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Magnetisation Measurements on Superconducting Beryllium Alloys

by **R. Burton**

Institut de physique expérimentale, Université de Genève

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Abstract. Measurements upon the compound Be_{22}Re have shown it to possess behaviour typical of a type II superconductor with Ginzburg-Landau parameter $\kappa_0 = 1.4$. The temperature dependence of κ_1 is much greater than that suggested by the theories which do not include anisotropic effects. Some microscopic parameters have been deduced in order to describe the superconducting state as fully as possible. Two phase binary alloys and several stoichiometric ternary alloys have yielded some information on flux trapping and flux jumping behaviour which have been interpreted in relation to filament and flux pinning effects.

Introduction

Previous results [1] obtained from measurements of the superconducting properties of beryllium-rhenium alloys have indicated some unusual features worthy of further investigation. The stoichiometric alloy Be_{22}Re which has a cubic structure [2] is unusual in that its very low content of transition element is sufficient to make an extremely large change in its superconducting properties. This comes about due to the new crystal structure made possible by the introduction of the transition metal and it has been suggested [3] that such an effect may have been responsible for the observation of superconductivity in thin films evaporated [4–6] at low temperatures. More recent work [7] on the pure metal in its usual hexagonal form has indicated a transition temperature of 26 mdegs; this is noteworthy in that it becomes the first member of Group IIA of the periodic table to exhibit superconductivity.

The work to be described below concerns measurements made upon Be_{22}Re , and non-stoichiometric compositions containing less rhenium, together with some ternary stoichiometric alloys with small additions of either tungsten, osmium or ruthenium as the third component.

Experimental

The specimens were prepared in a copper hearth arc furnace under a reduced pressure of argon. Ingots so obtained were then cut into the required form by spark erosion. The only difficulty involved in this operation was in accounting for the preferential evaporation of the beryllium. The specimens themselves were very brittle and of course polycrystalline. Unfortunately, the measurements to be described below

were made the more difficult to interpret because of the highly irreversible nature of the magnetisation curve; one would find a very interesting and rewarding specimen indeed if Be_{22}Re could be prepared in single crystal form.

Not a great deal of data exists about the phase diagram of the Be-Re system [8] but it appears that in the range of concentrations corresponding to the present work there are two phases, a eutectic, and that corresponding to stoichiometric Be_{22}Re [2] which is cubic. Quenched samples containing 1% rhenium give rise to about 15% by volume of the Be_{22}Re structure. This two phase nature is of central importance to the detailed behaviour of the non-stoichiometric alloys.

The magnetisation measurements were carried out using an integrating technique with a D.C. amplifier. Results were plotted directly with an X-Y recorder. The magnetic field source was a superconducting solenoid and as the specimen critical fields were not large, some investigation of the solenoid's flux trapping characteristics was appropriate. Owing to the geometry of the field windings, the trapped field displayed an oscillatory character which had a maximum amplitude of 50 gauss. The field at the centre was in fact zero and one could calculate that the extremities of the pick-up coils experienced fields of ± 10 gauss. These coils, which possessed brass formers screwed into a brass support acting as the common terminal, were situated adjacent to each other across the bore of the magnet with mutually parallel axes. The apparatus had a facility for raising the solenoid into warmer regions of the dewar if the trapped flux had to be removed for any purpose.

Although the apparatus was not intended to be used above 4°K, a quick modification proved to be very successful. The pick-up coils were simply enclosed in a thick walled copper can which was then furnished with a heater and resistance thermometer. The compensating coil carried a lead specimen, and a 1/10 mm copper foil strip of 0.75 cm width was clamped to the brass coil assembly and copper can. The whole was then placed inside an open glass tube which prevented contact with the liquid helium; radiation from the top of the dewar and convection inside the copper can were cut down by the liberal use of cotton wool. Measurements were now made using the lead and a 56 Ω 1/10 watt Allen Bradley resistor as thermometers, whilst the whole was allowed to warm – either freely as the helium level fell or by use of the heater. Most of the measurements were made with the helium below the level of the solenoid this being cooled by boiling off liquid helium from below. The method almost certainly owed its success to the thermal capacity and stabilising influence of the large quantity of copper-clad Nb-Zr wire. The lead in the compensating coil was extremely convenient as a thermometer and showed that discrepancies between it and the resistance thermometer only occurred if the copper can were heated to temperatures much above the equilibrium temperature it would have found in the absence of heating. Since the trapped field of the solenoid was zero at its centre, little influence upon the temperature, as determined from the lead critical field, was expected from this source once the slight broadening of the transition was accounted for. As a result of these investigations, it appears that a maximum error of 0.05°K was observed at 7.0°K which reduced to zero at 4°K and 9°K.

More sophisticated adjustments could have been made quite easily to the system to cut down this source of error but as will be explained later, the properties of this particular specimen made the execution of these modifications rather irrelevant.

Results

The data obtained from the measurements made upon the binary system Be-Re, and the ternary alloys containing Os, W and Ru are given in Table I; all fields refer to 4.17°K. It can be seen that the critical temperatures are somewhat lower than those reported in [1]. In the table, H_{c2} is the field suppressing diamagnetic behaviour, H_{max} is the field giving the maximum in the magnetic moment, H_{dia} is the upper limit for constant susceptibility with field, H_{c3} represents the field restoring full normal resistance and ϕ is the trapped flux.

Table I

	T_c	H_{c2}	Diameter mm	H_{max}	H_{c3}	Residual resistivity Ω cm	H_{dia}	ϕ % H_{c2}
Be _{0.99} Re _{0.01}	9.25	3350 ± 75	2.95	220	3350	1.57 10 ⁻⁷	130	3
Be _{0.99} Re _{0.01}	9.25	3200 ± 150	1.92	200			130	
Be _{0.98} Re _{0.02}	9.45	3250 ± 100	2.95	400	4000	2.03 10 ⁻⁷	190	5
Be _{0.96} Re _{0.04}	9.50	3200 ± 150	2.95	450			300	9
Be ₂₂ Re ₁	9.33	3400 ± 50	3.00	850	5900	5.35 10 ⁻⁶	400	18
Be ₂₂ Re ₁ annealed	9.55	3400	9.0	1900			—	65
Be ₂₂ (Re _{0.95} W _{0.05}) ₁	9.45	4100 ± 100	3.70	1200		7.8 10 ⁻⁶	400	30
Be ₂₂ (Re _{0.95} W _{0.05}) ₁	9.45	4100 ± 100	9.0	1900			500	50
Be ₂₂ (Re _{0.95} Os _{0.05}) ₁	9.2	3500 ± 50	3.0	1150		4.2 10 ⁻⁶		25
Be ₂₂ (Re _{0.99} Ru _{0.01}) ₁	9.2	3550 ± 100	3.0	900				20

Some specimen magnetisation curves are given in Figures 1, 2 and 3; they all refer to 4.17°K and were obtained from beryllium containing 1, 2 and the stoichiometric 4.35 atomic percent of rhenium respectively. As can be seen from Table I, the resistive transition of the stoichiometric alloy coincides nicely with the provisions of the theory [9], so that we can take the end point of the magnetisation curve as being representative of H_{c2} , the upper critical field described by ABRIKOSOV. The diagrams also point up the troublesome gradual approach to zero magnetic moment in high fields. A direct result of this can be seen in Figure 4, which gives the temperature dependence of H_{c2} for the alloy Be₂₂Re, where the recorder sensitivity influences the estimate for H_{c2} rather strongly. The points between 6.6 and 8.7°K, which were all measured on the same ranges of the X/Y recorder, are exactly parallel to the line joining the other experimental results but are displaced by about 80 oe. On increasing the Y sensitivity near to T_c , so that the relative sensitivity reverts to its original value, the estimate for H_{c2} increases again. A further product of the non-linear approach to zero magnetic moment is that with good alignment of field and specimen, a limiting sensitivity means that as the scale of the magnetisation curve increases, one moves progressively nearer to H_{c3} in making one's assessment of H_{c2} . This process was evident in several experiments but could be controlled below 4.2°K by taking measurements when the alignment/sensitivity was such that the return of resistance and the end point of the magnetisation curve almost coincided. In view of these features, together with a spread in the transition corresponding to about 200 oe, a detailed description of the temperature dependence of H_{c2} above 4.2°K is out of the question and one is conse-

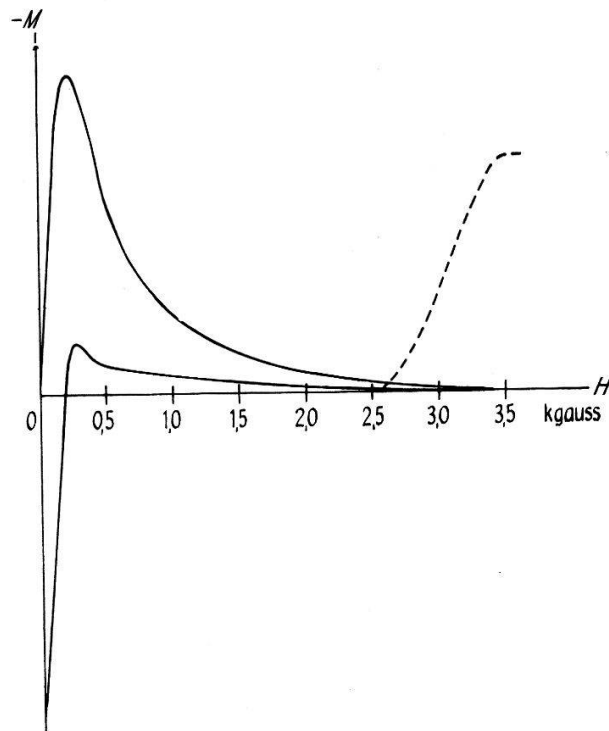


Figure 1

The magnetisation curve of $\text{Be}_{99}\text{Re}_1$ at 4.17°K (Resistance curve dashed).

quently unable to do better than to set a linear variation for H_{c2} within this temperature range.

Having determined H_{c2} , it is now possible to proceed to calculate κ_1 , the Ginzburg-Landau parameter defined by the relation:

$$H_{c2} = \sqrt{2} \kappa_1 H_c$$

where H_c is the thermodynamic critical field. Quite clearly this field cannot be deduced from the magnetic measurements so that we must make recourse to the value reported

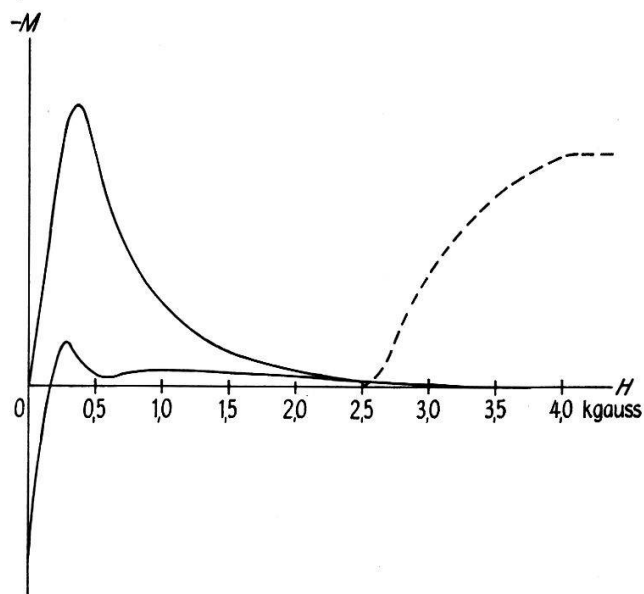


Figure 2

The magnetisation curve of $\text{Be}_{98}\text{Re}_2$ at 4.17°K .

for the electronic specific heat coefficient [1], γ . In this way, we find that with γ given by $0.59 \text{ mj/mole } ^\circ\text{K}^2$ and a molar volume of 5.06 cm^3 , the critical field at 0°K is:

$$H_c(0) = (0.17)^{-1/2} \gamma^{1/2} T_c = 775 \text{ oe.}$$

Intermediate values for H_c may now be calculated to within 2 or 3 percent of the true value by means of the parabolic approximation. Judging by the Debye and superconductive critical temperatures, Be_{22}Re will be weak coupling so that these results will represent a lower limit for H_c .

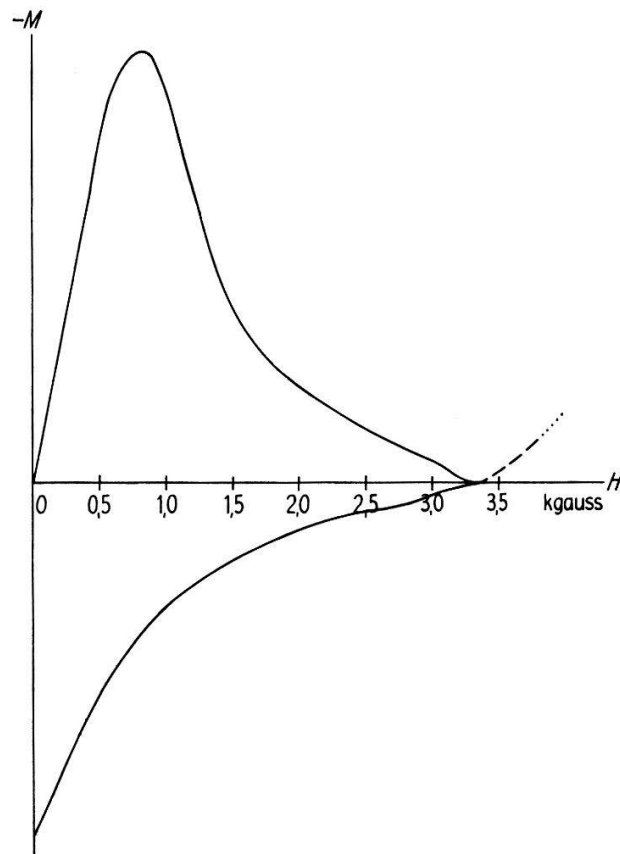


Figure 3

The magnetisation curve of Be_{22}Re at 4.17°K .

The results of the calculations are given in Figure 5 in the form of a plot of κ_1/κ , where κ is the value κ_1 at T_c . Points for the tungsten ternary alloy are also included after having made appropriate adjustments to $H_c(0)$ [10]. Owing to the approximations employed, the variation of κ_1 with temperature is determined from the outset in the range of temperature above 4.2°K so that the graph only refers to the restricted region where $t (= T/T_c)$ is less than 0.5. The normalising values for κ , as obtained from the slopes of the critical magnetic fields at T_c , were 2.80 and 3.34 for the binary and ternary alloys respectively.

It is seen from the figure that κ_1 enjoys a temperature dependence well in excess of that predicted by GOR'KOV [11] and EILENBERGER [12] in which $\kappa_1(0)/\kappa$ is 1.26 in the pure limit; the present increase represents a factor much nearer to the empirical 1.6 observed in a large number of pure elements [13]. Since these theories above do not consider anisotropy of the Fermi surface, this possibility, which has been discussed by HOHENBERG and WERTHAMER [14], appears to be required to play a significant

role. The observed results also indicate that the specimens are somewhere near the pure limit of behaviour.

A convenient value for κ may be obtained from the resistivity using [15, 16]:

$$\kappa = \kappa_0 + 7.5 \cdot 10^3 \gamma^{1/2} \rho$$

where κ_0 applies to pure Be_{22}Re or pure $\text{Be}_{22}(\text{Re}_{0.95}\text{W}_{0.05})$ and the resistivity is measured in Ω cm. This gives $\kappa = \kappa_0 + 1.37$ for the binary alloy and $\kappa = \kappa_0 + 1.98$ for the ternary sample. Using the κ values obtained from the critical fields, viz. 2.80 ± 0.1 and 3.34 ± 0.15 , κ_0 becomes 1.43 ± 0.1 and 1.36 ± 0.15 for the two alloys respectively.

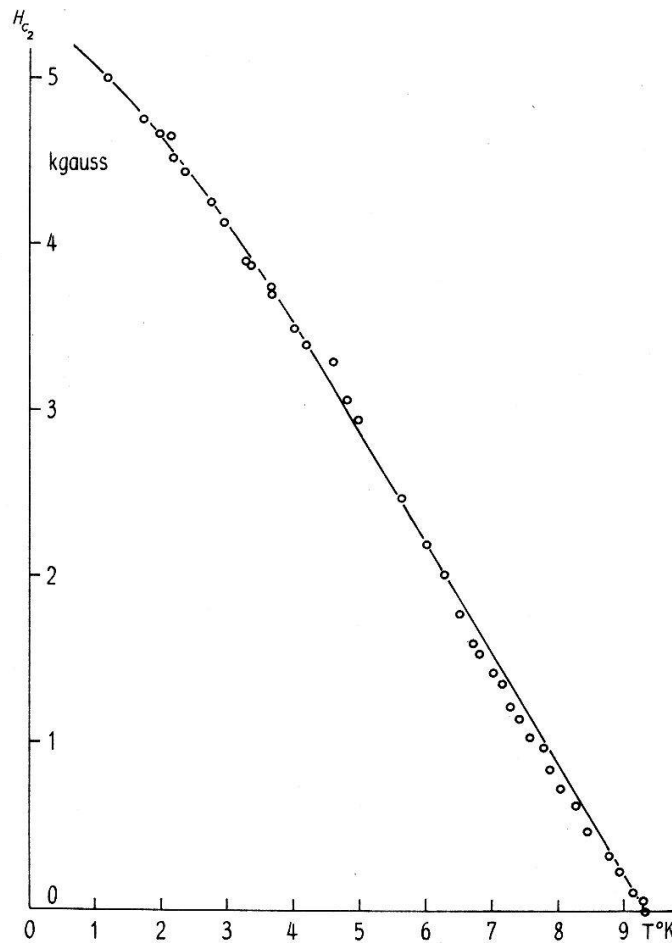


Figure 4

The upper critical field of Be_{22}Re .

A further rough check for the value of κ for the Be_{22}Re may be obtained from ΔC , the discontinuity in the specific heat at T_c , after calculating dH_c/dT by Rutgers formula.

$$dH_c/dT = \left(\frac{4\pi\Delta C}{T_c} \right)^{1/2} = 146 \text{ oe}/^\circ\text{K}.$$

This compares with $167 \text{ oe}/^\circ\text{K}$ for the parabolic $H_c(0)$ deduced from γ so that κ_0 changes correspondingly from 2.80 to 3.2. These two values are certainly as close as can be expected from this sort of comparison as is evident from other work. The results thus indicate that we have a rather unusual superconductor in Be_{22}Re it being,

to the present author's knowledge, the only compound so close to existing as a type one superconductor.

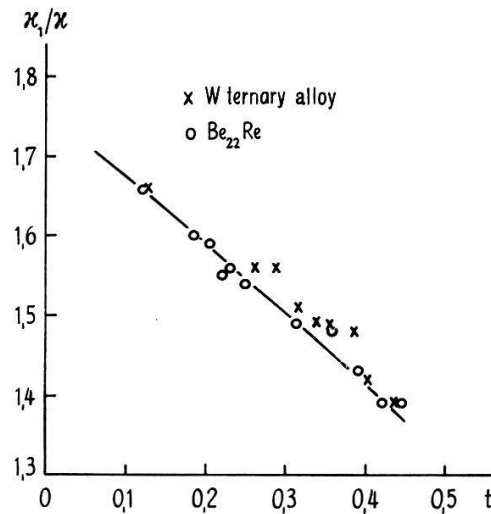


Figure 5

The temperature dependence of κ_1 .

In order to get an approximate idea of other parameters characterising this alloy, we start from the result, [17]

$$H_{c2} = \frac{4 \pi \lambda^2(T) H_c^2(T)}{\phi_0}$$

where ϕ_0 is the flux quantum, $2.1 \cdot 10^{-7}$ gauss cm², and λ is the penetration depth, although so far, theoretical justification for this formula only appears to exist for $l \ll \xi_0$ where l is the electron transport mean free path and ξ_0 is the coherence length. From the results at 4.17°K one can now obtain the penetration depth at 0°K, $\lambda(0)$, from the Gorter Casimir dependence;

$$\lambda = \lambda(0) (1 - t^4)^{-1/2}$$

whence $\lambda(0) = 1190 \text{ \AA}$. In reality, since the B.C.S. theory and the experimental results show deviations from the above relation, this figure should be reduced to about 1000 \AA —the experimental results falling roughly half way between the two. Nonetheless, so that we do not introduce an arbitrary character into the calculations, we continue with $\lambda(0) = 1190 \text{ \AA}$ and use the Gor'kov result, $\kappa_0 = 0.96 \lambda_L(0)/\xi_0$ together with the B.C.S. theory to evaluate the microscopic parameters. Taking $\kappa_0 = 1.43$ we find that $\xi_0/\lambda_L = 0.67$ and that $\lambda(0)/\lambda_L(0) = 1.15$ in the limit of infinite mean free path. The relations [18, 19] to be given immediately below now enable us to calculate l , and by a reiteration process we can obtain a better result for $\lambda(0)/\lambda_L(0)$.

$$l = \frac{6 \pi^2 \hbar}{e^2 \rho S} \quad \lambda_L(0) = \frac{3 \hbar (\gamma \pi)^{1/2}}{e k S}$$

In these expressions, S is the free electron Fermi surface in cm⁻² which we eliminate, ρ and e are in emu, \hbar is in erg sec and k is in erg deg⁻¹. The calculation for l yields 560 \AA so that $2 l/\pi \xi_0 = 0.51$ and from MILLER's [20] tables, $\lambda(0)/\lambda_L(0) = 1.67$. Reiterating a second time with the new mean free path of 380 \AA , we find virtually no change in $2 l/\pi \xi_0$ so that there is very little change in $\lambda(0)/\lambda_L(0)$.

With the relation [19]

$$1/v_F = \frac{6 h \gamma}{k^2 S}$$

where (v_F) is the average Fermi velocity in cm sec⁻¹, we are now in a position to provide some useful parameters describing the alloy Be₂₂Re. The errors included in Table II take no account of the lack of rigour of the approximations made in the analysis. The principal source of error from this aspect derives from the temperature dependence of λ and one could say that, as it is only near 0°K that deviations from $\lambda(T) = \lambda(0) (1 - t^4)^{-1/2}$ occur, the quantities quoted will give the correct values near T_c . In principle, these values of λ/λ_L at T_c could now be used to obtain good values of $\lambda(0)/\lambda_L(0)$ from MILLER's work; matching has not been done in this way however simply because of the aforementioned discrepancy which is observed in practice between experiment and theory.

Table II
Data for Be₂₂Re

T_c	= 9.33°K	$\lambda(0)$	= 1190 ± 40 Å	$\lambda_L(0)$	= 720 ± 30 Å
ΔT	= 0.3°K	l	= 380 ± 40 Å	ξ_0	= 480 ± 60 Å
$H_c(0)$	= 775 ± 20 oe	κ_0	= 1.43 ± 0.13	$\langle v_F \rangle$	= 3.10 ± 0.15 · 10 ⁷ cm sec ⁻¹

We now consider some of the features which characterise the other, non-stoichiometric alloys. Table I shows some systematic changes in the binary compositions as the rhenium content increases to that concentration corresponding to stoichiometry. During this process, it is seen that H_{c2} remains roughly constant suggesting that departures from stoichiometry in the structure are small and may even be non-existent. The trapped flux increases with the rhenium concentration so that it always remains roughly equal to the maximum magnetic moment – although opposite in sign of course. Systematic increases of H_{dia} , H_{c3} and H_{max} are all seen to follow as the rhenium content is increased.

In an effort to sort these observations into some consistent form and perhaps to make some useful deductions, we should start from the reasonable assumption that the reproducible value for H_{c2} derives from the inclusion of the stoichiometric Be₂₂Re phase. In addition, the coexistence of resistance and diamagnetism in Figure 2 suggests that this comes about as a result of isolated inclusions of this phase; multiply connected surface filaments from the sheath must be excluded because of the absence of hysteresis. These inclusions are thus of such size, distribution and geometry that they are incapable of trapping flux – at least near to H_{c2} . It is to be noted that as the Be₂₂Re is embedded in a very low resistance phase, there will be no sheath formation around the inclusions. In principle, κ_2 could be calculated from the reversible dM/dH at H_{c2} in Figure 2, but due to demagnetising effects which increase the low field susceptibility and decrease dM/dH , this calculation must overestimate the value. In the event however we find that $\kappa_2 \sim 6$ at 4.17°K.

The flux trapping observed in these specimens follows very closely the analysis suggested by CAMPBELL et al. [21]. Our Figure 1 corresponds to the magnetisation curve anticipated for a superconductor with widely spaced pinning points and the progression up to Figure 3 reflects an increasing density of inhomogeneities. More particularly, the two cases in Figures 1 and 3 refer to small and large values for $a \alpha$

respectively where a is the specimen diameter and α is given by $8\pi m F_0/l^2$. In this expression, m is the slope of the ideal B/H curve between H_{c1} and H_{c2} , F_0 is the pinning force on one line and l is the separation of the pinning centres. A very rough estimate suggests a factor of the order of 10^2 between the two values for $a\alpha$. An important difference between the present work and that of Ref. [21] is that we have varied the superconducting phase in a normal matrix whereas the previous workers varied the normal pinning phase within a superconducting matrix. The results suggest that the magnetisation curve is not sensitive to this quite fundamental difference in the structure.

Although the figures in Table I show that the trapped flux roughly follows the volume of the superconducting phase, the reasoning above shows how important the inter-relation between the inclusions is in determining the details of the magnetisation curve. It is along these lines that an explanation for the variation of H_{dia} and H_{max} must be sought. Essentially the behaviour of these two fields is determined by the same effect. H_{max} will be higher for greater rhenium content because a greater density of superconducting filaments can support an increased flux gradient [22]. Thus one can say that the pinning of flux lines is increased along the specimen radius. Analogously, the H_{dia} behaviour comes about because an increasing superconducting phase at the surface means that the flux lines are pinned more frequently along their length so that their consequent ingress into the superconductor is delayed to higher fields more or less linearly with the concentration. A secondary explanation for the increase of H_{dia} may arise from the variation of H_{c3} . GALAIKO [23] has indicated that the nucleation field for vortices is elevated when the surface critical current is raised. What is responsible for the apparent reduction in H_{c3} as the rhenium content decreases is not very clear, proximity effects are a possibility. It is quite obvious that these will play a part in determining the results, yet it is not easy to determine the magnitude of their influence; it seems probable that the inclusions are sufficiently large to avoid significant modifications.

Long-Term Effects and Flux Jumping

In addition to the above results, long-term changes were observed in the character of the magnetisation curves. The $\text{Be}_{0.99}\text{Re}_{0.01}$ sample showed quite a considerable difference between its behaviour on preparation and that recorded after several runs some six months later and given in Figure 1. In place of the single maximum observed in the curve in decreasing field, there was originally a double peak. The $\text{Be}_{0.98}\text{Re}_{0.02}$ sample showed the same effect only it was less marked; the structure in its maximum looked like the superimposition of two peaks. These alloys have high melting points and annealing effects seem unlikely; the evidence suggests that differential thermal expansion of the two phases on cycling the temperature must change the structure, this will break up the fine filaments so altering the flux retention properties. Surface damage to the inclusions might also be involved. Of the two possibilities, the latter would require irreversibility at higher fields which is not seen, so it is probably due to a finer dispersion of superconducting particles that the flux trapping increases with time.

Measurements upon the ternary alloy containing W when of diameter 9 mm, displayed systematic flux jumping behaviour and a magnetisation curve is given in

Figure 6. The flux jump marked 'A', appeared in the third quadrant (i.e. negative field going increasingly negative) at 4.2°K; it moved to values of H in the second quadrant linearly with the temperature which suggests that the flux annihilation concept was not responsible for its initial appearance. Furthermore, on being reduced to a diameter of 3.7 mm, this same specimen only displayed a flux jump at the very lowest temperature viz. 1.2°K. The size dependence of the flux jumping could find a facile explanation in assuming that a particular defect was responsible and that this was removed in the reduction process. Alternatively, the larger specimen would require higher internal temperatures to dissipate heat caused by flux motion which would give rise to instabilities. Certainly heating effects are of demonstrable importance in flux jumping behaviour, but nevertheless, as can be seen in the figure, the first jump 'A' is followed by a region of perfect diamagnetism up until the second occurs. The internal heating theory cannot hold for this case and if one assumes that the first flux jump reduced all currents in the specimen to subcritical values, it is seen that this second flux jump must have been provoked by some other instability, a like explanation follows for the two succeeding jumps. By way of explanation, it is quite clear that there is a change in character at the surface which allows gradual penetration – or expulsion – at high fields and provokes flux jumps joined by diamagnetic lines in low fields and that this should reasonably be related to H_{dia} . This field is seen to be reduced on decreasing the diameter from 9 mm to 3.7 mm. Allied to this effect will probably be a very slight dilation of the complete fluxoid lattice throughout the specimen as the external magnetic pressure is relaxed so causing small rearrangements of screening currents which could be critical – or in other words – so increasing the curvature of flux lines between pinning points that breakdown occurred.

The above assertion that H_{dia} is reduced on reducing the diameter is quite contrary to what one would expect from demagnetising effects and it is possible that experimental reasons could have been responsible. The pick-up coil system for the larger specimens was different from that for the small specimens, as was the superconducting magnet itself. These effects lead to greater imprecision in estimating H_{dia} but nonetheless, the results are very suggestive of an increased value and it should be

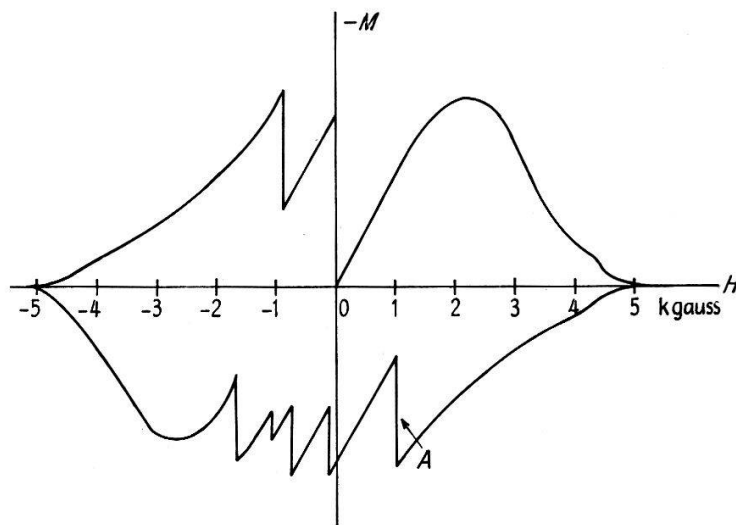


Figure 6

The magnetisation curve of $\text{Be}_{22}(\text{Re}_{0.95}\text{W}_{0.05})$ at 2.32°K.

considered. The only explanation possible seems to be along the lines of a size dependence in the pinning at the outer surface or some rather complicated co-operative effect between current paths in the specimen. This latter phenomenon might be capable of giving rise to metastable situations and flux jumps. Quite clearly some additional experiments upon size effects, their bearing upon H_{dia} and its role in flux jumping behaviour, are appropriate.

As a closing remark, the above behaviour observed in the tungsten ternary alloy was not generally applicable; the Be_{22}Re with diameter 3 mm displayed about fifteen small jumps between 900 and 1800 oe in *increasing* field at 1.2°K. It is evident that even small changes in the physical parameters of a sample can change the flux jumping behaviour markedly so that we are very far from the situation whereby one could forecast the effects to be anticipated in a given specimen.

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