UPPER CRITICAL FIELDS OF TRANSITION METAL ALLOY SUPERCONDUCTORS*

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The persistence of superconductivity at very high magnetic fields has commonly been attributed[1-4] to the existence of a network of small cross-section "high-critical-field" supercurrent-carrying filaments (possibly associated with dislocations[2,3]) embedded in a matrix of low-critical-field material. We present below an alternative interpretation based on (1) pulsed-magnetic-field data on the low-current-density resistive critical fields $H_r(J \lesssim 10\ \mathrm{A/cm^2})$ of concentrated transition metal alloys, (2) the Ginzburg-Landau-Abrikosov-Gor'kov (GLAG) theory,[5-7] and (3) a paramagnetically limited critical-field criterion due to Clogston.[8] The arguments set forth add weight to evidence already cited by Goodman[9] in support of a negative-surface-energy picture for alloy superconductors with short electronic mean free path.

The data of Fig. 1, which are typical of results obtained on several cold-rolled alloys, show that for low-current densities ($J \lesssim 10\ \mathrm{A/cm^2}$) a detectable resistance (~5% of the normal state resistance in this study) appears at a magnetic field which is nearly independent of (1) the amount of cold working and (2) the relative orientations of H, J, and the rolling plane (which apparently determines the orientation of an anisotropic defect structure having considerable influence on H_r at higher current densities[10,11]). Although (1) might be interpreted via a filamentary model,[2,3,12] the evidence (1) and (2) may, on the other hand, indicate that H_r $(J \lesssim 10)$ is a parameter which is simply related to the electronic character of the bulk alloy superconductor quite independent of dislocation considerations. The latter possibility is supported by the data of Fig. 2, which show that for alloys in the systems Ti-V, Ti-Nb, Zr-Nb, and Ti-Mo, H_r $(J=10,\ T=1.2°\mathrm{K})$ is a smoothly varying function of the average number of "valence" electrons per atom

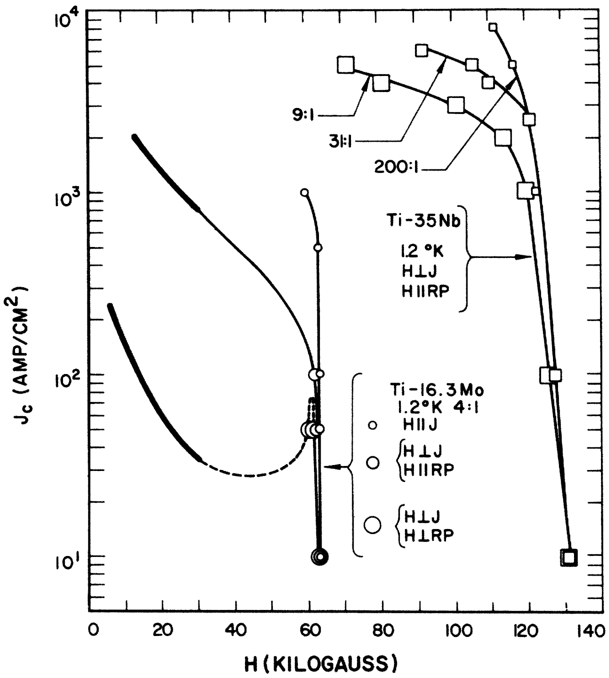

FIG. 1. Typical illustrations of the independence of H_r $(J \lesssim 10)$ upon cold working and relative orientations of H, J, and rolling plane (RP) defect structure. The ratios indicate cold-rolling thickness reductions; heavy lines represent steady-field data; and the dashed line is an approximate representation based on observed resistance transitions.

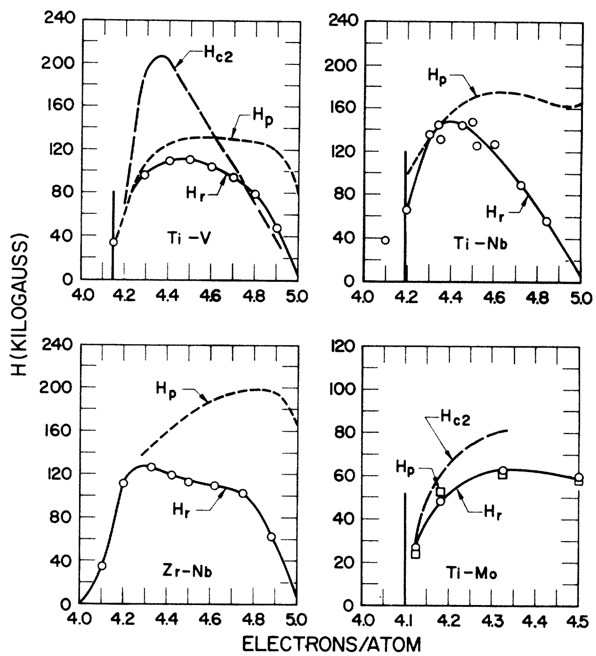

FIG. 2. H_r $(J=10,\ T=1.2°\mathrm{K})$ vs average valence electron concentration for cold-rolled alloys in the systems Ti-V, Ti-Nb, Zr-Nb, and Ti-Mo. Comparison is made with H_{c_2} and H_p calculated, respectively, according to the GLAG theory [Eq. (3)] and Clogston's correlation [Eq. (4)]. Vertical lines indicate approximate alloy phase stability limits.

e/a. The peaking evident for three of these systems between 4 and 5 e/a also occurs typically for such nondislocation-controlled alloy parameters as critical temperature T_c, thermodynamic critical field H_c, and electronic specific heat coefficient γ.

The GLAG theory predicts that the high-field super-normal transition in an alloy superconductor should occur at a field determined by just such bulk electronic parameters. According to this theory there exist two classes of superconductors distinguishable on the basis of their respective values for the coupling parameter κ of the Ginzburg-Landau theory.[5] For concentrated alloys, where $\kappa > 1/\sqrt{2}$, magnetic-field penetration into the bulk of the material commences at a field $H_{c1} < H_c$ forming a macroscopically uniform "mixed state" characterized, according to Abrikosov,[6] by a regular lattice array of quantized supercurrent vortices (analogous in some respects to the superfluid vortices thought to occur in He II[13]) extending throughout the bulk of the material.[14] This mixed state persists to an "upper critical field,"[15]

$$H_{c2} = \sqrt{2}\,\kappa H_c, \tag{1}$$

where flux penetration is complete and a second-order transition to the normal state occurs.[16] Gor'kov[7] has suggested that when the electronic mean free path is much less than the Bardeen-Cooper-Schrieffer[17] (BCS) coherence length, ξ_0, then

$$\kappa = 7.53\times 10^3\, \rho_n \gamma^{1/2}, \tag{2}$$

where γ is expressed in erg cm^{-3} deg^{-2}, and ρ_n (the normal state resistivity) is expressed in ohm-cm. From Eqs. (1) and (2) and the approximations $\gamma T_c^2/H_0^2 \approx 0.17$ [Eq. (3.40) of BCS] and $H_c \approx H_0 \times[1-(T/T_c)^2]$, it follows that

$$H_{c2} \approx 2.58\times 10^4\, \rho_n \gamma T_c[1-(T/T_c)^2]. \tag{3}$$

For values of ρ_n, γ, and T_c typical of Group IV-Group V transition metal alloys, this equation predicts a pronounced peaking in H_{c2} (much more pronounced in fact than in γ, H_c, or T_c) between 4 and 5 e/a in qualitative accord with our experimental results on H_r ($J=10$, $T=1.2$°K), Fig. 2. Furthermore, for concentrated alloys, ρ_n, γ, and T_c, and consequently H_{c2}, should be relatively independent of the degree of cold working, in accord with the behavior of H_r ($J=10$) in Fig. 1.

A more direct comparison between theory and experiment is possible for Ti-Mo and Ti-V alloys. Using the present pulsed-field resistivity data (ρ_n) and the calorimetric data (γ, T_c) of Hake[18] on Ti-Mo alloys and Cheng et al.[19] on Ti-V alloys, we have calculated values of H_{c2} ($T=1.2$°K) from Eq. (3). These values are compared with H_r ($J=10$, $T=1.2$°K) in Fig. 2. Fair quantitative accord is obtained except in the vicinity of 4.3 to 4.5 e/a in the Ti-V system where the maximum discrepancy approaches a factor of two.

The failure of Eq. (3) for Ti-V alloys in this composition range might be attributed to the neglect in the GLAG formulation of paramagnetic free energy terms. As pointed out by Pippard and Heine,[20] the energy gain $2\mu_B H$ (where μ_B is the Bohr magneton) resulting from electron spin alignment along H should become important in fields of the order of 100 kilogauss, where it begins to approximate the opposite-spin-paired superconducting state gap energy $2\epsilon_0 \approx 3.5kT_c$. That this circumstance might impose a limitation on high-field superconductors was noted independently by Chandrasekhar[21] and Clogston.[8] For $T/T_c \ll 1$, Clogston has estimated an approximate paramagnetically limited critical field,

$$H_p \approx (\epsilon_0/\sqrt{2}\,\mu_B)[1-(T/T_c)^2] = 1.84\times 10^4 T_c[1-(T/T_c)^2], \tag{4}$$

simply by equating the usual super-normal free-energy difference $H_c^2/8\pi$ to the Pauli paramagnetic energy $\frac{1}{2}\chi_p H_p^2 = \mu_B^2 N(E_F) H_p^2$, where $N(E_F)$ is the electronic density of states at the Fermi level. (Because H_p is merely a limiting value, the magnetic-field dependence of ϵ_0 is not considered.) A more rigorous derivation would encounter uncertainties arising from (1) the nonvanishing Knight shift in superconductors and (2) diamagnetic, exchange, and correlation contributions to the susceptibility. Nevertheless, in Fig. 2 we compare values of H_p calculated from Eq. (4) with H_r ($J=10$, $T=1.2$°K).[22] It appears that paramagnetic energy considerations are relatively unimportant for the Group V-rich alloys, for which ρ_n is relatively low, and H_r ($J=10$, $T=1.2$°K) values are probably in fair accord with Eq. (3). However, for the Group IV-rich alloys, H_p so closely approximates H_r ($J=10$, $T=1.2$°K) as to suggest that a firm theoretical basis for the introduction of paramagnetic energies into the GLAG formulation should be sought.

The above considerations suggest that the GLAG theory may serve as a first approximation in accounting for the properties of high-field alloy superconductors. Aside from modification to include paramagnetic energies, extensions of the theory are required to take account of the effect of transport supercurrents, and to explain the ability of extended lattice defects in alloy superconductors to cause the typical (1) flux trapping[23] and (2) critical current enhancement, anisotropy, and "peak effect"[10] at large transport supercurrent densities (all apparent in Fig. 1). Attempting an analogy with the trapping of superfluid vortices on wires in He II,[13] one may speculate that extended lattice defects (especially dislocations) might serve as supercurrent vortex anchors.[24] Such stabilization of the flux-enclosing vortex structure might allow flux trapping and relatively large high-field critical currents.

A more detailed description of this work will be published elsewhere, along with additional data on the similarly behaving systems Ti-Ta, Hf-Nb, and Hf-Ta.

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[12]Filamentary model arguments that H_r ($J \rightarrow 0$) should be independent of the amount of cold working would also predict an absence of high-field superconductivity in a dislocation-free alloy, contrary to predictions of the GLAG theory.

[13]For a review of theory and experiment, see W. F. Vinen in Progress in Low-Temperature Physics, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1961), Vol. III, p. 1 ff.

[14]Independent vortex theories for hard superconductors (similar in some respects to that of Abrikosov) have been proposed by A. J. Glick and R. A. Ferrell, Bull. Am. Phys. Soc. 7, 324 (1962) and G. B. Yntema (private communication).

[15]Extensions of Abrikosov's theory by Gor'kov (reference 7) and E. A. Shapoval {J. Exptl. Theoret Phys. (U.S.S.R.) 41, 877 (1961) [translation: Soviet Phys.—JETP 14, 628 (1962)]} introduce temperature-dependent coefficients into Eq. (1). Existing data do not permit a choice between Eq. (1) and Gor'kov's proposal, but a nearly parabolic temperature dependence of H_r ($J=10$) observed in this work appears to contradict Shapoval's extension.

[16]The GLAG model appears to be in qualitative accord with the recent measurements of F. J. Morin, J. P. Maita, H. J. Williams, R. C. Sherwood, J. H. Wernick, and J. E. Kunzler [Phys. Rev. Letters 8, 275 (1962)], who showed that the high-field superconducting transition in V_3Ga occurs without latent heat after nearly complete flux penetration and involves a large fraction of the electronic assembly. It is significant that the calorimetrically determined bulk high-field transitions occur at fields nearly coincident with resistive critical fields H_r ($J=1$ A/cm^2) in accord with the experimental identification of H_r ($J \lesssim 10$ A/cm^2) with H_{C2} in the present paper.

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[24]Interesting mechanisms for trapping of supercurrent vortices have been advanced by G. B. Yntema (private communication).