1357 (1961).

 $^{10}R.$  Kubo and Y. Obata, J. Phys. Soc. Japan <u>11</u>, 547 (1956).

<sup>11</sup>The filamentary character of the superconducting state of these "hard" superconductors in relatively weak magnetic fields is apparently the origin of the complete flux penetration in our particles.

<sup>12</sup>In the schematic band structure given in reference 9, the properties of the Ga s and p electrons are treated in terms of admixtures of the wave functions of these electrons into the s and d bands at the V sites. All atomic diamagnetism is neglected.

 $^{13}\langle r^{-3}\rangle$  for V was obtained from A. Abragam, J. Horowitz, and M. H. L. Pryce, Proc. Roy. Soc. (London) <u>A230</u>, 169 (1955) and independently using Watson's Hartree-Fock functions [R. E. Watson, Massachusetts Institute of Technology Report, Solid State Molecular Theory Group  $-\underline{12}$ , 1959 (unpublished); R. E. Watson, Phys. Rev.  $\underline{119}$ , 1934 (1960)].  $\xi$  is assumed to lie between 0.5 and 1.0, representing the expansion of the 3*d* wave functions to be expected in a metal.

<sup>14</sup>P. Morel, J. Phys. Chem. Solids <u>10</u>, 277 (1959).

<sup>15</sup>C. H. Cheng, K. P. Gupta, E. C. van Reuth, and

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<sup>16</sup>See reference 9 for the values of s and d hyperfine fields.

<sup>17</sup>J. Butterworth, Phys. Rev. Letters <u>5</u>, 305 (1960).

<sup>18</sup>The possibility that orbital paramagnetism is important to the NMR properties of V metal was suggested by L. Orgel, J. Phys. Chem. Solids 21, 123 (1961).

## UPPER LIMIT FOR THE CRITICAL FIELD IN HARD SUPERCONDUCTORS

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Recently a number of reports have been made of extremely high critical fields observed in certain hard superconductors.<sup>1-7</sup> It is generally believed that these high critical fields arise from some sort of filamentary structure of the hard superconductors, possibly associated with dislocations.<sup>1-10</sup> A recent Letter,<sup>11</sup> reporting observations of nuclear magnetic resonance in the intermetallic compounds V<sub>3</sub>Si and V<sub>3</sub>Ga, shows that the spin susceptibility of these materials is reduced in the superconducting state at T = 0 by more than 75% over the normal state. This observation sets a severe upper limit on the attainable critical field for these materials.

In a homogeneous, bulk superconductor, the transition from the superconducting to the normal state in a magnetic field occurs because of the extra free energy associated with the superconducting state due to the Meissner effect. If  $F_N$  and  $F_S$  are the free energies per unit volume of the normal and superconducting state, the critical field  $H_0$  is given by

$$F_N = F_S + H_0^2 / 8\pi.$$
 (1)

In a thin cylindrical conductor, the free energy associated with the Meissner effect is greatly reduced by partial penetration of the magnetic field. If the conductor is very thin, the critical field can be extremely large. Hauser and Hel-fand<sup>9</sup> find an enhancement factor of 45 for filaments of 400Å diameter.

We wish to point out that the critical fields

observed and predicted for various superconductors are so high that they are approaching a limit that will exist even in the limit of no Meissner effect. In the normal state, a metal has a paramagnetic susceptibility  $\chi_p$  due to the density of states at the Fermi level. In a magnetic field, the free energy will be lowered by an amount  $\frac{1}{2}\chi_p H^2$ . According to the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity,<sup>12</sup> a superconductor at absolute zero will have no susceptibility due to electrons at the Fermi level. If this condition is realized in practice, in the absence of any Meissner effect, we should write in place of Eq. (1) at absolute zero.

$$F_N - \frac{1}{2}\chi_{\rho} H_0^2 = F_S.$$
 (2)

In this equation we ignore the presence of any orbital paramagnetism that will be essentially the same in the normal and superconducting state. In terms of the density of states N(0),  $\chi_p = 2\mu_B^{2N}(0)$ , assuming a g factor equal to 2. According to the BCS theory<sup>12</sup> the free-energy difference  $F_N - F_S = \frac{1}{2}N(0)\epsilon_0^2(0)$ , where  $\epsilon_0(0)$  is the energy gap at T = 0. Equation (2) therefore becomes

$$(\mu_B H_0)^2 N(0) = \frac{1}{2} N(0) \epsilon_0^2(0)$$

or

$$\mu_{B}H_{0} = (1/\sqrt{2})\epsilon_{0}(0) \tag{3}$$

with the density of states cancelling out. If we

assume  $2\epsilon_0(0) = 3.5kT_c$ , Eq. (3) yields

$$H_0 = 18400 T_c$$
 gauss. (4)

Equation (2) is essentially a result of perturbation theory. The use of perturbation theory in a similar problem has been discussed by Suhl and Matthias.<sup>13</sup> The difficulties discussed in that case do not arise for the present problem since the transition induced by the magnetic field will be of first order with the energy gap remaining finite.

If the susceptibility of the superconducting state is reduced from that of the normal state by a fraction  $\alpha$ , the right-hand side of Eq. (4) should be divided by  $1/\sqrt{\alpha}$ . If  $\alpha = 0.75$ , the critical field given in Eq. (4) is greater by a factor 1.16. If many-body effects are considered in the normal state of the metal, the susceptibility  $\chi_p$  will be reduced by a factor 1 + VN(0) where V is the average matrix element used by BCS.<sup>11</sup> The critical field given by Eq. (4) will be increased by a factor  $[1 + VN(0)]^{\nu 2}$ . Using data from reference 11 this factor will be at most about 1.18. These two effects taken together could increase the critical fields by 30% over Eq. (4).

Low-current critical fields have been measured by Wernick et al.<sup>7</sup> as a function of temperature on a series of  $\beta$ -wolfram compounds. For many of these materials the critical fields are so high that they can be measured only near  $T_c$ . The values near T = 0 must be obtained by extrapolation and are estimated to lie within the limits given in Table I. We also include in Table I the transition temperatures  $T_c$  observed for these materials, and the maximum critical field allowed by Eq. (4). It is evident that the critical field for  $V_{2.95}$ Ga will be limited by our criterion to values considerably smaller than those estimated. For Nb<sub>3</sub>Sn and V<sub>3</sub>Si the theoretical limit enters at the upper range of the estimated values.

Table I. Maximum and estimated critical fields at T = 0.

| Material                                  | Estimated critical<br>field<br>(kilogauss) | Т <sub>с</sub><br>(°К) | Maximum critical field<br>from Eq. (4)<br>(kilogauss) |
|---|--|------------------------|---|
| V <sub>2.95</sub> Ga                      | 350 - 700                                  | 14.5                   | 266   |
| Nb <sub>3</sub> Sn<br>V Si                | 180 - 340                                  | 17.8                   | 328   |
| V <sub>3</sub> 51<br>V <sub>1.95</sub> Ga | 80 - 90                                    | 5.0                    | 92  |

For  $V_{1.95}$ Ga the limit set by Eq. (4) may have already been reached. An interesting application of Eq. (4) has been made by Berlincourt and Hake<sup>14</sup> to the low current density critical fields of various transition metal alloys.

We conclude that the critical fields that obtain for the  $\beta$ -wolfram compounds are so high that they may be effectively limited at low temperatures by the normal-state paramagnetism. If this is the case, critical fields higher than about 300 kilogauss will not be realized unless materials can be discovered with higher transition temperatures.

<sup>4</sup>J. E. Kunzler, in <u>Proceedings of the International</u> <u>Conference on High Magnetic Fields, Massachusetts</u> <u>Institute of Technology, November, 1961</u> (Massachusetts Institute of Technology Press, Cambridge, Massachusetts and John Wiley & Sons, Inc., New York, 1962), p. 574.

<sup>5</sup>H. R. Hart, I. S. Jacobs, C. L. Kolbe, and P. E. Lawrence, in <u>Proceedings of the International Con-</u> <u>ference on High Magnetic Fields, November, 1961</u> (Massachusetts Institute of Technology Press, Cambridge, Massachusetts, and John Wiley & Sons, Inc., New York, 1962), p. 584.

<sup>6</sup>R. G. Treuting, J. H. Wernick, and F. S. L. Hsu, in <u>Proceedings of the International Conference on</u> <u>High Magnetic Fields, Massachusetts Institute of</u> <u>Technology, November, 1961</u> (Massachusetts Institute of Technology Press, Cambridge, Massachusetts, and John Wiley & Sons, Inc., New York, 1962), p. 597.

<sup>7</sup>J. H. Wernick, F. J. Morin, F. S. L. Hsu, D. Dorsi, J. P. Maita, and J. E. Kunzler, in <u>Proceedings of the International Conference on High Magnetic</u> <u>Fields, Massachusetts Institute of Technology, November, 1961</u> (Massachusetts Institute of Technology Press, Cambridge, Massachusetts, and John Wiley & Sons, Inc., New York, 1962), p. 609.

<sup>8</sup>R. Shaw and D. E. Mapother, Phys. Rev. <u>118</u>, 1474 (1960).

<sup>9</sup>J. J. Hauser and E. Helfand, Phys. Rev. <u>127</u>, 386 (1962).

<sup>10</sup>J. J. Hauser and E. Buehler, Phys. Rev. <u>125</u>, 142 (1962).

<sup>11</sup>A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, preceding Letter [Phys. Rev. Letters <u>9</u>, 262 (1962)].

<sup>-12</sup>J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. <u>108</u>, 1175 (1957).

<sup>13</sup>H. Suhl and B. T. Matthias, Phys. Rev. <u>114</u>, 977 (1959).

<sup>14</sup>T. G. Berlincourt and R. R. Hake (private communication).

<sup>&</sup>lt;sup>1</sup>J. E. Kunzler, Revs. Modern Phys. <u>33</u>, 1 (1961).

<sup>&</sup>lt;sup>2</sup>J. E. Kunzler, J. Appl. Phys. <u>33</u>, 1042 (1962).

<sup>&</sup>lt;sup>3</sup>T. G. Berlincourt, R. R. Hake, and D. H. Leslie, Phys. Rev. Letters 6, 671 (1961).