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Report

THE PARAMAGNETIC LIMIT IN TYPE II SUPERCONDUCTORS

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THE PARAMAGNETIC LIMIT IN TYPE II SUPERCONDUCTORS

by

R. HANCOX

ABSTRACT

The critical field of a type II superconductor is reduced by the paramagnetic susceptibility of the normal phase. Theory and experiment are compared and it is shown that for high field superconductors the paramagnetic limit is 30 to 40% higher than is generally assumed. The temperature variation of the critical field is calculated, and used to estimate the critical field of the superconducting compound V_3Ga .

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C O N T E N T S

INTRODUCTION

If the range of coherence ξ in a superconductor is less than the penetration depth λ it is a superconductor of the second kind, and because there is a negative interphase surface energy it no longer exhibits a complete Meissner effect. Many of the properties of such a superconductor can be calculated from the Ginzburg-Landau-Abrikosov-Gor'kov (GLAG) theory using the dimensionless parameter.

$$\kappa \approx \lambda/\xi \qquad \text{... (1)}$$

The GLAG theory predicts an upper critical field H_{c2} at which a superconductor returns to the normal state. The transition is of second order, and H_{c2} is given by

$$H_{c2} = \sqrt{2}\ \kappa\ H_c \qquad \text{... (2a)}$$

where H_c is the thermodynamic critical field. More detailed consideration of the theory shows that there is a slight temperature variation of κ and that equation (2a) is more accurately

$$H_{c2} = \sqrt{2}\ \kappa_1\ H_c \qquad \text{... (2b)}$$

where the ratio κ_1/κ is unity at the transition temperature T_c and increases to about 1.25 at zero temperature. Since the parameter κ can be estimated for many materials, equation (2) can be verified. For example, the alloy V-15% Ti at a temperature of 1.2°K has $\kappa = 21$ and $H_c = 1.95$ kG, giving a calculated $H_{c2} \approx 74$ kG compared with a measured value of 69 kG.

Not all materials, however, exhibit a critical field as high as that given by equation (2). This has been explained by both Clogston [(1)] and Chandrasekhar [(2)], who pointed out that the free energy of the normal state is reduced in a magnetic field due to the Pauli paramagnetic susceptibility of normal metals. Clogston calculated that this imposed an upper limit for the critical field of any superconductor, given by

$$H_p = 18400\ T_c \qquad \text{... (3)}$$

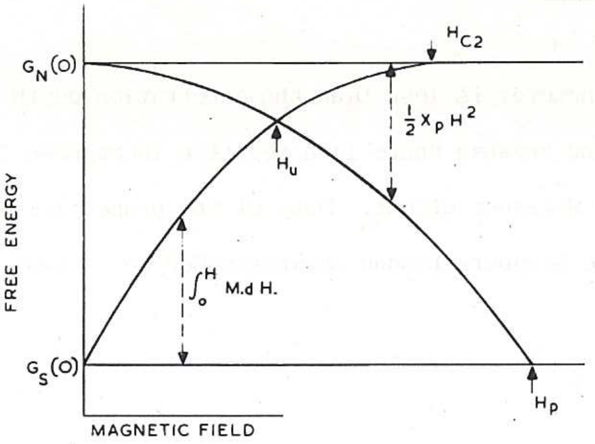

Fig. 1 (CLM-R60)
Free energy diagram for the superconducting and normal states

These two criteria for the critical field of a type II superconductor, represented by equations 2 and 3, are shown diagrammatically in Fig.1 in which the free energies of the normal and superconducting states are plotted as a function of the magnetic field. At zero field the energy difference is equal to the condensation energy of the superconducting electrons

$$G_N(0) - G_S(0) = \tfrac{1}{2}\,\varepsilon^2\,N(0) = H_c^2/8\pi,$$

where $2\,\varepsilon$ is the superconducting energy gap ($\approx 3.5\,\kappa\,T_c$) and $N(0)$ is the density of the states at the Fermi surface. As the magnetic field is increased the energy of the superconducting state increases due to the magnetisation of the superconductor and in the absence of the paramagnetic effect a transition would occur when $\int_0^{H_{c2}} MdH = H_c^2/8\pi$ at the upper critical field H_{c2} defined by equation (2). Alternatively, in the absence of any magnetisation the transition would occur when $\tfrac{1}{2}\,\chi_p H_p^2 = H_c^2/8\pi$ at the Clogston limit H_p defined by equation (3). In practice both effects are always present and a first order transition occurs when the free energies of the normal and superconducting states are equal, represented by H_u in Fig.1.

From Fig.1 it is obvious that the upper critical field calculated from GLAG theory (equation (2)) is only correct when it is much lower than the paramagnetic limit (equation (3)) and that otherwise the observed critical field will be less than either H_{c2} or H_p.

EXPERIMENTAL EVIDENCE FOR THE PARAMAGNETIC LIMIT

Confirmation of the ideas outlined above was obtained by Berlincourt and Hake[3], from a study of the critical fields of a range of superconducting alloys. Calculated values of H_{c2} and H_p were compared with measured critical fields as a function of alloy composition. The results of the Ti-V system, for which most information was available, are shown in Fig.2 and it is seen that the critical field is determined by both H_{c2} and H_p and is always less than either of them.

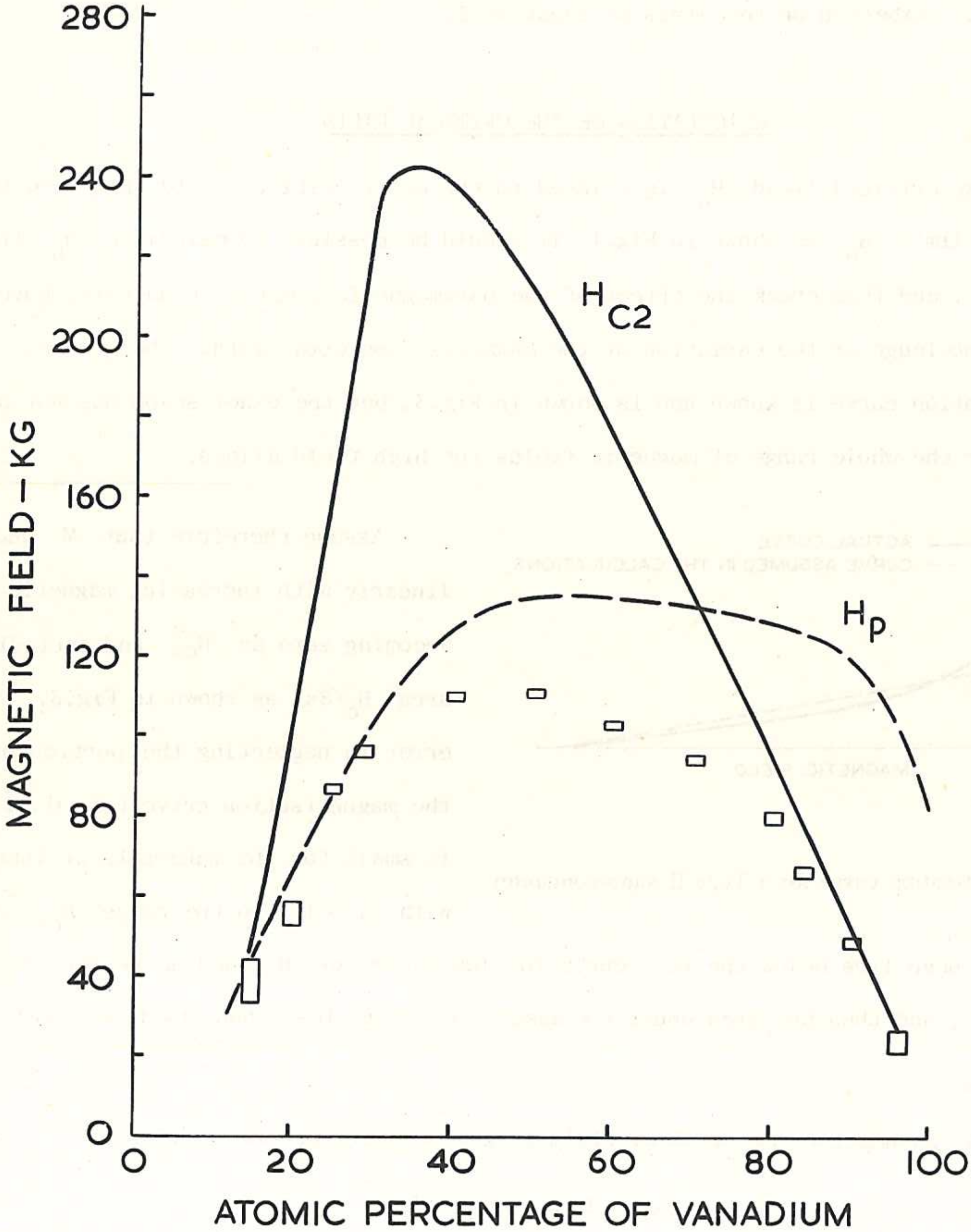

Fig. 2 (CLM-R60)

Experimental results of Berlincourt and Hake for Ti-V compared with calculated values of the upper critical field H_{c2} and the Clogston limit H_p

More recently Kim, Hempstead and Strnad[4] have developed a method of measuring H_{c2} by the extrapolation of low field flux flow data, and confirmed some of the calculated values of H_{c2} shown in Fig.2. Similar measurements by Shapira and Neuringer[5] have confirmed the calculated values of H_{c2} for two Nb-Ti alloys. There is, therefore conclusive evidence that the measured critical field of several alloys is well below the upper critical field H_{c2} expected on the basis of equation 2.

CALCULATION OF THE CRITICAL FIELD

Since the critical field H_u is related to the upper critical field H_{c2} and the paramagnetic limit H_p as shown in Fig.1, it should be possible to calculate H_u from H_{c2} and H_p, and thus check the effect of the paramagnetic limit. To do this, however, requires a knowledge of the variation of the magnetisation with field. The general form of the magnetisation curve is known and is shown in Fig.3, but the exact shape has not been measured over the whole range of magnetic fields for high field alloys.

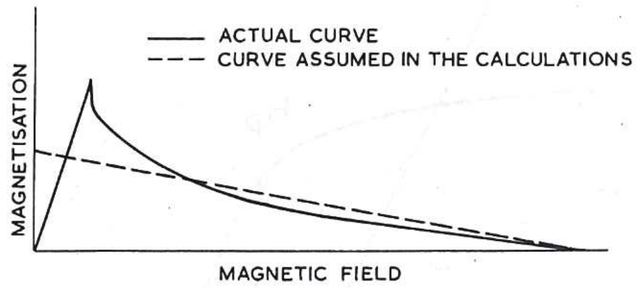

Fig. 3 Magnetisation curve for a Type II superconductor

Assume therefore that M decreases linearly with increasing magnetic field, becoming zero at H_{c2} and enclosing an area $H_c^2/8\pi$ as shown in Fig.3. The error in neglecting the portion of the magnetisation curve for $0 < H < H_{c1}$ is small for the materials of interest with $\kappa \gg 1$. In the range $H_{c1} < H < H_{c2}$ the assumed curve lies below the real curve for low values of H, and above for high values of H, and thus the area under the assumed curve is less than under the real curve, except at H_{c2}.

With this assumption the critical field at zero temperature is found to be

$$H_u = H_p H_{c2}/(H_p + H_{c2}) \qquad \ldots (4)$$

Equation 4 has been evaluated for the Ti-V system and compared (neglecting small temperature effects) in Fig.4 with the measurements of Hake and Berlincourt taken at $1.2^\circ K$. It is seen that in general the calculated critical field H_u is about 30% below the measured resistive transitions.

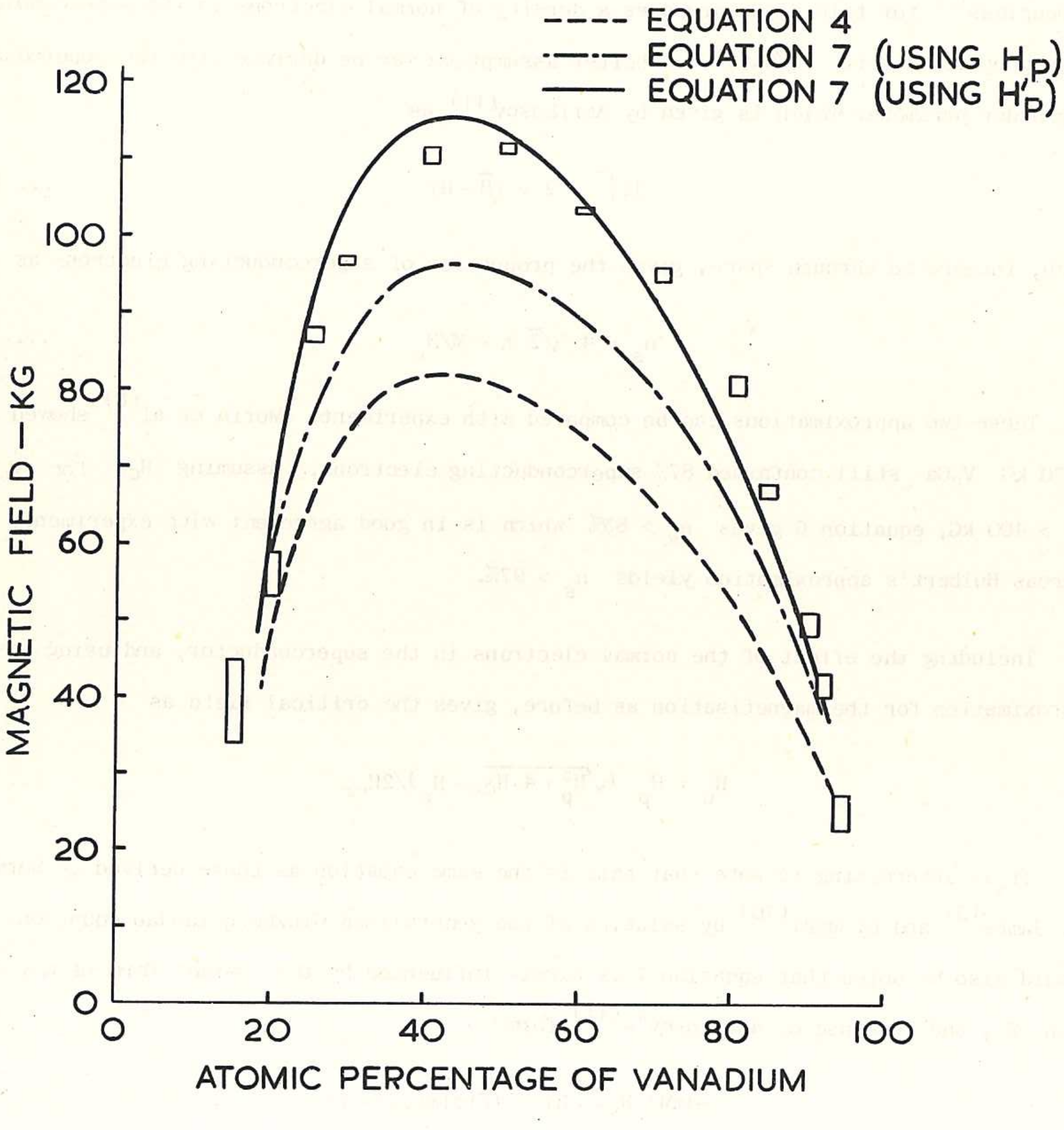

Fig. 4 (CLM - R 60)

Comparison between calculated critical fields for the Ti-V system and the experimental results of Berlincourt and Hake

It has already been pointed out by Hulbert[6] that the paramagnetic limit calculated by Clogston is only true in the limit $\kappa \to \infty$ since it is assumed that all the electrons in the superconductor are paired. In general where $H_{c2} \approx H_p$ the superconducting energy gap will be reduced by the magnetic field, adding a paramagnetic contribution to the free energy of the superconductor, and increasing the free energy difference between the normal and superconducting states. Hulbert, using the variation of energy gap with field deduced by Douglass[7] for thin films proposes a density of normal electrons in the superconducting state proportional to $(H/H_{c2})^2$. A better assumption may be derived from the superconducting order parameter which is given by Abrikosov[11] as

$$|\psi|^2 = 2\,\kappa\,(\bar{H} - H) \qquad \ldots (5)$$

which, integrated through space, gives the proportion of superconducting electrons as

$$n_s = 4\,\sqrt{2}\,\pi\,\kappa\,M/H_c \qquad \ldots (6)$$

These two approximations can be compared with experiment. Morin et al[8] showed that at 70 kG V_3Ga still contained 87% superconducting electrons. Assuming H_{c2} for V_3Ga as > 400 kG, equation 6 gives $n_s > 83\%$ which is in good agreement with experiment, whereas Hulbert's approximation yields $n_s > 97\%$.

Including the effect of the normal electrons in the superconductor, and using the same approximation for the magnetisation as before, gives the critical field as

$$H_u = H_p\;(\sqrt{H_p^2 + 4\,H_{c2}} - H_p)/2H_{c2} \qquad \ldots (7)$$

It is interesting to note that this is the same equation as those derived by Sarma and St. James[9] and by Maki[10] by solution of the generalised Ginzberg-Landau equation. It should also be noted that equation 7 is hardly influenced by the assumed form of magnetisation M, and that use of Abrikosov's[11] form

$$-4\pi M/(H_{c2} - H) = 1/1.18(2\kappa^2 - 1) \qquad \ldots (8)$$

which is more accurate when $H \approx H_{c2}$, gives exactly the same equation.

The critical field H_u calculated from equation 7 is also compared with the experimental results of Berlincourt and Hake in Fig.4, and once again H_u is found to be less than the measured critical fields.

MAGNITUDE OF THE PARAMAGNETIC LIMIT

The discrepancy between the calculated and measured values of the critical field in Ti-V alloys is thought to be due to an over-estimate of the paramagnetic effect. Before accepting this view, however, it is necessary to consider other sources of error.

It is possible that the measured critical fields do not represent the limit of superconductivity in the bulk of the material but only surface effects. It is well known that there is a surface critical field H_{c3} which is 70% higher than the bulk critical field H_{c2}. The agreement between the measured critical fields obtained by several authors, and the independence of results on the size and shape of the specimens suggests, however, that the measured fields are bulk properties. Again, the agreement between the calculated H_{c2} of Berlincourt and Hake and the measured values of H_{c2} of Kim et al make it unlikely that the upper critical field data is wrong. Another possible source of error is the use in theory of the reversible magnetisation curve for a heavily cold worked material which would undoubtedly show an irreversible magnetisation. The results of Shapira and Neuringer, however, were obtained with annealed specimens and again show the same discrepancies.

Having ruled out the more obvious causes for the difference between measured and calculated critical fields it is permissible to question the magnitude of the paramagnetic limit H_p. In discussing this question Clogston pointed out that the calculated value of the electron spin susceptibility would be reduced by $\sim (1+N(0)V)$ if many-body effects were considered in the normal state, and hence H_p would be increased by $(1+N(0)V)^{\frac{1}{2}}$. For Ti-V alloys $N(0)V$ is about 0.29, and hence H_p will be increased by about 14%. It is also uncertain whether all the d band electrons, which lead to superconductivity in the transition metal alloys, are paired, although in V_3Ga and V_3Si it has been shown that at least 75% are paired at zero temperature, leading to an uncertainty in H_p of up to 16%.

Another source of error is that Clogston assumes the energy gap to be equal to 3.5 kT_c, the classical B.C.S. value, but in alloys with a low Debye temperature the gap will be slightly greater, and H_p will be increased by up to 14%. Thus it is found that in many of the materials of particular interest H_p should be 30-40% higher than the value given by equation 3.

Using this increased value of the Clogston limit H_p', the critical field has again been calculated from equation 7 and compared in Fig.4 with the measured values of Berlincourt and Hake. With H_p increased by 30% the fit between theory and experiment is reasonable. A similar calculation also gives agreement with the critical fields of the two Nb-Ti alloys measured by Shapira and Neuringer.

TEMPERATURE DEPENDENCE OF THE PARAMAGNETICALLY LIMITED CRITICAL FIELD

The temperature dependence of the paramagnetic limit has been calculated by Maki[12], but is not expressed in a usable analytic form. Equation 7 may be used at any temperature, however, by including the temperature dependence of the thermodynamic critical field H_c and the temperature dependent Ginzberg-Landau parameter κ_1 used in equation 2b. This leads to a family of curves for the temperature dependent critical field $H_u(t)$, shown in Fig.5, the exact shape depending on the ratio H'_p/H_{c2} at zero temperature.

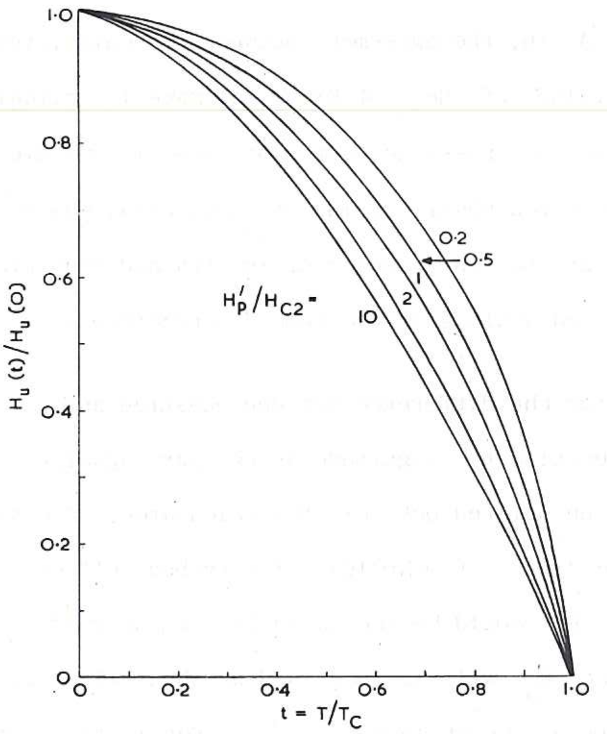

Fig. 5 Variation of critical field H_u with temperature

Using the curves of Fig.5 the effect of temperature on the critical field of Nb-56% Ti alloy has been calculated and compared with the experimental values of Shapira and Neuringer. Agreement is reasonable for H_{c2} = 200 kG (which is close to their measured value) and H'_p = 260 kG which is 40% above the value calculated by Clogston.

The curves of Fig.5 may also be compared with the experimental results of Jones, Hulm, and Chandrasekhar[13] for Nb-Ti and Nb-Zr alloys, which have been interpreted in the past as showing a variation of the form of the temperature dependent parameter κ_1/κ with alloy composition. Since, however, for these alloys H_p is almost constant whilst H_{c2} varies with composition, it is more reasonable to suppose that the experimental curves simply reflect a varying paramagnetic effect. The same criticism applies to several other experimental studies of the variation of κ_1/κ, and for this reason there is some uncertainty as to the exact shape of the curves of Fig.5, which assumed the computed value of κ_1 by Helfand and Werthamer[14]. The relative shapes of the curves do not depend on the values assumed for κ_1.

There has been considerable interest in the compound V_3Ga due to the suggestion of Wernick, et al[15] that its critical field may exceed 500 kG, based on the extrapolation of measurements up to 80 kG. This appeared to be contradicted by the Clogston limit, however, since T_c for V_3Ga is about $14.6^{o}K$ and therefore H_p is 270 kG. To overcome this apparent contradiction, it has been suggested that the critical temperature should be much higher, or that the dependence of critical field on temperature was different from other materials, resulting in a rapid levelling of the curve as the temperature decreased. To resolve this question, equation 7 has been fitted to the high temperature experimental measurements in order to estimate the zero temperature critical field. A reasonable fit is obtained for $H_p' = 380$ kG (40% above Clogston's value) and $H_{c_2} = 630$ kG (equivalent to $\kappa = 75$), yielding $H_u = 280$ kG. Thus although V_3Ga will have a higher critical field than Nb_3Sn it will be no-where near the suggested value of 500 kG.

CONCLUSIONS

The measured critical field of superconductors of the second kind is determined by a combination of the upper critical field and the paramagnetic limit. It has been shown that for many high field materials of interest the paramagnetic limit is 30-40% higher than the generally accepted value. When this together with the affect of a magnetic field on the paramagnetic contribution to the free energy of a superconductor is taken into account, there is a reasonable agreement between calculated and measured critical fields.

The temperature dependence of the paramagnetically limited critical field has been considered.

Finally, the critical field of V_3Ga has been calculated and fitted to low field experimental results. The critical field at zero temperature is estimated to be 280 kG.

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