

SURFACE NORMAL REGIONS IN SUPERCONDUCTING $Zr_{70}Cu_{30}$ INDUCED BY THERMAL RELAXATION

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Penetration depth measurements show that thermal heat treatment in amorphous $Zr_{70}Cu_{30}$ induces a normal region 5000 Å thick at the surface of ultrarapid quenched ribbons. Upper critical field measurements indicate that the new induced phase is a normal one while the rest of the sample remains as a homogeneous superconducting phase.

IN PREVIOUS WORK we investigated thermal relaxation effects in different normal and superconducting properties of the amorphous $Zr_{70}Cu_{30}$ system. It was shown [1] that thermal heat treatment can systematically change the density of low energy excitations (TLS) that determine the phonon scattering in the thermal conductivity at low temperatures. The measurements of the superconducting penetration depth [2], the electrical resistivity and critical temperature [3] show that the as-quenched $Zr_{70}Cu_{30}$ is an intermediate coupling superconductor that follows the BCS–Gorkov theory in the short electron mean free path limit, indicating no direct relation between the density of TLS and the superconducting behavior.

In this paper we study the effects of thermal relaxation in the spatial homogeneity of the sample, using the two characteristic lengths, the coherence length obtained from the upper critical field H_{c2} and the weak field penetration depth, obtained by measuring the reversible Meissner flux expulsion as a function of temperature. The flux expelled from the sample is given by [4]

$$\Delta\Phi(T) = HD[d - 2\lambda(T)], \quad (1)$$

where D and d are the width and thickness of the sample respectively. The maximum expulsion of field corresponds to $T = 0$, $\Delta\Phi_M = HD[d - 2\lambda(0)]$. We see that the knowledge of the sample dimensions together with the measurement of the variation of magnetic flux with temperature allow for the determination of the absolute value of λ as well as its temperature dependence.

The penetration depth can be expressed [5] by

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$\lambda(T) = \lambda(0)f(T)$, where $f(T)$ is a temperature dependent function that characterizes the electrodynamic response of the superconductor. Using the two fluid model and local London electrodynamics it is found that $f(T) = y = (1 - t^4)^{-1/2}$. Deviations [5] from this empirical law are expected for $y < 1.5$ if the superconductor follows the BCS theoretical model. We have recently shown [2] that $Zr_{70}Cu_{30}$ as-quenched samples follow extremely well the temperature dependence predicted by the BCS theory in the dirty limit, with $2\Delta(0)/kT_c = 3.8$ where $\Delta(0)$ is the superconducting gap at $T = 0$. It was also shown [2] that the experimental penetration depth of $Zr_{70}Cu_{30}$ can be very well fitted by

$$\lambda(T) = A + By, \quad (2)$$

in the temperature region $1.3 \leq y \leq 2.5$, where $B/\lambda(0) = 1.17$, in agreement [2] with BCS predictions. In this paper we characterize the thermally induced evolution of the electrodynamic response of the material by the experimental slope B . Although it has been observed that annealing changes the temperature dependence of $\lambda(T)$, the variation is not big and is irrelevant for the discussion in this paper.

The experimental temperature range in our measurement was from $y = 1.05$ to $y = 5$. Since the penetration depth of this material is large, [$\lambda(0) \approx 1 \mu\text{m}$], deviations from the linear dependence given by equation (2) were evident for $y > 3$. These deviations are accounted for by standard size effect theoretical expressions [5].

Using the microscopic Gorkov's relation [5] for dirty superconductors it is possible to relate the coefficient B in equation (2) the electrical resistivity and the critical temperature

$$B = 1.288 \times 10^{-2} (\rho/T_c)^{1/2}. \quad (3)$$

Expression (3) was shown [2] to be valid for non-annealed samples. In this work we show that it is also obeyed by the heat treated samples in the whole relaxation region. Figure 1 shows B/B_i as a function of T_c/T_{ci} ,

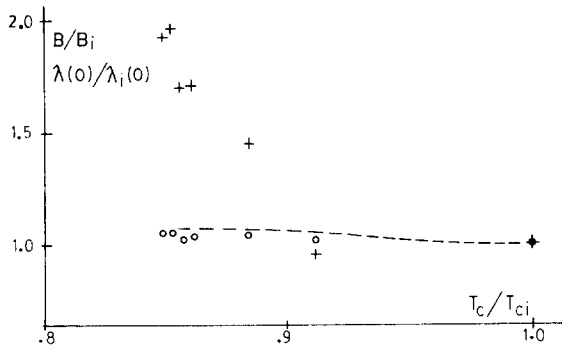


Fig. 1. The zero temperature penetration depth, $\lambda(0)$, obtained from the total flux expulsion, +, and the coefficient of the temperature dependence, B , of the penetration depth defined in equation (2), \circ , as a function of the normalized critical temperature. Both quantities are normalized by the corresponding values of the as-quenched sample. The dotted line represents expression (3), see text.

where B_i and T_{ci} are the values corresponding to the as-quenched sample. The dotted line corresponds to expression (3) where the experimental ρ and T_c have been used to calculate B . Since the resistivity increases [3] by 1% with annealing the change in B shown by the dotted line in Fig. 1 is mainly due to the 15% decrease [3] in T_c .

It is seen that expression (2) describes correctly not only the absolute value of λ in the non-annealed sample [2] but also the variation induced by thermal treatment.

In the same figure we have plotted the value of the penetration depth at $T = 0$, obtained from the maximum expulsion of field, Φ_M , normalized by the corresponding value of the as-quenched sample, $\lambda_i(0)$. We see that while B remains almost constant, in accordance with theoretical expectations, annealing increases $\lambda(0)$ by almost a factor of two. This means that although the temperature dependence of $\lambda(T)$ is well described by theory, the total expulsion of field decreases strongly as a function of annealing. It is interesting to mention that the size effects can be taken into account by theoretical expressions [5] only if B is used as $\lambda(0)$ instead of the value of $\lambda(0)$ obtained from $\Delta\phi_M$. That is, the $\lambda(0)$ obtained from the total flux expulsion overestimates the size effects in the annealed samples. These results indicate that B is the parameter that characterizes the electrodynamic response of the superconducting pairs. Consequently, the use of expression (1) at $T = 0$ is inadequate to obtain the characteristic penetration depth of annealed samples.

The discrepancy could be solved if annealing modifies the thickness d appearing in equation (1). Since the measurement of the geometrical thickness show that it does not change with annealing, we postulate that there

is an effective superconducting thickness that is reduced with heat treatment. If this is the case the apparent increase of the zero temperature penetration depth is due to the growth of a non-superconducting region at the surface of the ribbon. As we will show later, other experiments indicate that this region is a normal metallic one.

It is important to remark that the presence of a normal layer could change, in principle, the temperature dependence of $\lambda(T)$ due to proximity effects. On the other hand, the reduction of superconductivity induced by proximity is propagated to a distance of the order of coherence length which in this material is two orders of magnitude smaller than λ and consequently, its influence in the temperature dependence should not be serious.

If we assume that the growth of the normal region is the same in both surfaces of the ribbon the experimental data indicate that when $T_c/T_{ci} = 0.85$ the normal thickness is approximately 5.000 Å. It is not possible to proceed with heat treatments any further because of the nucleation of crystalline regions, detected by a weak structure in the Debye-Scherrer X-ray diagrams, a decrease in the electrical resistivity [1, 3] a broadening of the superconducting transition and a strong modification of the temperature dependence of $\lambda(T)$, precluding any linear region when plotted as a function of y .

The heat treatment discussed in this paper reduced the superconducting transition width from 100 mK to less than 10 mK.

We do not know the type of transformation that takes place in the surface of the amorphous ribbons but it is clear that after annealing the system cannot be considered homogeneous from a superconducting point of view. Although we have not been able to detect crystallinity, either by X-ray diffraction experiments or by the resistivity measurements, the transformation of the material to the normal state implies strong variation of material properties near the surface of the ribbon. Since many physical properties are often deduced from experiments that are sensitive to surface properties we thought convenient and important to verify our conclusions by means of other available techniques.

The upper critical field, H_{c2} , is sensitive to inhomogeneities either due to a non uniform distribution of electron mean free paths [6] or to the presence of regions with different critical temperatures [7]. Since H_{c2} is determined by the superconducting coherence length this will be the minimum size of the inhomogeneity that can be detected measuring H_{c2} . On the other hand since the penetration depth is very large in this dirty superconductors it can be argued [7] that it is not a useful parameter to detect inhomogeneities of dimensions much smaller than $\lambda(T)$. This is not correct

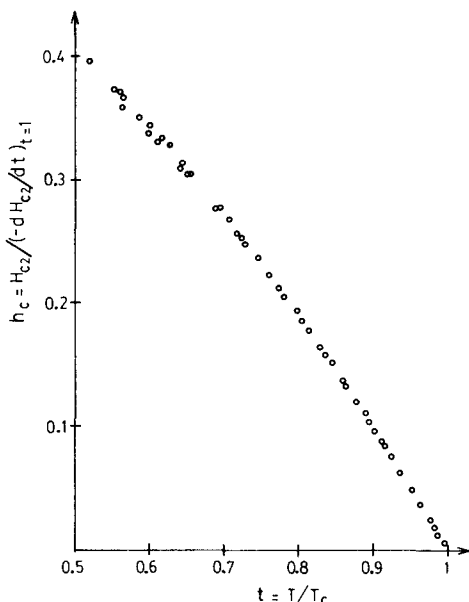


Fig. 2. Normalized upper critical field H_{c2} as a function of reduced temperature showing the universal behaviour of the annealed samples. The data correspond to normalized critical temperatures $T_c/T_{ci} = 1$, $T_c/T_{ci} = 0.954$ and $T_c/T_{ci} = 0.909$.

because λ is determined by measuring the change in magnetic flux using a SQUID, that is sensitive to changes of a fraction of a flux quantum independently of the size of the penetration depth. What is important is that the inhomogeneity or the distribution of inhomogeneities has to allow the percolation of magnetic flux through the surface cross section perpendicular to the magnetic field. From this point of view we see that the magnetic flux would be sensitive to either normal or superconducting inhomogeneities. On the contrary, the measurements of the upper critical field will be strongly weighted by the superconducting regions with higher critical fields. These measurements will be ineffective to detect normal nucleation centers. From this point of view, if our ideas about the evolution of $Zr_{70}Cu_{30}$ under heat treatment are correct we expect the temperature dependence of H_{c2} to follow a universal behavior. In Fig. 2 we show the normalized H_{c2} of $Zr_{70}Cu_{30}$ as a function of reduced temperature for different stages of annealing [1, 3] indicating a clear universal behavior. It is interesting to mention that this behavior was obtained either for perpendicular or parallel critical fields, although their absolute values were not necessarily the same.

The measurement of the parallel critical field gave further support to the existence of the surface normal region induced by thermal annealing. Since it is known that the surface critical field, H_{c3} , is diminished by the presence of a normal layer at the sur-

face of the sample, we decided to investigate the parallel critical field of amorphous $Zr_{70}Cu_{30}$ as a function of thermal heat treatment. To our knowledge there is no clear report on the existence of H_{c3} in amorphous superconductors. There are two reasons that can explain the absence of a surface critical field in most measurements. On one side it is not simple to accomplish the necessary boundary condition of parallelism between the applied field and the sample surface. Most of the surface can be rough at a scale of the coherence length ($\xi \approx 100 \text{ \AA}$) and consequently the surface critical field would be strongly diminished and confused with the intrinsic transition width at H_{c2} . Other possibility is that the normal region we have detected at the surface of the sample, is already nucleated in the as-quenched samples with a thickness too small to be detected from the flux expulsion results but thick enough to decrease or suppress the surface critical field.

We have detected the superconducting transition with the field parallel and perpendicular to the surface of the ribbon by means of electrical resistivity measurements. Five samples were investigated but only in two we found evidence of surface superconductivity. The perpendicular critical field was defined at 50% of the resistive transition. The slope of this critical field is independent of the percentage of the transition used to define H_{c2} . While this is the behaviour for the perpendicular orientation we found that for the parallel one the slope was strongly dependent on the percentage used to define the critical field. The parallel transition was characterized by a long tail at high critical fields that made uncertain the maximum critical field determination. This fact plus the limitation imposed by the maximum field available from our superconducting coil (35 kOe) made impossible the measurement of the maximum critical field in most of our temperature range. As a consequence, and taking in consideration that the ideal H_{c3} of the material is almost impossible to measure we decided to determine the slope of the critical field defined at different percentages of the superconducting transition. The slope obtained from the definition of the critical field at 95% of the superconducting transition coincides with that of H_{c2} defined at 50% of the perpendicular superconducting transition. In any case the extrapolation of the different transitions to $H = 0$ defined a unique T_c . Annealing reduced the tail in the parallel transition and made sharper the whole parallel superconducting transition. In Fig. 3 we plot the slope of the parallel critical field normalized by the slope of H_{c2} . The number in every curve indicates the value of the corresponding T_c/T_{ci} . It is seen that the slopes of the parallel critical field are reduced with annealing even at high percentages of the superconducting transition,

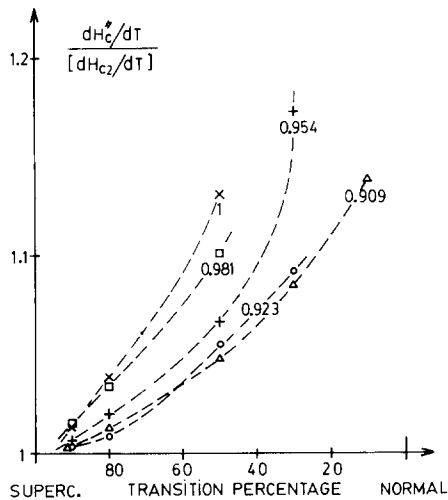


Fig. 3. The slope of the parallel critical field defined at different percentages of the superconducting transition, normalized by the slope of H_{c2} . The number in every curve indicates the value of the corresponding T_c/T_{ci} .

where the weight of the bulk critical field is more important.

The penetration depth measurements as well as the critical field determination indicate the existence of a normal region at the surface, while the bulk of the material seems to remain in a homogeneous superconducting state. We have not been able to identify the nature of the new phase, the X-ray diffraction measurements do not show structure and preliminary electron diffraction measurements [8] did not show any evidence of crystalline material.

It is interesting to mention that two recent investigations [9, 10] of the surface behaviour of amorphous magnetic materials also indicate that the surface of the material is more unstable than the bulk when the material is heat treated. It is not clear yet if the origin of both effects is the same but it is remarkable that the surface thickness in which the transformations occur is of the same order of magnitude.

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