, if short annealing times are used such as  $\frac{1}{2}$  hr, the resistivity ratios increase with decreasing annealing temperature. The effect of using a bad vacuum ( $1.5 \times 10^{-3}$  mm) for  $\frac{1}{2}$  hr is to decrease the resistivity ratio, especially at the lower annealing temperature.

TABLE I. Effect of annealing temperature on the transition temperature.

Specimen number	Annealing time in hr	Vacuum in mm	Annealing temp. in °C	$T_c$ in °K	$R_0/R_4^\circ\text{K}$
7	0	$10^{-5}$	as grown	1.463	4100
8	0	$10^{-5}$	as grown	1.457	3850
12	$\frac{3}{2}$	$10^{-5}$	2700	1.904	1960
11	16	$5 \times 10^{-6}$	2200	1.476	120
13	16	$5 \times 10^{-6}$	2200	1.457	520
10	16	$5 \times 10^{-6}$	1500	1.500	2020
15	$\frac{1}{2}$	$10^{-5}$	2700	1.857	2430
16	$\frac{1}{2}$	$10^{-5}$	2200	1.563	3040
17	$\frac{1}{2}$	$10^{-5}$	1500	1.523	3300
22	$\frac{1}{2}$	$1.5 \times 10^{-3}$	2700	1.826	1870
21	$\frac{1}{2}$	$1.5 \times 10^{-3}$	2200	1.450	1330

#### IV. DISCUSSION

It should be pointed out that as the critical field is measured resistively,  $H_{\text{crit}}$  represents the field necessary to destroy the last superconducting filament. On the other hand, when the critical field is measured by susceptibility, it represents a bulk property. Consequently, the critical field will have a different value depending on the method of measurement. For sufficiently low current densities, the critical field determined by a resistance measurement will be higher than the one determined by a susceptibility measurement.

The fact that the critical field versus current density curves are independent of the size of the specimen indicates that the filaments are homogeneously distributed throughout the volume. The increase in critical field with plastic deformation can be explained if one assumes that the filaments responsible for hard superconductivity are dislocations. As no dislocation can terminate within the lattice, the dislocations form a continuous network which can carry the current from one terminal to another. An edge dislocation for example, has the property that a certain dilatation of the

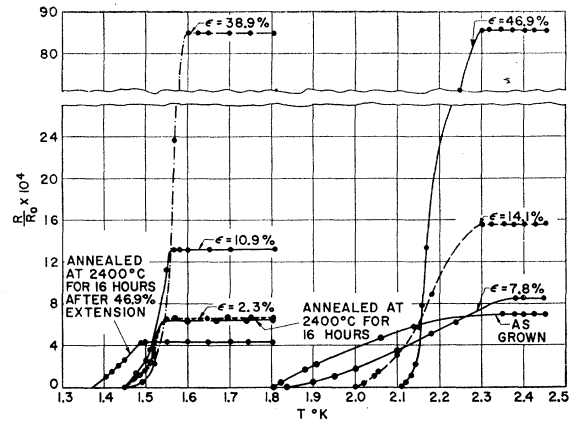


FIG. 6. Effect of annealing and plastic deformation on the critical temperature of Re single crystals.

lattice is associated with it. Matthias<sup>9</sup> developed the empirical rule that the transition temperature  $T_c \sim c(V^x/M)T(n)$  where  $V$  is atomic volume,  $M$  is the atomic mass,  $T(n)$  is a term depending on the electronic concentration, and  $x$  is a number between 4 and 5. Therefore, the expanded region associated with an edge dislocation can be expected to have a slightly higher critical temperature than the bulk of the material. The extremely high critical field produced by these dislocations can be explained<sup>10</sup> if one considers a dislocation as a circular cylinder with a radius smaller than the penetration depth. It was also shown by one of the authors<sup>10</sup> that various portions of the dislocation network will have different critical fields because of their various orientations relative to the externally applied field. Consequently the current density versus field curves can be explained in terms of the following parameters:  $H_{cb}$ , the critical field of the bulk;  $H_{cf}$ , the critical field of the filaments;  $\rho$ , the density of filaments;  $r$ , the radius of the filament; and  $a$ , the radius of the

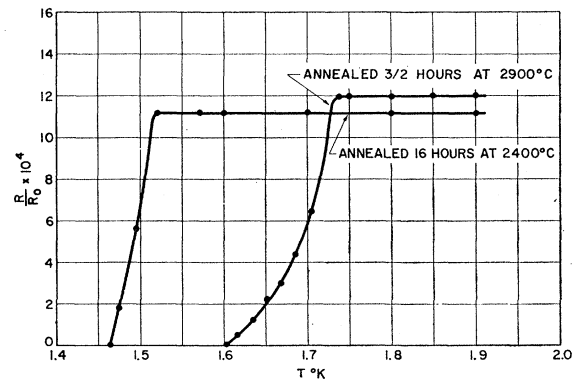


FIG. 7. Effect of annealing temperature on the critical temperature of polycrystalline Re.

<sup>9</sup> B. T. Matthias, *Progress in Low-Temperature Physics*, edited by J. C. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2, Chap. 5, p. 138.

<sup>10</sup> J. J. Hauser (to be published).

sample considered. As a dislocation normal to the externally applied field has a lower critical field than one parallel to it, the current will try to run in the dislocations which are closest to the direction of the externally applied field. This in turn will lead to a distribution of  $H_{cf}$  as a function of the number of dislocations between  $H_{cf \min}$  and  $H_{cf \max}$ .

The current density versus critical field curves can be divided in three basic regions according to the magnitude of the current density. The fundamental formula describing the hard superconductor is

$$H_{cf \text{ av}} = H_a + 0.2I/\rho\pi a^2 r, \quad (1)$$

where  $H_a$  is the applied field which causes the transition from superconducting to normal,  $\rho\pi a^2$  the number of filaments in the sample and therefore  $I/\pi a^2 = j$  is the current density for the sample as a whole and  $j/\rho$  is the current per filament. The second term on the right of Eq. (1) represents the field at the surface of each filament produced by the current circulating in all the filaments.

In the very high current density limit, when  $0.2j/\rho r > H_{cf \text{ av}} - H_{cb}$ , the filaments are no longer important. As long as the applied field  $H_a$  is smaller than  $H_{cb}$ , the current flows in the penetration depth. When the applied field exceeds the critical field of the bulk, the current is rejected in the filaments, but in this case the filaments are not capable of carrying the current density and therefore the filaments turn normal with the bulk. Actually, the filaments with  $H_{cf \min}$  turn normal first, but as the current density is thereby increased in the remaining filaments, the transition is accelerated and this is why  $H_{cf \text{ av}}$  is used in relation (1). Consequently, in the very high current density limit, the hard superconductor behaves as a soft superconductor and should be described by the relation:

$$H_{cb} = H_a + 0.2I/a. \quad (2)$$

When the current density is very low, and the applied field exceeds  $H_{cb}$ , the current is rejected into the filaments which are now able to remain superconducting. Consequently, in this region one is really measuring the filaments of the material. The critical field versus current density curve is now described by the relation (1). Increasing plastic deformation increases the number of dislocations and thereby increases  $\rho$ , the density of filaments. Consequently, the second term on the right of relation (1) decreases and as  $H_{cf}$  is a constant of the material, this leads to an increase of  $H_a$  as shown in Figs. 1-4. The slope in this region is  $\partial j/\partial H_a = -\rho r/0.2$  and therefore the slope becomes steeper with increasing plastic deformation as can be seen in Figs. 1-4. In this region  $0.2j/\rho r < H_{cb \min} - H_{cb}$ , so that when the bulk becomes normal, all the filaments can carry the current. This steep region present in highly deformed hard superconductors is actually missing here, the deformation being too mild. As soon as a current is applied, one

is in the intermediate current plateau where the number of filaments is reduced. If relation (1) is fitted to the single crystal described in Fig. 3, one obtains  $\rho r = 5.4 \times 10^{-4}$ . Assuming that  $r$ , the radius of a dislocation is approximately  $10^{-7}$  cm, the density of filaments  $\rho$  is equal to  $5.4 \times 10^3$ . The radius of a dislocation could actually be somewhat larger if one takes into account the coherence of the superelectrons, instead of only considering the core of the dislocation. This density of filaments is much smaller than the density of dislocations to be expected even in a well annealed single crystal. This result is nevertheless quite reasonable, because although every filament is expected to be a dislocation, the converse is not true as the current will only tend to choose the dislocations oriented as closely as possible in the direction of the externally applied field. If one further assumes that  $H_{cb} = 800$  gauss and  $H_{cf \text{ av}} = 8000$ , one obtains 25 amp/cm<sup>2</sup> as the transition value between low current density and intermediate current densities. The intermediate current densities portion of the curve is defined by  $H_{cf \min} - H_{cb} < 0.2j/\rho r < H_{cf \max} - H_{cb}$  and corresponds to the transition region between very low and very high current densities. This value of 25 amp/cm<sup>2</sup> is not exact but this is to be expected if one considers the simplicity of the assumptions made as compared to the complexity of the real problem. For example, it was assumed that  $H_{cb}$  is a constant throughout the sample and this might not be true if the sample is not completely chemically homogeneous. Furthermore, the density of dislocations might not be isotropically homogeneous. Finally even if  $\rho$  and  $H_{cf}$  were completely homogeneous, the model could still be obscured by some intricacy of the intermediate state. For example, an inhomogeneity in  $H_{cb}$  along the sample would allow the field to penetrate in certain regions, and thereby would distort the magnetic field. Consequently as  $j$  tends towards zero,  $H_a$  tends towards  $H_{cf \text{ av}}$  and eventually  $H_{cf \text{ av}}$  approaches  $H_{cf \max}$ . It was implicitly assumed during this discussion that plastic deformation only changes the number of dislocations and not their nature, which means that  $H_{cf}$  and  $r$  are unchanged by the deformation process. This seems to be true certainly in the case of Nb where the critical temperature remains unchanged to  $\pm 0.1^\circ\text{K}$ .

These results are in qualitative agreement with the data obtained by Kunzler *et al.*<sup>11</sup> on Nb<sub>3</sub>Sn. There again, a plateau can be observed in the current density versus critical field curves measured at 4.2°K. The plateau occurs at current densities which are several orders of magnitude higher than the ones described here. This can be explained in terms of the much greater number of filaments present in an intermetallic compound severely strained as compared to the mild tensile deformations used in this experiment and also by a higher

<sup>11</sup> J. E. Kunzler, E. Buehler, F. S. L. Hsu, and J. H. Wernick, Phys. Rev. Letters **6**, 89 (1961).

$H_{cb}$ . It was also shown by Kunzler *et al.*<sup>12</sup> that Nb<sub>3</sub>Sn samples prepared by sintering a powder in a Nb core had 50 times the current-carrying capacity at 88 kgauss and 4.2°K for a given field than Nb<sub>3</sub>Sn bulk samples prepared stoichiometrically. This difference can again be accounted for if one assumes that these two types of samples contain a different number of filaments. However, measurements at liquid hydrogen temperatures and at low current densities show that the current density versus critical field curves for these two different samples, both approach the same limit which is the critical field of the filaments contained in both samples.

However if one assumes that dislocations are responsible for the phenomenon of hard superconductivity, one may ask why the dislocations present in such soft superconductors as Pb, Sn, In, etc., do not produce the same effects. It is possible that the extra elastic energy associated with a dislocation can only influence superconductivity if its magnitude is large enough as compared to the energy gap. Indeed, all hard superconductors have a high Young's modulus which means that the dislocations will be very narrow. All the soft superconductors have a low Young's modulus which will lead to very wide dislocations. Furthermore, all the soft superconductors are more of the close metal type than the hard superconductors. A close metal has atoms which are analogous to hard bubbles in a bubble model, i.e., small bubbles and this again will lead to wide dislocations. Therefore, all the soft conductors have very wide dislocations, associated with a small amount of extra elastic energy per atom, and therefore the superconducting properties are not altered by a dislocation. It is true, however, that if a soft superconductor such as lead is deformed at liquid helium temperatures as was done by Shaw and Mapother,<sup>4</sup> a certain amount of hardness can develop as the  $E$  modulus will increase with decreasing temperature. There are, however, certain exceptions such as Pb-Bi alloys which behave as hard superconductors and have a low  $E$  modulus. The importance of dislocations in such alloys would have to be justified by a different mechanism.

The experiments performed on Re yielded a slightly different result in the sense that the transition temperature was affected by plastic deformation as shown in Fig. 6. A Re single crystal grown by the floating-zone technique can have its transition temperature raised from 1.8° to 2.1°K by a tensile strain of 47%. On the other hand, an identical Re single crystal annealed at 2400°C for 16 hr prior to extension has a constant transition temperature of 1.45°K independent of the amount of tensile deformation. This effect can be explained in terms of the equilibrium number of vacancies present at a certain annealing temperature. The Re single crystal which was annealed before deformation has certainly reached thermal equilibrium in 16 hr and can therefore

be expected to have a homogeneous vacancy content representative of the holding temperature. Consequently, the sample being homogeneous displays a sharp transition temperature and the width of the transition is approximately 0.1°K. The as-grown crystal is such that as one goes from the starting end of the crystal to the other end, the crystal is annealed for shorter and shorter times at higher and higher temperatures. Therefore, the vacancy content will be inhomogeneous and will increase from the starting end to the last part to freeze which will contain the maximum number of vacancies. If one assumes that the transition temperature is related to the number of vacancies, different portions of the crystal having a different number of vacancies will also have a different transition temperature. Consequently, the inhomogeneity in vacancy content will broaden the transition and in the as-grown single crystal the width of the transition is approximately 0.5°K. The transition temperature was actually measured in three different portions of the sample. The width of these transitions were smaller than the original one and the transition temperatures increased from one end to the other, and was higher at the last end to freeze. The effect of plastic deformation on such an as-grown crystal is to homogenize the vacancies throughout the sample, thereby narrowing the transition as can be seen in Fig. 6. As would be expected from such a model, the transition temperature is raised to approximately the middle of the original transition, i.e., to 2.1°K. If such a crystal is annealed at 2400°C for 16 hr it regains the transition properties of an annealed crystal.

Figure 7 illustrates the fact that even for a polycrystal of Re the transition temperature is higher, the higher the annealing temperature. The relative magnitude of the transition temperatures for an as-grown and an annealed single crystal will depend on the purity of the single crystal as the as-grown treatment corresponds to some average annealing treatment below the melting point of the material.

In order to exhibit more clearly the effect of vacancies on the transition temperature, various single crystals of Re were subjected to different annealing treatments summarized in Table I. The as-grown crystals display a very high resistivity ratio around 4000 as a result of the 6 electron beam melting passes which were used. Specimens 12, 11, 13, and 10 are as-grown crystals which were annealed subsequently in a good vacuum. It can be seen that the transition temperature is highest, the higher the annealing temperature except maybe for the sample annealed at 1500°C. This would be consistent with the fact that the higher the annealing temperature the greater the number of vacancies. However, as vacancies decrease the resistivity ratio as shown by sample 12, one would expect that the lower annealing temperatures resulting in a smaller number of vacancies would lead to a higher resistivity ratio, which is not the case. If one assumes that, during annealing, the samples could pick up such interstitial impurities as nitrogen

<sup>12</sup> J. E. Kunzler, F. S. L. Hsu, and E. Buchler, *Bull. Am. Phys. Soc.* **6**, 144 (1961).

from the vacuum and that the solubility of such an impurity is higher at the lower temperatures, this would explain the anomaly in the resistivity ratio. Furthermore, as nitrogen can raise the transition temperature of Re,<sup>13</sup> this could also account for the discrepancy shown by the sample annealed at 1500°C. With this idea in mind, the annealing treatments were repeated at the same temperatures but for shorter times so as to allow thermal equilibrium to occur but not interstitial diffusion. Now, as shown by samples 15–17, the transition temperature is again highest, the higher the annealing temperature, but the resistivity ratios increase with decreasing annealing temperature presumably because of the lower vacancy content. As an additional test, samples 21 and 22 were annealed in a bad vacuum in order to promote the pickup from the vacuum. By comparison of samples 15 and 22 annealed at 2700°C and samples 16 and 21 annealed at 2200°C it is observed that the resistivity ratio of the sample annealed at the lower temperature is more depressed than the one annealed at the high temperature probably because of the greater solubility at the low temperature. The transition temperature in Nb is unchanged by vacancies, either because the material is too impure, or because the energy of formation of vacancies is higher in Nb than in Re.

## V. CONCLUSIONS

The current density critical field curve for hard superconductors such as Nb and Re display three distinct regions. The high-current-density portion of the curve where the filaments are unable to carry the current is analogous to the curve displayed by a soft superconductor. The intermediate-current-density portion of the curve, i.e., the plateau, depends on the number of filaments present in the sample. The low-current-density portion, where one is dealing principally with the filaments, can be described by Eq. (1). At very low

current densities, as  $I$  tends toward zero the number of filaments becomes unimportant, as the second term on the right of Eq. (1) becomes negligible. Consequently, no matter how much plastic deformation is applied on the sample, one can never hope to exceed the critical field of the best filaments. Immediately above the yield point of the material, where very few new dislocations have been created, the critical field increases only very slightly. The critical field increases markedly with increasing amounts of plastic strain especially when the strain is in a portion of the stress-strain curve where many new dislocations are being created. As the strain hardening decreases, the increase in critical field approaches saturation. Annealing a plastically deformed sample restores the original critical field properties. As the filaments must be continuous and as their radii must be smaller than the penetration depth, the above experimental results can be taken as evidence to identify filaments with dislocations. The increase in critical field with plastic deformation is therefore produced by the increase in dislocation density accompanying plastic deformation. The limiting critical field at zero current will be left unchanged, as it is independent of the number of dislocations and only depends on the nature of the dislocations present.

Finally, in the case of Re, it was shown that the transition temperature is higher, the higher the annealing temperature presumably because of the higher vacancy content. Plastic deformation does not affect the transition temperature of a well annealed single crystal but raises the transition temperature of an as-grown crystal by redistributing the inhomogeneous vacancy content. The effect of vacancies can be shown more unambiguously with short annealing times. Long annealing times promote impurity pickup from the vacuum which tends to obscure the effect of vacancies, especially from a resistivity ratio point of view.

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<sup>13</sup> B. T. Matthias and W. H. Zachariasen, J. Phys. Chem. Solids 7, 98 (1958).