

contamination. It can be concluded from these figures that the helium metastable beam might be an excellent probe for measuring the state of surface cleanliness. Figure 4 further illustrates the possibilities of using the time and temperature of flash technique in investigating the energy states of gas adsorption.

Some disagreement exists concerning the magnitude of the various rare-gas Penning cross sections. The dependence of these cross sections on energies of the colliding atoms might explain the disagreement since differing techniques were used in the measurements. In Table I, Penning cross sections for the ionization of argon by helium and neon metastable atoms obtained in the present work are compared with other

reported values. The present values for helium, with one exception, compare well with others within experimental error (30%). Agreement in the case of neon is not good. Benton *et al.*, Phelps, and Biondi carried out their measurements in an afterglow following a pulsed discharge; other measurements used beam techniques.

#### ACKNOWLEDGMENTS

Thanks are due to Professor L. B. Loeb, under whom this work was done, for his support and guidance; to Dr. J. T. Dowell, who pointed out the need for such a study; and to Dr. Dowell and P. D. Burrow for useful discussions.

## Critical Magnetic Field and Transition Temperature of Synthetic High-Field Superconductors

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Measurements of the critical field  $\hat{H}$  and transition temperature  $\hat{T}$  of superconducting indium in porous glass have been made using a low-frequency mutual-inductance technique. The pore sizes of the glasses are well characterized, so that 96% of the pore volume is within  $\pm 10\%$  of the mean pore diameter  $d$ . Pore diameters from 65 to 250 Å were used. Below  $t$  ( $\equiv T/\hat{T}$ ) = 0.5,  $\hat{H}$  can be represented approximately by

$$\hat{H} = (3415 \pm 40)(1 - t^2)/d^{(1.00 \pm 0.14)},$$

where  $\hat{H}$  is in kilo-oersteds and  $d$  is in Angstrom units. This is in agreement with the predictions of de Gennes and Maki of  $H_{c2}$  for type II superconductors in the dirty limit, assuming that the electronic mean free path is proportional to  $d$ . Above  $t=0.6$ , there are deviations from de Gennes's prediction for the  $d$  dependence and the  $t$  dependence of  $\hat{H}$ . For the small pore sizes the temperature dependence of  $\hat{H}$  is qualitatively similar to the Abrikosov prediction of  $H_{c2}$  for type II superconductors; however, near  $t=1$  for the largest pore size the temperature dependence of  $\hat{H}$  is similar to that for a type I superconductor. The superconducting transition temperature  $\hat{T}$  shows a strong dependence upon  $d$ , so that  $\hat{T}(65 \text{ Å})$  is 4.23°K compared with 3.4°K for the bulk indium. The dependence of  $\hat{T}$  on  $d$  is conveniently represented by

$$\hat{T} - T_{\text{bulk}} = 1 - 0.0028 d,$$

where  $d$  is in Angstrom units. The change in  $\hat{T}$  may be due to strain, mean-free-path, or surface effects. The samples are similar to inhomogeneous type II superconductors in their magnetic properties, showing hysteresis and flux jumping.

### I. INTRODUCTION

**S**YNTHETIC high-field, high-current superconductors have been made by impregnating porous glass with metal. Magnetic properties of these composites have been described by Bean, Doyle, and Pincus,<sup>1</sup> Bean,<sup>2</sup> and more recently by Watson.<sup>3</sup> The behavior of the samples was similar to inhomogeneous type II superconductors, since they showed hysteresis in the magnetization, flux jumping, and a current-carrying capacity apparently limited by the Lorentz force con-

dition. It was also found that the critical field  $\hat{H}$  and the superconducting transition temperature  $\hat{T}$  depended strongly upon the pore size of the glass. ( $\hat{H}$  and  $\hat{T}$  refer to the normal superconducting transition of the filamentary structure.  $H_c$  and  $T_c$  refer to the bulk metal.)

In this paper measurements of the critical field  $\hat{H}$  and the superconducting transition temperature  $\hat{T}$  are presented for samples of porous glass containing indium and covering a wide range of pore sizes.

It was found in these measurements that  $\hat{H}$  depended strongly upon  $d$ , the pore diameter of the glass. Below  $t=0.5$ , where  $t = T/\hat{T}$ ,  $\hat{H}$  varied as  $1/d$ . In the same temperature range  $\hat{H}$  varied approximately as  $(1 - t^2)$ .

<sup>1</sup> C. P. Bean, M. V. Doyle, and A. G. Pincus, *Phys. Rev. Letters* **9**, 93 (1962).

<sup>2</sup> C. P. Bean, *Rev. Mod. Phys.* **36**, 31 (1964).

<sup>3</sup> J. H. P. Watson, *J. Appl. Phys.* **37**, 516 (1966).

These results are in accordance with de Gennes's<sup>4</sup> and Maki's<sup>5</sup> prediction of  $H_{c2}$  for dirty type II superconductors. At higher temperatures there are considerable deviations from de Gennes's and Maki's prediction.

$\hat{T}$  also depended upon  $d$ . Over the range of pore diameters used, 65 to 25 Å,  $\hat{T}$  varied linearly with  $d$ , becoming larger as  $d$  was reduced. The increase in  $\hat{T}$  may be due to strain; however, surface effects<sup>6</sup> and mean-free-path effects<sup>7</sup> may be important.

## II. POROUS GLASS

The porous glass was prepared by leaching a phase-separated alkali-borosilicate glass<sup>8</sup> to remove the boron-rich phase and leave the porous body. Typical porous glasses contain 96% SiO<sub>2</sub>, 3% B<sub>2</sub>O<sub>3</sub>, small amounts of Na<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and other oxides.<sup>9</sup> Electron microscope studies,<sup>10-12</sup> have shown that the porous glass can be viewed as a randomly packed collection of silica balls, all about 300 Å in diameter. In glasses of the larger pore sizes the balls are distorted appreciably from sphericity. Comparing the density of silica with that of porous glass shows that the density is within 3% of that of a collection of randomly dense-packed uniform spheres as determined by Scott.<sup>13</sup>

Several methods may be used to infer the pore size of the glass. These methods rely upon the nitrogen adsorption and desorption isotherms. In the first method the volume of the pores is found by measuring the volume of the gas  $V_s$  adsorbed by the glass at the saturation vapor pressure of the gas. The surface area  $S$  of the pores is determined by the volume of the first monolayer adsorbed;  $S$  is calculated from the Brunauer-Emmett-Teller (BET) equation.<sup>14</sup> It is explicitly assumed that the pores are all cylindrical and of equal diameter given by  $4V_s/S$ . This method was used here to measure the pore size of the glass.

The second method used the so called Kelvin equation which relates the vapor pressure over a curved surface to its radius of curvature. The curvature of the liquid gas interface in a pore can be determined from the radius of the pore, the surface tension of the liquid, and the angle of contact. The evaporation pressure  $P$  corresponding to the steepest part of the desorption curve is then characteristic of the pore diameter  $d$ , after allowing for the BET multilayer thickness. Then,

assuming that the angle of contact is zero the pore diameter  $d$  is given by

$$d = (4\sigma V/R_g T) \ln(P/P_0) - 2s, \quad (1)$$

where  $V$  is the molar volume,  $\sigma$  is the surface tension of the adsorbate,  $s$  is the multilayer thickness at a pressure  $P$ ,  $P_0$  is the saturation vapor pressure,  $R_g$  is the gas constant, and  $T$  is the temperature (°K).

The second method was modified by Shull<sup>15</sup> to describe the distribution of pore radii  $L(r)$ . The pores are assumed to approximate a variety of cylinders with different radii and the method determines  $L(r)$  from the shape of the desorption branch of the isotherm. For a typical porous glass  $L(r)$  is Gaussian and 96% of the cylinder volume is within  $\pm 3$  Å of a mean radius of 20.3 Å.

The three methods of measurement described above give different pore-size values. These methods when applied to porous glass can give values differing by 8% which is more than twice the experimental error in each measurement.

The fact that the spaces in the glass are not cylinders but pockets joined by "gates" of various size needs some consideration. The gates control the desorption since the evaporating meniscus may be formed at these gates. As the pressure is lowered all pockets controlled by gates of a certain size will empty, except for a certain small fraction of gas trapped in the body of the material. The desorption curve indicates the volume of the pores controlled by gates of a certain size. The steepness of the desorption branch of the isotherm for porous glass indicates that most of the pore volume of the glass is accessible through gates of approximately the same size. The pore radius given by the last two methods is assumed proportional to the average gate size. The first method does not disagree with the other methods by more than a few percent, so the pore diameter as measured by the first method also gives a good relative measure of the minimum cross sectional diameters of the filaments; furthermore, this technique is more convenient experimentally.

The gates control the pressure required to fill the glass with metal because of capillary action. In the impregnation curves shown by Charles,<sup>12</sup> 70% of the pore volume was filled by a 6% pressure increase above the initial impregnation pressure. From electron-microscope studies, Charles<sup>12</sup> described the filaments of the metal in the glass as a network of beads of uniform diameter touching one another. The necks between the beads must occur at the gates and the cross sectional areas of the necks must be almost equal to the gate size.

## III. EXPERIMENTAL

The samples used in this investigation were made from porous glass cylinders 10 mm diam and 10 mm long, except sample *G* which was 3.2 mm in diameter

<sup>4</sup> P. G. de Gennes, *Physik Kondensierten Materie* **3**, 79 (1964).

<sup>5</sup> K. Maki, *Physics* **1**, 21 (1964).

<sup>6</sup> V. L. Ginsburg, *Phys. Letters* **13**, 101 (1964).

<sup>7</sup> D. M. Ginsberg, *Phys. Rev.* **138**, A1409 (1965).

<sup>8</sup> H. P. Hood and M. E. Nordberg, U. S. Patent Nos. 2,286,275 and 2,106,744.

<sup>9</sup> The samples specified in this work by a pore diameter of 65 Å were Corning's Code 7930. The other porous glasses were prepared by T. H. Elmer, Exploratory Chemical Research Department, Corning Glass Works.

<sup>10</sup> G. B. Carrier (private communication).

<sup>11</sup> R. J. Charles, *J. Am. Ceram. Soc.* **47**, 154 (1964).

<sup>12</sup> R. J. Charles, *J. Appl. Phys.* **35**, 2252 (1964).

<sup>13</sup> G. D. Scott, *Nature* **188**, 908 (1960).

<sup>14</sup> S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.* **60**, 309 (1938).

<sup>15</sup> C. G. Shull, *J. Am. Chem. Soc.* **70**, 1405 (1948).

and 25 mm long. The porous glasses were impregnated with indium at pressures up to 70 000 pounds per square inch (psi). Some of the samples were cracked during impregnation. The impregnated glass is black and shiny in appearance.

The transition temperature in zero field  $\hat{T}$  ( $^{\circ}\text{K}$ ) and the critical field  $\hat{H}$  ( $^{\circ}\text{K}$ ) were determined by a mutual inductance technique.<sup>16</sup> The amplitude  $h_0$  of the 17-cps ac magnetic field was 0.43 Oe. The measurements were made in a constant magnetic field as the temperature was slowly swept through the transition region. The changes in  $\chi'$  and  $\chi''$ , the real and imaginary parts of the complex susceptibility, were measured and were used to locate the transition. A Magnion Inc. superconducting Nb-Zr solenoid (3060 (Oe)/A) produced the constant magnetic field. The current supply manufactured by Alpha Scientific Laboratories (Model A1-50-50) had a stability of 1 part in  $10^5$ .

#### IV. RESULTS

$\chi'$  and  $\chi''$  change rapidly in the transition region. In Fig. 1 the changes in  $\chi'$  and  $\chi''$  are shown for transitions in various magnetic fields for sample *G*, most other samples have broader transitions. The temperature of the transition was assigned at the temperature of the peak in  $\chi''$ . Although the transition is broadened by the magnetic field and often the peak height is lowered, the position of the peak could usually be located to about  $0.010^{\circ}\text{K}$ . An indication of the width of the transition is given in Table I as  $\Delta T$  ( $^{\circ}\text{K}$ ), the temperature difference between the initial change and the peak of  $\chi''$ . In general the samples with the fewest surface cracks had the smallest values of  $\Delta T$ . Many of the samples showed another superconducting transition at  $3.4^{\circ}\text{K}$ , the transition temperature of bulk indium. At magnetic fields greater than 300 Oe these transitions were not detected. The samples with few surface cracks showed only small changes of  $\chi'$  and  $\chi''$  at  $3.4^{\circ}\text{K}$ , indicating that only a small amount of bulk indium was present.

TABLE I. Extrapolated critical fields and transition temperatures for samples of various pore diameters.

	$d$ ( $\text{\AA}$ )	$\hat{H}(0)$ (kOe) <sup>a</sup>	$\hat{T}$ ( $^{\circ}\text{K}$ )	$\Delta T$ ( $^{\circ}\text{K}$ )
<i>A</i>	65	$48.5 \pm 3$	4.21	0.05
<i>B</i>	65	...	3.71	0.44
<i>C</i>	65	$58.4 \pm 2$	4.17	0.05
<i>D</i>	106	$30.18 \pm 2$	4.06	0.11
<i>E</i>	106	$32.9 \pm 2$	4.09	0.04
<i>F</i>	117	$32.9 \pm 2$	4.04	0.07
<i>G</i>	160	$23.7 \pm 1$	3.91	0.05
<i>H</i>	250	$11.6 \pm 1$	3.68	0.18
<i>I</i>	250	...	3.43	0.38
<i>J</i>	250	...	3.67	0.18

<sup>a</sup> Extrapolated value.

<sup>16</sup> W. L. Pillinger, P. S. Jastram, and J. G. Daunt, Rev. Sci. Instr. **29**, 159 (1958).

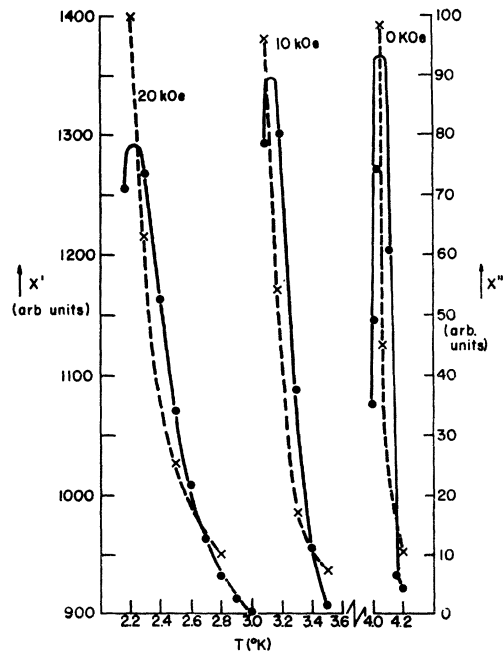


FIG. 1. The real (broken line) and the imaginary (solid line) parts of the complex susceptibility (in arbitrary units) plotted against temperature in various applied dc magnetic fields for sample *G* (160  $\text{\AA}$ ).

The transition temperature  $\hat{T}$  showed a strong dependence on the pore diameter of the glass. In Fig. 2, the transition temperature  $\hat{T}$  is plotted versus pore diameter and the width  $\Delta T$  is indicated by the bar length. Except for samples *B* and *I*, which have very broad transitions and a large amount of cracking,  $\hat{T}$  appears to be a linear function of pore diameter. A least-squares fit gives the following relation between 65  $\text{\AA}$  and 250  $\text{\AA}$ :

$$\hat{T} - T_c = 1.0 - 0.0028d,$$

where  $d$  is the pore diameter in Angstrom units and  $T_c$  is the transition temperature of bulk indium.

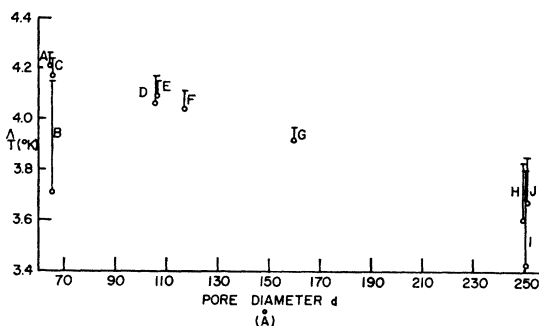


FIG. 2. The transition temperature  $\hat{T}$  ( $^{\circ}\text{K}$ ) ( $h_0 = 0.43$  Oe) plotted against pore diameter ( $\text{\AA}$ ) for various samples. The circles indicate the peak in  $\chi''$  and the bars indicate the temperature at which  $\chi''$  begins to change.

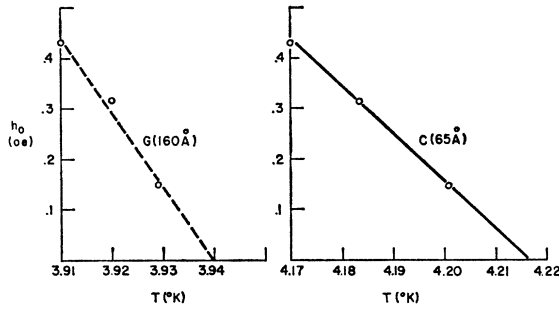


FIG. 3. The amplitude of the ac magnetic field  $h_0$  (Oe) versus the transition temperature (the temperature corresponding to the peak in  $\chi''$ ) for sample (65 Å) and for G(160 Å). The lines shown and the linear extrapolations to  $h_0=0$ .

It was found that  $\hat{T}$  depended slightly on the amplitude,  $h_0$ , of the 17-cps ac magnetic field. In Fig. 3,  $h_0$  is plotted versus the transition temperature  $\hat{T}$  for samples C(65 Å) and G(160 Å). On extrapolating the curves to  $h_0=0$  the increase in  $\hat{T}$  is less than 0.050°K. On the basis of the extrapolations in Fig. 3, the shift in  $\hat{T}$  due to the finite measuring fields was ignored.

The critical field  $\hat{H}$  is shown in Fig. 4 versus  $T$ , and in Fig. 5 versus  $t(T/\hat{T})$ . The strong dependence of  $\hat{H}$  on pore diameter is clearly demonstrated. The values of  $\hat{H}$  were continued to temperatures as low as 1.5°K unless the transition became too broad to clearly identify the peak in  $\chi''$ . In Fig. 6,  $\hat{H}$  is plotted versus the pore diameter for different values of the reduced temperature. This plot clearly shows the weakening

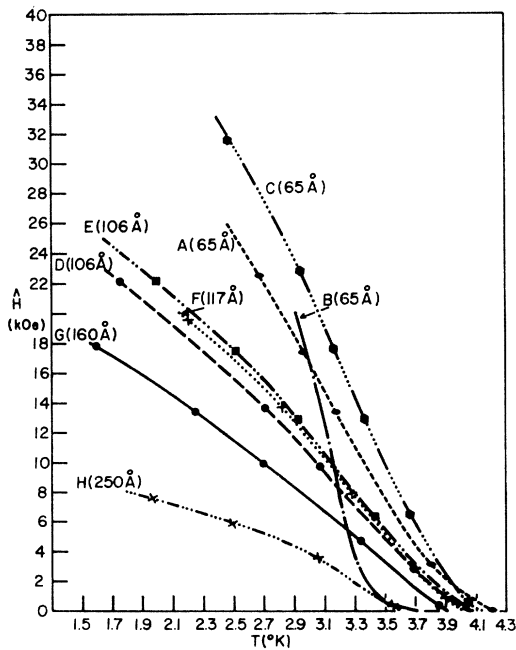


FIG. 4. The critical field  $\hat{H}$  (kOe) versus temperature (°K) for samples with various pore diameters.

dependence on  $d$  as the temperature increases. At  $t=0.95$ ,  $\hat{H}$  appears to be independent of  $d$ .

### V. DISCUSSION

#### The Superconducting Transition

It has been suggested by Maxwell and Strongin<sup>17,18</sup> that peaks in  $\chi''$  at the superconducting transition of Sn-Pb alloys can be explained in terms of a superconducting filamentary mesh. The mesh, it was suggested, was formed by lead which had migrated to the dislocation lines.

The peak in  $\chi''$  was explained in terms of an average conductivity model in which formation of unconnected filamentary superconducting inclusions increased the average current density and thereby the dissipation.

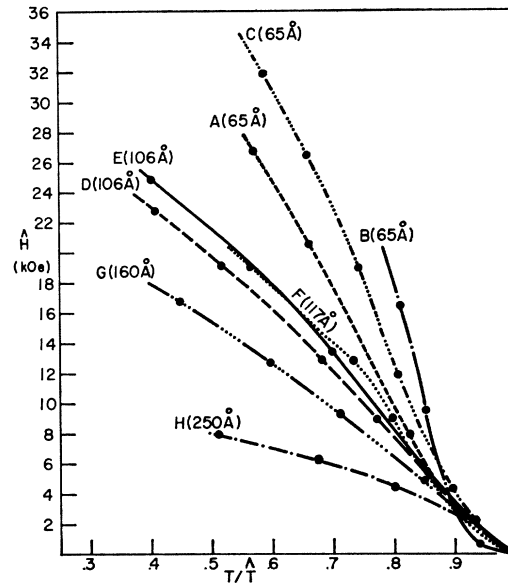


FIG. 5. The critical field  $\hat{H}$  versus reduced temperature  $T/\hat{T}$  where  $\hat{T}$  is the transition temperature in zero magnetic field.

As the multiply connected superconducting structure is formed, the currents flowing shield the interior of the sample from the magnetic field and the total dissipation is reduced. The dependence of the peak in  $\chi''$  on frequency and magnitude of the exciting voltage was also investigated and found to be in agreement with the average conductivity model.

In the present work it was known that there was a filamentary network present and peaks in  $\chi''$  similar to those described by Maxwell and Strongin were found. The shift of  $\hat{T}$  with  $h_0$ , the amplitude of the ac magnetic field, was explained by Maxwell and Strongin by assuming a limited current carrying capacity of the filaments.

<sup>17</sup> E. Maxwell and M. Strongin, Phys. Rev. Letters **10**, 212 (1963).

<sup>18</sup> E. Maxwell and M. Strongin, Phys. Letters **6**, 49 (1963).

The ratio of the shifts found in the present work for samples *C* and *G* were found to be approximately in the inverse ratio of the squares of their pore diameters. The shifts observed indicated that the error in  $\hat{T}$  caused by not correcting for finite ac field amplitude is less than  $0.05^\circ\text{K}$  in all cases. This correction also gives an upper limit to the broadening of the transition due to nonhomogeneous ac magnetic fields across the sample. These inhomogeneities arise from the large demagnetizing factor of most of the samples and from nonuniformity of the ac magnetic field used. A distribution of transition temperatures as in an inhomogeneous sample can also broaden the transition. As indicated in Fig. 2, the transition temperature  $\hat{T}$  depends upon the pore diameter; the width of the transition will therefore be dependent on the pore size distribution. The width of the transition also appears to be correlated with the number of surface cracks; if there is appreciable bulk indium in these cracks the average conductivity of the sample may be different from the average conductivity due to the filaments. If the indium in the cracks has a lower transition temperature than that in the filaments, the transition temperature  $\hat{T}$  will be broadened and lowered depending on the amount of indium in the cracks. This is probably the case for samples *B*, *I*, and possibly *H*; however, the remaining samples are probably more representative of a filamentary structure appropriate to the pore size of the glass.

Yntema, Otter, Stetser, and Warner<sup>19</sup> have recently described the transitions of composite superconductors made by compacting insulating powders and indium powders. These composites are comparable with samples *H*, *J*, and *I*, and shifts in the transition temperature of the same order of magnitude were observed. These shifts in the transition temperature were reasonably well explained on the basis of the stress produced by the differential thermal contraction of the insulator and the metal. For a given metal and insulator the strain is fixed by the temperature change; the stress produced is proportional to  $1/d^2$  and consequently the shift in the transition temperature should be proportional to  $1/d^2$ .

For films of tin, Hall<sup>20</sup> found that shifts in the transition temperature were correlated with the differential thermal expansion for six different substrates; also the shifts produced by stressing the film by bending the substrate were investigated. Shifts in the transition temperature of indium films have also been observed by Toxen.<sup>21,22</sup> It was concluded that the increase in the transition temperature was due to the stress produced by the differential thermal contraction of the film and the substrate; in particular, Toxen found that the increase was proportional to  $1/d_t$  where  $d_t$  was the film thickness.

<sup>19</sup> G. B. Yntema, F. A. Otter, D. A. Stetser, and B. M. Warner, *Bull. Am. Phys. Soc.* **10**, 345 (1965).

<sup>20</sup> P. M. Hall, *J. Appl. Phys.* **36**, 2471 (1965).

<sup>21</sup> A. M. Toxen, *Phys. Rev.* **123**, 442 (1961).

<sup>22</sup> A. M. Toxen, *Phys. Rev.* **124**, 1018 (1961).

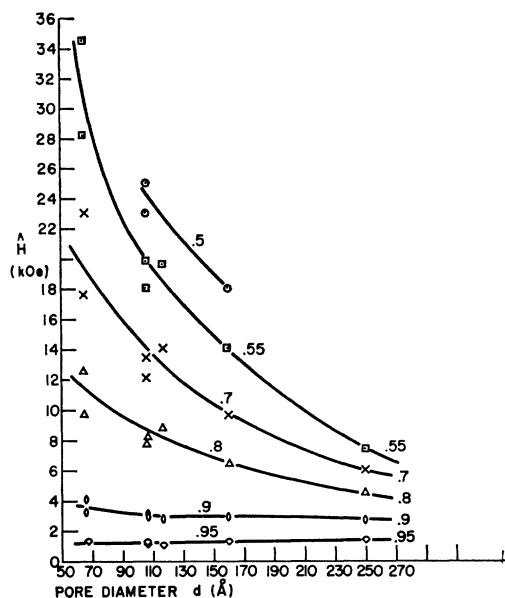


FIG. 6. The critical field  $\hat{H}$  versus sample pore diameter at various values of the reduced temperature.

Recently, Strongin, Kammerer, and Paskin<sup>23</sup> have found that the shift in the transition temperature of aluminum films cannot entirely be accounted for by stress. Following a proposal by Ginzburg,<sup>6</sup> they suggest that the superconducting properties of a layer of thickness  $d_o$  near the surface of the metal film of thickness  $d_t$  may become altered by the presence of a polarizable dielectric layer, namely, aluminum oxide, on the surface. They take account of this using two different electron-electron coupling constants,  $V_o$  near the surface and  $V_n$  in the rest of the film. This approach accounts for their results and they also show that it accounts for Toxen's results.<sup>21,22</sup> When this model is applied to cylindrical geometry it does not account for the linear dependence found here.

Recently, Ginsberg<sup>7</sup> has shown that by reducing the electronic mean free path the transition temperature can be raised. When the mean free path is reduced, both the Debye frequency and the contribution to the electron-electron coupling from the transverse phonons can be changed. Assuming that the mean free path is equal to the pore diameter, this leads to a  $1/d$  dependence for the transition temperature. According to this model there may be an appreciable change in the Debye temperature.

It is possible that all of the mechanisms discussed above may contribute to the increase of  $\hat{T}$ .

### The Critical Field

When a dc magnetic field is applied the resistive transition moves to a temperature which depends upon

<sup>23</sup> M. Strongin, O. F. Kammerer, and A. Paskin, *Phys. Rev. Letters* **14**, 949 (1965).

the applied field  $H$ . The peak in  $\chi''$  is lowered in height and broadened, as shown for sample  $G$  in Fig. 1.

The broadening can be understood as the result of a pore size distribution. For a given field  $H$  each pore size has a different transition temperature; this broadens the transition and lowers the peak height of  $\chi''$ . At lower temperatures because of the  $1/d$  (see below) dependence of the critical field only the indium of the characteristic or smaller pore size contributes significantly to the peak in  $\chi''$ ; the rest of the indium is normal at the highest fields. Samples that have a broad transition in zero dc magnetic field can have the transition narrowed at high field where only indium of the characteristic pore size contributes to the peak in  $\chi''$ .

The demagnetizing factor has a small contribution to the width because the magnetization is very small near  $\hat{H}$  as the penetration of the dc magnetic field is almost complete.<sup>3</sup>

Recently, de Gennes<sup>4</sup> and Maki<sup>5</sup> have predicted the upper critical field,  $H_{c2}$ , as a function of temperature for dirty type II superconductors.

A table of de Gennes's and Maki's value of  $H_{c2}$  versus temperature is given in the Appendix. The prediction is valid over the whole range of temperature between  $t=0$  and 1, as distinct from most predictions for pure type II superconductors which are valid only near  $t=1$ . Near  $t=1$ , de Gennes's and Maki's result coincides with the Ginzburg-Landau<sup>24</sup> result  $H_{c2} = \sqrt{2}\kappa H_c$  when  $\kappa$  is evaluated according to the Abrikosov-Gor'kov<sup>25</sup> prescription for dirty superconductors  $\kappa \approx 0.75 \lambda_L(0)/l$  where  $\lambda_L(0)$  is the London penetration depth in the pure metal at  $t=0$  and  $l$  is the electronic mean

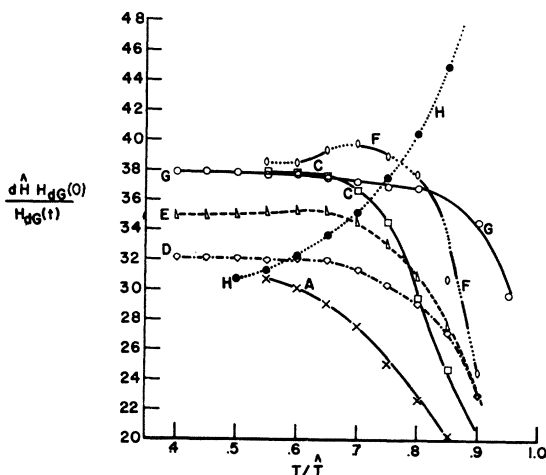


FIG. 7. The product of  $\hat{H}d$  divided by  $H_{dG}(t)/H_{c2}(0)$  the upper critical field according to de Gennes and Maki plotted against reduced temperature.

<sup>24</sup> V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950).

<sup>25</sup> A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **39**, 1791 (1960) [English transl.: Soviet Phys.—JETP **12**, 1243 (1961)].

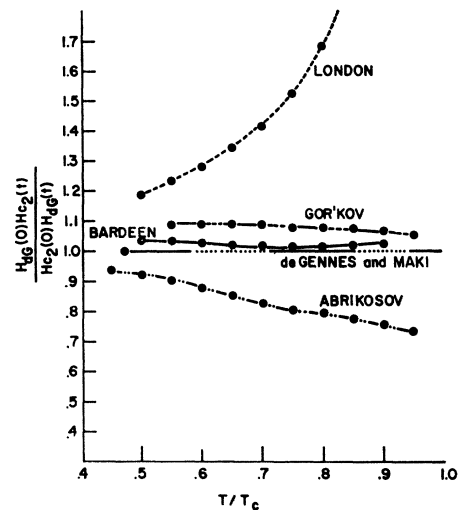


FIG. 8. Various predictions for  $H_{c2}(t)/H_{c2}(0)$  divided by the de Gennes and Maki prediction  $H_{dG}$  plotted against reduced temperature.

free path. In this region of temperature de Gennes and Maki found  $H_{c2}$  varies approximately as  $(1-t)$  and near  $t=0$ ,  $H_{c2} \approx 0.87\lambda_L(0)H_c(0)(1-t^2)/l$ .

If we identify  $\hat{H}$  with  $H_{c2}$  and assume that the electronic mean free path  $l$  is proportional to the pore diameter  $d$ , then  $d\hat{H}(t)H_{c2}(0)/H_{c2}(t)$  ( $=S$ ) should be a constant for all samples between  $t=0$  and 1.  $S$  is plotted against reduced temperature in Fig. 7. For  $t$  less than 0.6,  $S$  is largely constant with temperature for most samples.  $H(250 \text{ \AA})$  deviates from the constant value; sample  $G(160 \text{ \AA})$ , however, is fairly constant below  $t=0.8$ . Above  $t=0.6$  for all samples, except  $H(250 \text{ \AA})$  and  $F(117 \text{ \AA})$ ,  $S$  falls with  $t$ , indicating that  $\hat{H}$  lies below  $H_{c2}$  in this region. For  $F(117 \text{ \AA})$ ,  $S$  shows a maximum before falling with increasing temperature. The behavior of  $H(250 \text{ \AA})$  will be discussed below. Predictions of  $H_{c2}$  valid in this region of temperature have been made for pure type II superconductors by Gor'kov<sup>27</sup>, Ginzburg,<sup>28</sup> Bardeen,<sup>29</sup> and Helfand and Werthamer<sup>30</sup> (similar to the Gor'kov expression). These predictions are compared in Fig. 8. The only prediction that lies below the de Gennes<sup>4</sup> and Maki<sup>5</sup> value in this region is that of Abrikosov; however, it does not fit the results described here very well.

From Fig. 6, it is apparent that above  $t=0.6$  the dependence of  $\hat{H}$  on  $d$  changes. At  $t=0.6$ ,  $\hat{H} \approx 1/d$ ; but at  $t=0.95$ ,  $\hat{H}$  is independent of  $d$ . Using the method of least squares the best fit to  $\log \hat{H}$  versus  $\log d$  at  $t=0.55$  can be obtained, as shown in Fig. 9. The result is in

<sup>26</sup> R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. **120**, 88 (1960).

<sup>27</sup> L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **37**, 833 (1959) [English transl.: Soviet Phys.—JETP **10**, 593 (1960)].

<sup>28</sup> V. L. Ginzburg Zh. Eksperim. i Teor. Fiz. **30**, 593 (1956) [English transl.: Soviet Phys.—JETP **3**, 621 (1956)].

<sup>29</sup> J. Bardeen, Phys. Rev. **94**, 554 (1954).

<sup>30</sup> E. Helfand and N. R. Werthamer, Phys. Rev. Letters **13**, 686 (1964).

good agreement with the de Gennes and Maki prediction of  $H_{c2} \sim 1/d$ . The expression found at  $t=0.55$  was

$$\hat{H}(0.55) = (2020 \pm 220)/d^{(1.00 \pm 0.14)}.$$

Assuming that the  $1/d$  dependence is correct, a least-squares fit to  $\hat{H}$  versus  $1/d$ , as shown in Fig. 10, gives

$$\hat{H}(0.55) = (2015 \pm 46)/d + (0.4 \pm 2).$$

The critical field of bulk indium lies within the standard deviation of the value of 0.4 kOe obtained from this plot. If it is assumed that  $\hat{H}(0.55)/\hat{H}(0) = 0.59$  as predicted by de Gennes, then  $\hat{H}(0) = (3415 \pm 60)/d + (0.4 \pm 2)$ . Reasonable estimates of the value of  $\hat{H}$  at 0°K can be made from Fig. 7 and these values are shown in Table I. From the extrapolations of the individual curves

$$\hat{H}(0)_{\text{extrap}} = (3451 \pm 300)/d$$

and the best fit for the power of  $d$  is  $1.04 \pm 0.10$ . Comparing the de Gennes value at 0°K with the average extrapolated value gives

$$3451/d = 0.87 \lambda_L(0) H_c(0)/l.$$

Taking the free-electron value of the penetration depth,  $\lambda_L(0) = 1.76 \cdot 10^{-6}$  cm, the critical field  $H_c(0) = 0.283$  kOe<sup>25</sup> and the electronic mean free path  $l = d/\alpha$ , it is found that  $\alpha \simeq 8$ , whereas it might be expected that  $\alpha$  should be near unity. From the above discussion it appears that the temperature dependence and the dependence on  $d$  of  $\hat{H}$  are in good agreement with the de Gennes prediction below  $t=0.6$ . From the value of  $\alpha$  it appears that absolute magnitude of  $H_{c2}$  is too low to account for the magnitude of  $\hat{H}$ . A value of  $\alpha$  near 2 can be obtained by using the penetration depth actually observed for pure indium of 640 Å.<sup>31</sup>

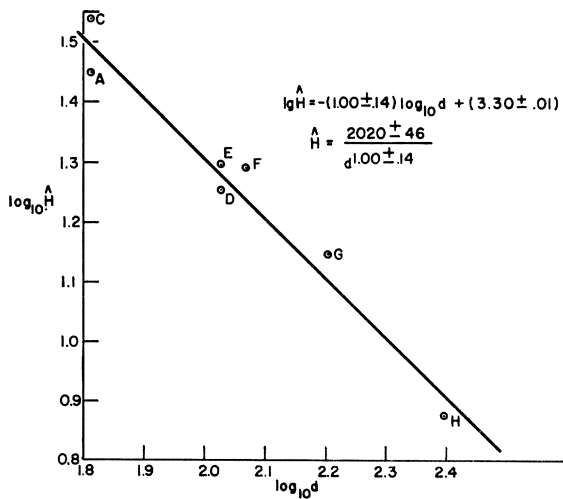


FIG. 9. The  $\log \hat{H}$  against  $\log d$  at  $t=0.55$  for various samples. The line shown is the best least-squares fit.

<sup>31</sup> J. M. Lock, Proc. Roy. Soc. (London) **A208**, 391 (1951).

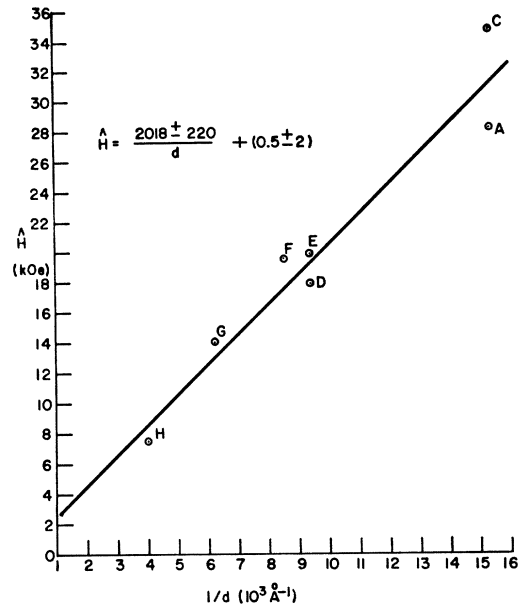


FIG. 10. The critical field  $\hat{H}$  against  $1/d$ . The line shown is the best least-squares fit.

For a thin film or a thin filament of a superconductor, parallel to a magnetic field, the critical field  $h$  can be raised when the small dimension  $d$  is less than the effective penetration depth  $\lambda_{\text{eff}}$ . The original theory due to London<sup>32</sup> and a later theory due to Ginzburg and Landau<sup>24</sup> lead to  $h \sim H_c \lambda_{\text{eff}}(t)/d$ . For the case of dirty superconductors the Bardeen, Cooper, and Schrieffer<sup>33</sup> theory gives  $\lambda_{\text{eff}} = \lambda_L (\xi_0/\xi(l))^{1/2}$  where  $\xi_0$  is the coherence length of the pure metal and  $\xi(l)$  is the coherence length shortened by the electronic mean free path  $l$ . Pippard<sup>34</sup> gives  $1/\xi(l) = 1/\xi_0 + 1/l$  as the form for  $\xi(l)$ . In the presence of diffuse boundary scattering for filaments of the size discussed here  $l \sim d$  and  $\xi(l) \sim l$  so  $h \sim (H_c \lambda_L(0)/d) (\xi_0/l)^{1/2} \sim H_c \lambda_L(0) \xi_0^{1/2}/d^{3/2}$ . More recently de Gennes and Tinkham<sup>35</sup> have examined these results for various values of  $l$ . They find that the results of the simple theory are of the correct form for the cases where  $l < d$  and  $d < l < (\xi_0 d)^{1/2}$ . They also consider a more realistic model of a thin film as being composed of close packed array of spheres and again  $h \sim d^{-3/2}$ . The best power fitting the dependence of  $\hat{H}$  on  $d$  at  $t=0.55$  is  $-1.00 \pm 0.14$ ; the prediction of  $-1.5$  of the above theory is well outside the standard deviation of  $\pm 0.14$  in the results found here. The temperature dependence of the London type theory compared with the de Gennes and Maki theory is shown in Fig. 7. Most of the samples deviate from this behavior; however, sample H (250 Å)

<sup>32</sup> F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950), Vol. I.

<sup>33</sup> J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

<sup>34</sup> A. B. Pippard, Proc. Roy. Soc. (London) **A238**, 175 (1956).

<sup>35</sup> P. G. de Gennes and M. Tinkham, Physics **1**, 107 (1964).

shows a temperature dependence qualitatively similar above  $t=0.5$ .

It is worth considering sample *B* in more detail. This sample has a very broad transition in zero dc magnetic field and the position of the peak in  $\chi''$  is probably representative of an appreciable amount of material not of the characteristic pore size. As the magnetic field increases, the peak in  $\chi''$  moves rapidly to low temperatures because of the low critical field of much of the material present. This results in  $\hat{T}$  being assigned a temperature appreciably lower than the value representative of 65 Å filamentary mesh. As the temperature is lowered the material of low critical field contributes less to the peak in  $\chi''$ ; consequently  $\hat{H}$  moves closer to the curve representative of 65 Å filaments. The low value of  $\hat{T}$  now makes the critical field on the reduced temperature plot lie appreciably above the curve representative of 65 Å filaments. This suggests that the critical field versus temperature curves for all the samples may be lowered in magnitude somewhat near  $t=1$  and raised somewhat at low temperature. For the samples used in the calculations the percentage increase in  $\hat{H}(0)$  must be less than  $(\Delta T/T)100$  which is 3% for the worst case.

## VI. CONCLUSIONS

The critical fields of synthetic high field superconductors appear to follow the de Gennes<sup>4</sup> and Maki<sup>5</sup> prediction for the dependence of  $H_{c2}$  on pore diameter and temperature for values of reduced temperature below  $t=0.6$ . Above  $t=0.6$  there is disagreement, some of which may be due to imperfections in the samples. From the temperature dependences of  $\hat{H}$  it appears that for all samples except *H* (250 Å) the behavior is similar to that of a type II superconductor. Sample *H* with a pore diameter of 250 Å seems to be largely type I in character.

The filamentary superconductors that are type II in nature probably show variations in the order parameter in the form of vortex structures.<sup>36</sup> Some of the filaments will be normal or almost completely normal, but the cores of the vortices will be pinned mainly in the silica. The density of pins is about  $10^{11}/\text{cm}^2$  which is higher than most dislocation densities in inhomogeneous type II superconductors. This high density leads to the very high current-carrying capacities that have been observed in the synthetic high-field superconductors.<sup>1,2</sup>

The dependence of the transition temperature  $\hat{T}$  upon pore diameter  $d$  does not fit the various proposed models very well. In order to investigate the nature of the effect, measurements on smaller pore sizes should be made. If the chemical character of the interior surface of the glass is changed by some means prior to impregnation, any changes produced in  $\hat{T}$  may be revealing.

<sup>36</sup> A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. 32, 1442 (1957) [English transl.: Soviet Phys.—JETP 5, 1174 (1957)].

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## APPENDIX

The equation given by de Gennes<sup>4</sup> and Maki<sup>5</sup> for  $H_{c2}$  for dirty type II superconductors is

$$\ln(T_c/T) = -\Psi(\frac{1}{2}) + \Psi(\frac{1}{2} + hH_{c2}D/2\Phi_0 kT);$$

$D = \frac{1}{3}\nu_F l$  where  $\nu_F$  is the electron velocity at the Fermi surface in the normal state and  $\Phi_0$  is  $2.10^{-7}$  G cm<sup>2</sup>, the

TABLE II. Upper critical field of dirty type II superconductors according to de Gennes (Ref. 4) and Maki (Ref. 5).

$H_{c2}(t)/H_{c2}(0)$	$t$
0.049	0.953
0.129	0.909
0.223	0.800
0.327	0.764
0.411	0.700
0.481	0.643
0.590	0.553
0.662	0.490
0.740	0.416
0.788	0.367
0.851	0.299
0.899	0.238
0.962	0.140
0.996	0.040

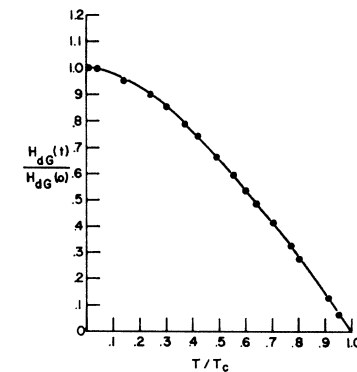


FIG. 11. The upper critical field  $H_{dG}(t)/H_{dG}(0)$  for dirty type II superconductors according to de Gennes and Maki plotted against reduced temperature.

flux quantum.  $\Psi(x) = \Gamma'(x)/\Gamma(x)$ , where  $\Gamma(x)$  is the gamma function. The above equation can be written

$$\ln(1/t) = -\Psi(\frac{1}{2}) + \Psi(\frac{1}{2} + H_{c2}(t)/\exp(-\Psi(\frac{1}{2}))H_{c2}(0) \cdot t).$$

Values of  $H_{c2}(t)/H_{c2}(0)$  are given in Table II and are shown in Fig. 11.