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SUPERCONDUCTIVITY **MASTER** OF COPPER CONTAINING SMALL AMOUNTS OF NIOBIUM

C. C. Tsuei and L. R. Newkirk

JANUARY 1973

A REPORT ON RESEARCH CONDUCTED
UNDER CONTRACT FOR THE
U.S. ATOMIC ENERGY COMMISSION

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California Institute of Technology

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by

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AEC Research and Development Report No. 43 under Contract No. AT(04-3)-822
Professor Pol Duwez and Dr. C. C. Tsuei, principal investigators

January 1973

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ABSTRACT

Superconductivity of copper containing small amounts of niobium has been investigated by measuring the electrical resistivity, superconducting volume fraction and by metallographic studies. Small amounts of niobium added to copper has a drastic effect on the low temperature resistivity of the alloys. The annealed alloy $\text{Cu}_{99.5}\text{Nb}_{0.5}$ shows zero resistance at a current density of 200 A/cm^2 below 3°K . The estimated superconducting volume fraction of this alloy at 2°K is about 50 times the physical volume fraction of the Nb in the alloy. When more Nb is added these effects unexpectedly become much smaller than those observed in the dilute alloys (<1.5 at. % Nb). Metallographic results indicate that in all the Cu-Nb alloys studied there are two distinct types of Nb particles in the Cu matrix. The large particles (average size $\sim 10 \mu\text{m}$) randomly distributed in the alloy are probably formed at high temperature when the bulk of the alloy is still in the liquid state. The small Nb particles (size $\gtrsim 1 \mu\text{m}$, interparticle distances $< 0.2 \mu\text{m}$) probably form through a solid state precipitation. It has been found that the large precipitates are more abundant in the alloy containing more than 1.5 at. % Nb, than in alloys containing less than 1.5 at. % Nb. The observed superconducting properties of alloys $\text{Cu}_{99.8}\text{Nb}_{0.2}$ and $\text{Cu}_{99.5}\text{Nb}_{0.5}$ have been attributed to the proximity effect of the small Nb particles whose interparticle distances are compatible with the coherence length in the Cu matrix. The very wide superconducting transition shown in both the resistivity and the inductance measurements suggests a distribution in the Nb particle sizes as well as in the interparticle distances.

I. INTRODUCTION

It is well established experimentally that pure copper does not become a superconductor even at the millidegree temperature range.¹ However if high purity copper is melted in a niobium crucible under a helium atmosphere, the resulting Cu ingot exhibits evidence of superconductivity² at about 6 to 8°K. The evidence consisted of observing both the persistent current at a current density about 5A/cm² and the flux quantization, using a Nb-contaminated Cu as part of a superconducting ring. It was uncertain, however, that the observed superconductivity was a bulk effect (i.e. a property of the Cu-Nb solid solution) or was due to the presence of niobium-rich filaments in a Cu matrix. The purpose of the present study is to clarify the nature of the superconductivity observed in the Cu-Nb alloys. A systematic study of Cu-Nb alloys of various compositions was performed by measuring the resistivity and the superconducting transition temperature (inductive method). The structures of some alloys, after various heat treatments were examined metallographically.

II. EXPERIMENTAL PROCEDURE

Alloys of compositions Cu_{100-x}Nb_x in which x= 0.1, 0.2, 0.5, 1.5, 3.0 and 5.0 were prepared by induction melting of the appropriate quantities of the constituents (99.999% pure Cu and 99.98%-pure Nb) in glassy carbon crucible under an argon atmosphere. The alloys were then cooled slowly in the crucible. The weight losses were less than 0.2% and the nominal compositions of the alloys were taken as the actual ones. After melting, there was a silvery coating on the ingot which was removed by boiling H₂SO₄. The ingot was rolled into an

approximately rectangular rod with a 25% reduction in cross section area. Then it was cut into two pieces which were machined into 2 x 20mm rods. These two rods were designated as specimens I and II.

Specimen I was etched in dilute nitric acid to reduce its diameter to less than 1 mm. Its electrical resistivity as a function of temperature was measured by using a standard four-probe technique at a current density of about 200 A/cm². The superconducting transition temperature of the same sample was also measured by a standard ac inductance Wheatstone bridge using a PAR lock-in amplifier to detect the imbalance of the bridge. With the lock-in amplifier operating in a linear region, it was found that the bridge output is proportional to the volume of a given superconductor. Based on this fact, the inductance measurement was used to roughly estimate the volume fraction of the sample from which the flux is excluded (hereafter called superconducting volume fraction) by monitoring the amplitude change of the output of the lock-in amplifier in the bridge circuit. This was done by attaching a small piece of pure Nb of known weight (\sim 10 mg) to the Cu-Nb sample and measuring the inductance change as a function of temperature. From the weight of the Nb and that of the Cu-Nb sample and from the changes of the bridge output at the superconducting transition temperatures of both the standard Nb and the specimen, the superconducting volume fraction (SVF) of the Cu-Nb alloy can be estimated within 10%.

The rod designated as specimen II was annealed at 800°C for about two days, and its diameter was reduced by etching. The resistivity and the superconducting transition temperature were then measured as for specimen I. The same samples were then examined under the optical microscope. For the purpose of comparison, metallographic study was also performed on two alloys (0.5 and 3.0% Nb) in the as cast condition.

III. RESULTS

The values of the resistivity (normalized to those at 15°K) are presented in Fig. 1 to 4 as a function of temperature and composition. The results for the as-rolled samples (specimen I) are shown in Fig. 1 and 2 and those for the annealed ones (specimen II) in Fig. 3 and 4. It is remarkable that, at a current density of about 200 A/cm^2 the annealed $\text{Cu}_{99.8}\text{Nb}_{0.2}$ and $\text{Cu}_{99.5}\text{Nb}_{0.5}$ show no electrical resistance below 3°K. By no resistance it is meant that the potential drop across a rod $\sim 10 \times 0.5\text{mm}$ is less than 10^{-8} volts at a current of 0.5A.

The superconducting volume fraction as a function of temperature can be estimated from the inductance change of samples and the calibration procedure described in section II. The results of such measurements are shown in Fig. 5-8 for the as rolled and annealed alloys. From the results shown in Fig. 1-8 and the microstructures shown in Fig. 9, the following observations can be made:

1. Small amounts of niobium added to copper has a drastic effect on the low temperature resistivity of the alloys at a current density of about 200 A/cm^2 . For the low concentrations, such as $\text{Cu}_{100-x}\text{Nb}_x$, with $x = 0.1$,

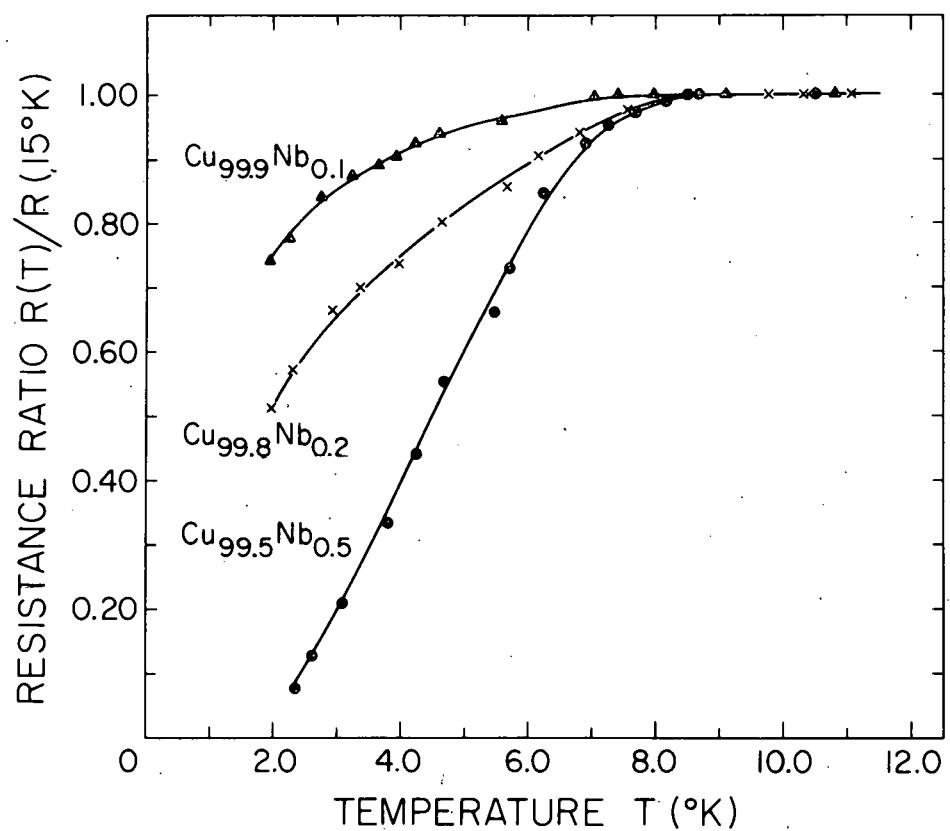


Fig. 1. Resistance ratio $R(T)/R(T = 15^{\circ}\text{K})$ as a function of temperature for copper alloys containing 0.1, 0.2, and 0.5 at. % Nb as rolled.

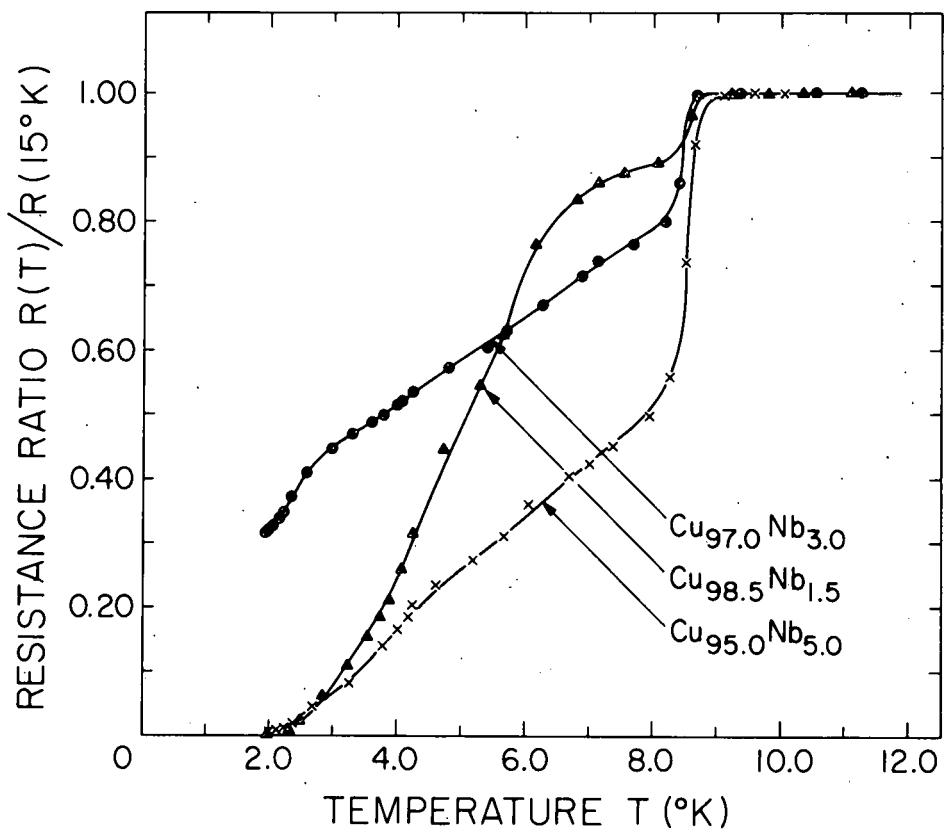


Fig. 2. Resistance ratio $R(T)/R(T = 15^{\circ}\text{K})$ as a function of temperature for copper alloys containing 1.5, 3.0, and 5.0 at. % Nb as rolled.

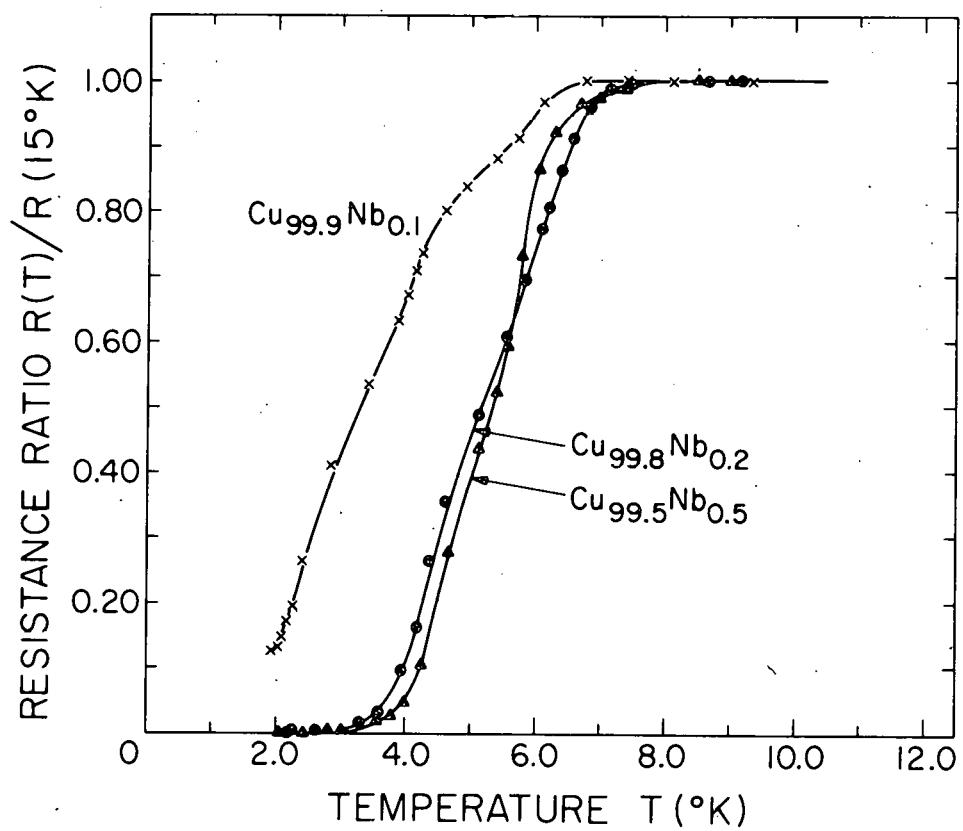


Fig. 3. Resistance ratio $R(T)/R(T = 15^{\circ}\text{K})$ as a function of temperature for copper alloys containing 0.1, 0.2 and 0.5 at. % Nb after annealing.

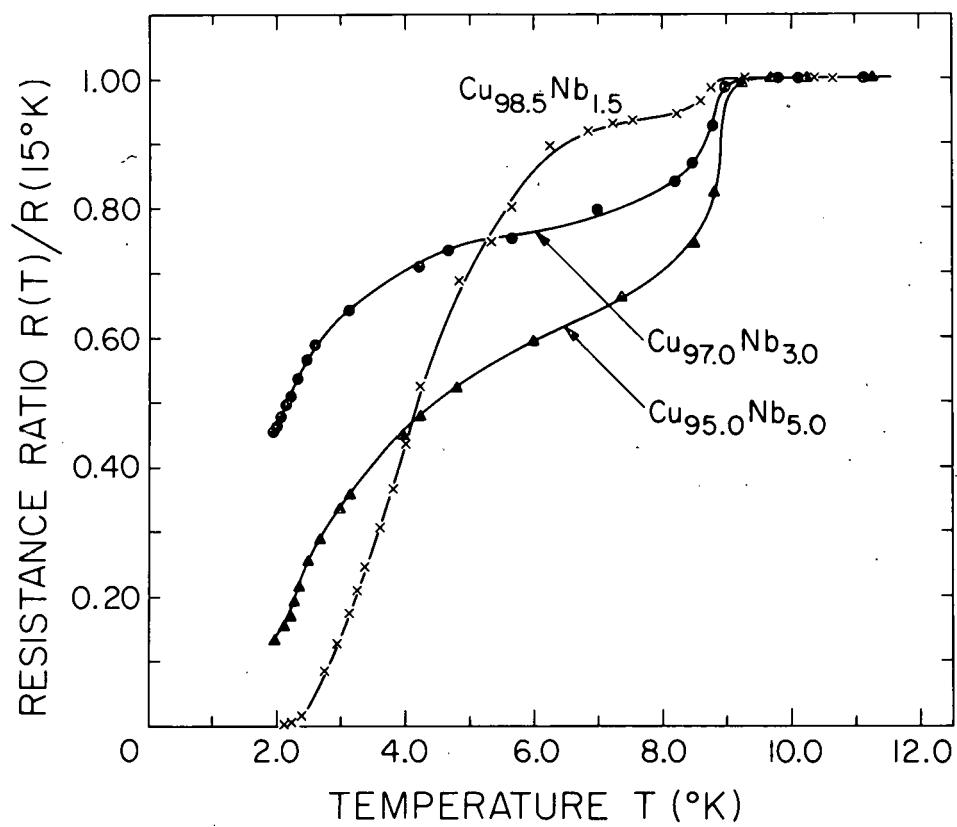


Fig. 4. Resistance ratio $R(T)/R(T = 15^{\circ}\text{K})$ as a function of temperature for copper alloys containing 1.5, 3.0 and 5.0 at .% Nb after annealing.

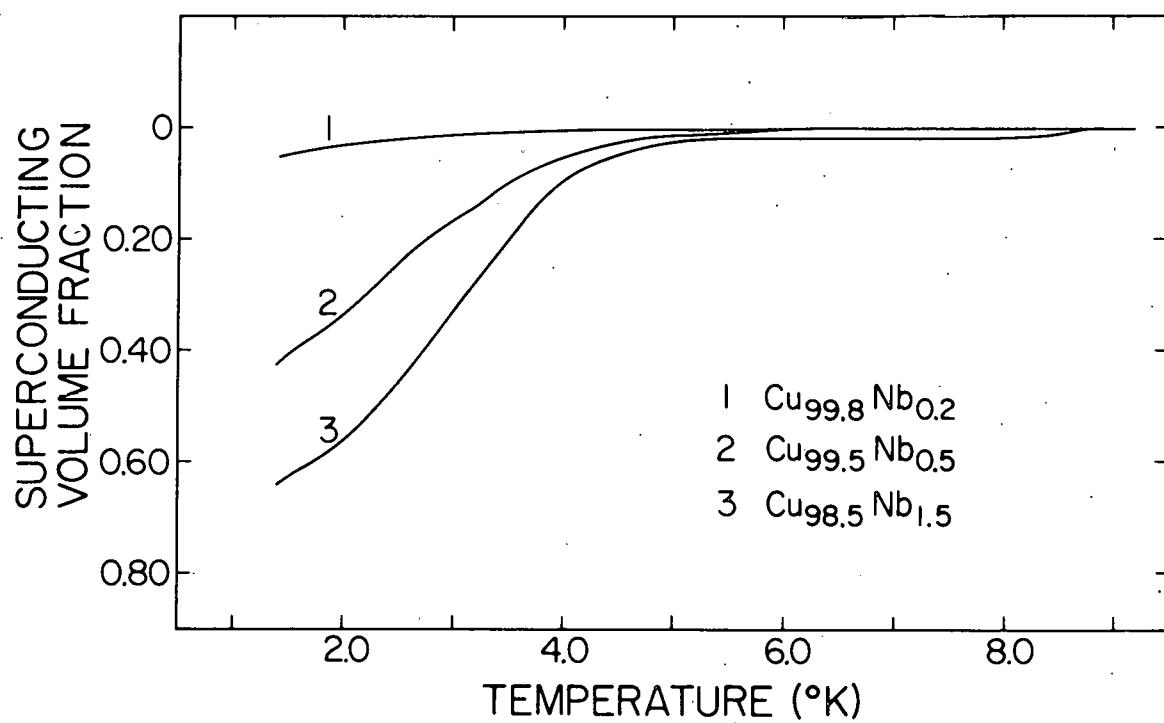


Fig. 5. Estimated superconducting volume fraction as a function of temperature for copper alloys containing 0.2, 0.5 and 1.5 at. % Nb as rolled.

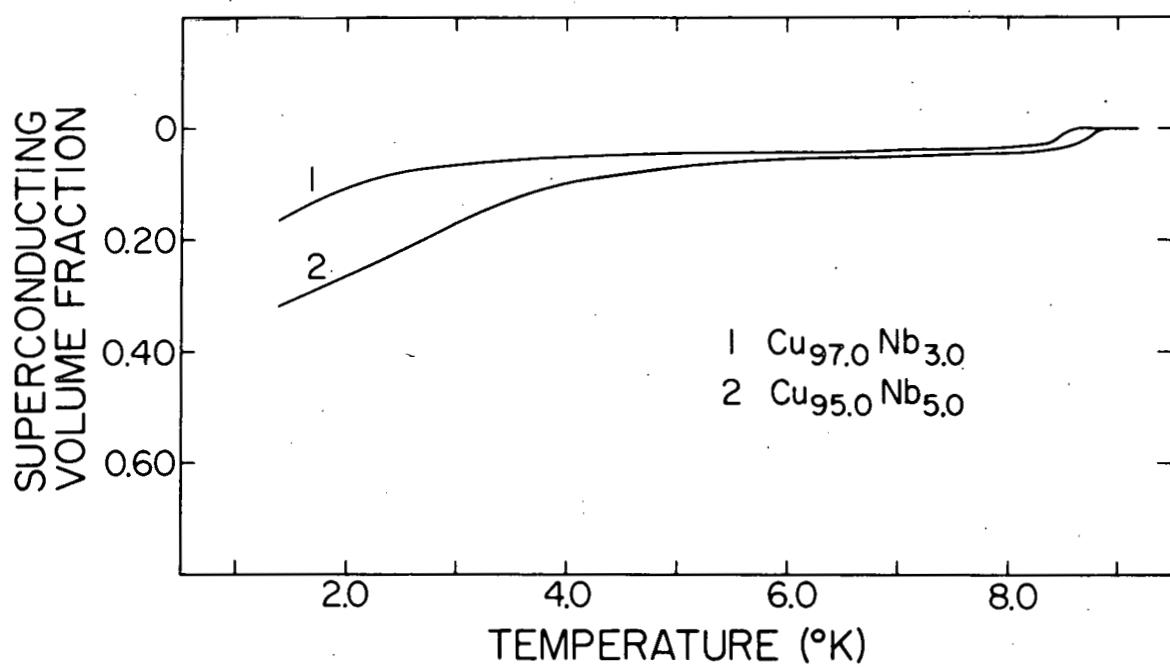


Fig. 6. Estimated superconducting volume fraction as a function of temperature for copper alloys containing 3.0 and 5.0 at. % Nb as rolled.

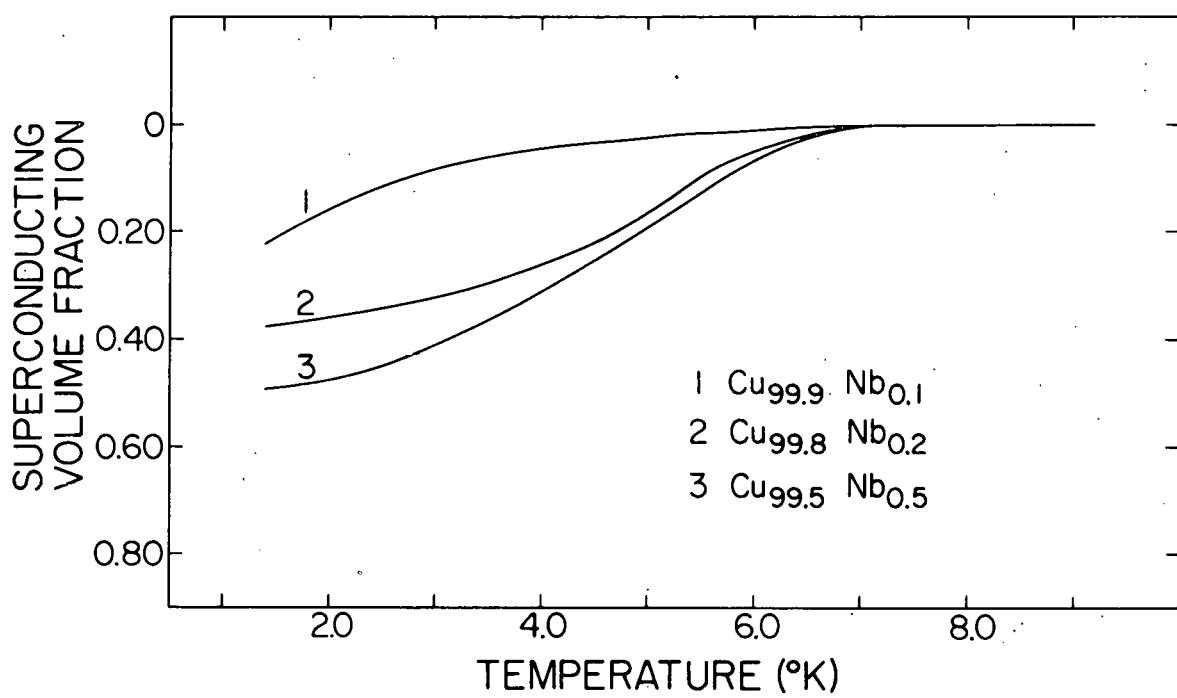


Fig. 7. Estimated superconducting volume fraction as a function of temperature for copper alloys containing 0.1, 0.2 and 0.5 at. % Nb after annealing.

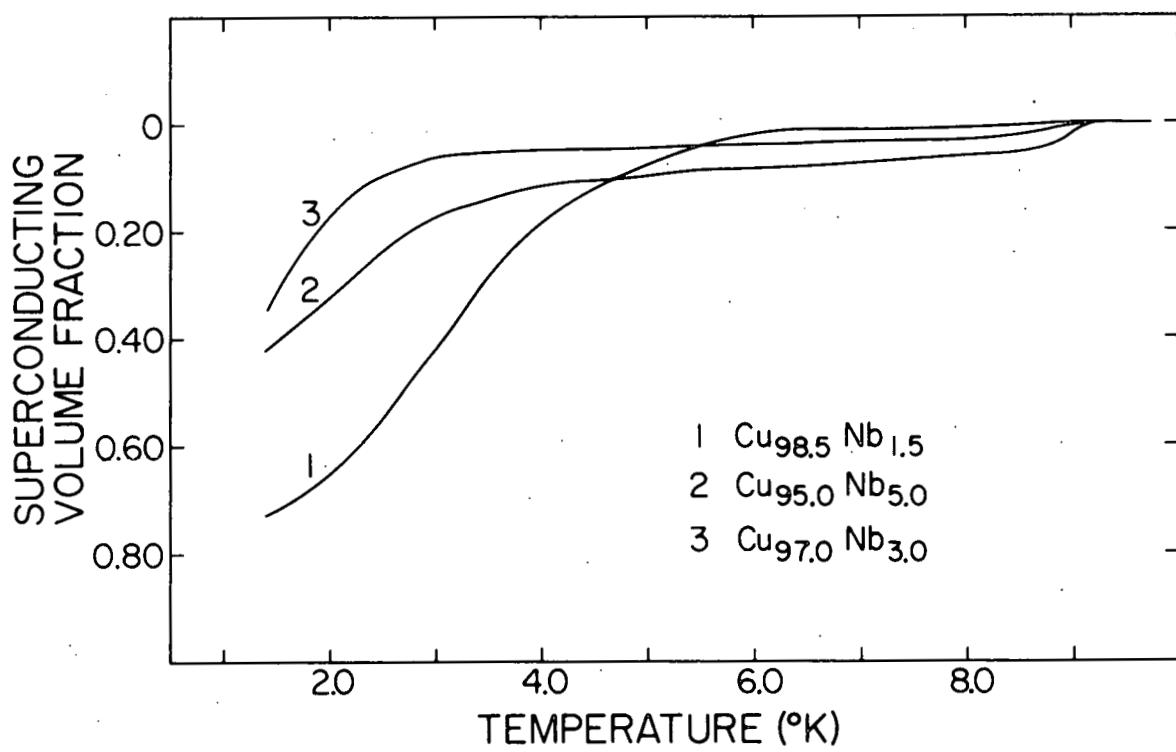


Fig. 8. Estimated superconducting volume fraction as a function of temperature for copper alloys containing 1.5, 3.0 and 5.0 at .% Nb after annealing.

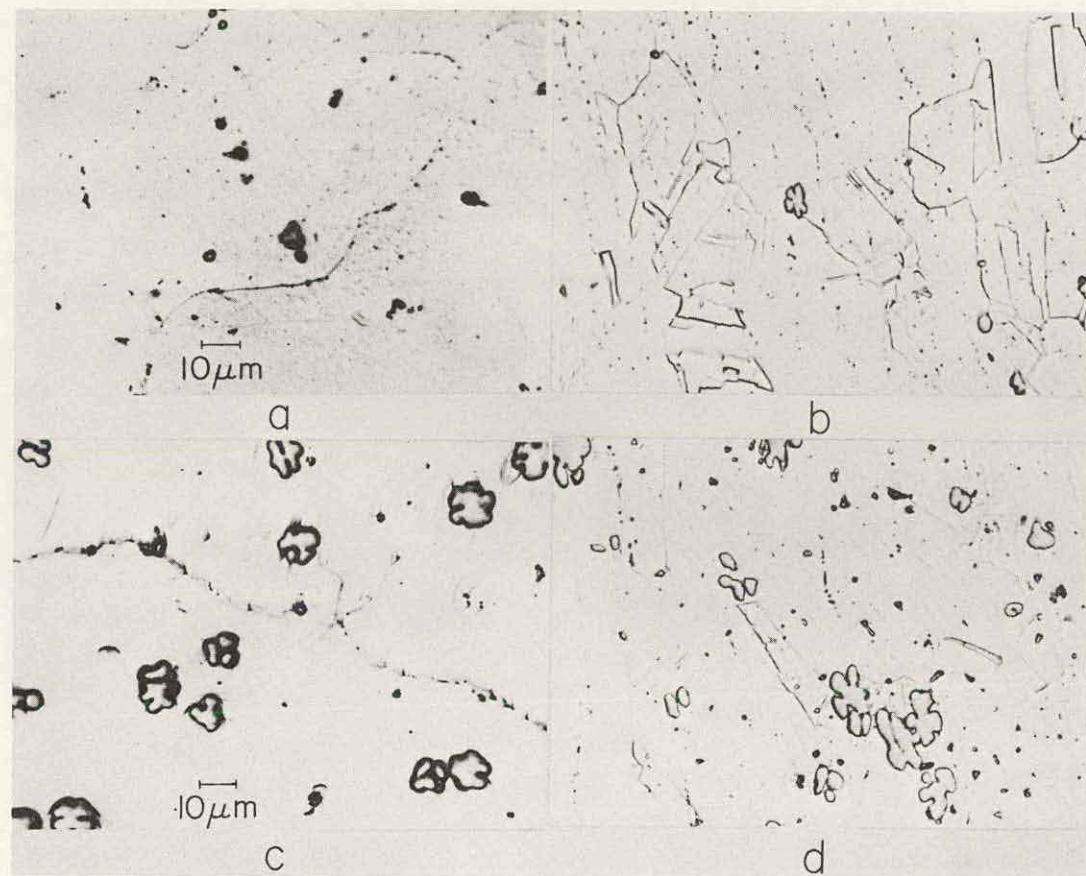


Fig. 9. Photomicrographs of copper-niobium alloys; a/0.5 at .% Nb as cast, b/0.5 at .% Nb after annealing, c/3.0 at .% Nb as cast, d/3.0 at .% Nb after annealing.

0.2 and 0.5, the low temperature resistivity for $T < 15^{\circ}\text{K}$ instead of being constant as that of pure copper decreases with decreasing temperature starting at about 8°K (Fig. 1). This effect becomes more pronounced with increasing Nb concentration. At 2°K , the resistivity of the alloy $\text{Cu}_{99.5}\text{Nb}_{0.5}$ is reduced to about 4% of the resistivity at 15°K . This trend is interrupted as more niobium is added to copper. For alloys with relatively high niobium content, the resistivity as a function of temperature first shows a sharp drop at about 9°K , then continues to decrease with decreasing temperature. The data presented in Fig. 2 indicate that the resistivity of the alloys $\text{Cu}_{98.5}\text{Nb}_{1.5}$ and $\text{Cu}_{95.0}\text{Nb}_{5.0}$ is nearly zero at 2°K . The alloy $\text{Cu}_{97.0}\text{Nb}_{3.0}$ exhibits a relatively high resistivity at 2°K ($\sim 30\%$ of the resistivity at 15°K). This indicates that the effect of adding Nb in Cu on resistivity of the alloys does not depend linearly on concentration.

2. The effect of annealing at 800°C for ~ 2 days on resistivity is shown in Figs. 3 and 4. For the most dilute alloy studied in this investigation, i.e. $\text{Cu}_{99.9}\text{Nb}_{0.1}$, annealing reduces the resistivity at 2.0°K to $\sim 10\%$ of its value at 15°K . This is to be compared with 75% for the same alloy in the as-rolled state. After annealing both $\text{Cu}_{99.8}\text{Nb}_{0.2}$ and $\text{Cu}_{99.5}\text{Nb}_{0.5}$ alloys become superconducting below 3°K . As indicated in Fig. 3, the resistivity of the annealed $\text{Cu}_{99.5}\text{Nb}_{0.5}$ decreases with decreasing temperature at a faster rate than that of annealed $\text{Cu}_{99.8}\text{Nb}_{0.2}$. The effect of annealing on the resistivity of the alloys with higher Nb concentration is manifested in two aspects: a) the magnitude of the resistivity drop around 9°K is reduced. b) below 8°K , the rate of decrease in resistivity is lower than that of the as-rolled samples. This effect, however, is less pronounced for the alloy $\text{Cu}_{98.5}\text{Nb}_{1.5}$.

3. From the results presented in Figs. 5-8, the estimated supercon-

ducting volume fraction (SVF) of the Cu-Nb alloys studied as a function of temperature is in general consistent with the results of the resistivity measurement. At low concentration i.e. for alloys $Cu_{100-x}Nb_x$, with $x = 0.1, 0.2, 0.5$ and 1.5 , the SVF increases with increasing Nb content for both the as rolled and the annealed samples.

It should be noticed that the magnitude of the SVF shown by these alloys is about fifty times the physical volume fraction of niobium. For example in the alloy $Cu_{99.5}Nb_{0.5}$ Nb would occupy at most $\sim 0.75\%$ of the total volume if all the Nb is assumed to be present as a second phase in the Cu matrix. The data shown in Fig. 7 indicate a superconducting volume fraction of about 50% at 2^0K . The alloys containing higher Nb concentrations, i.e. $Cu_{100-x}Nb_x$, $x = 3$ and 5 , show a relatively small SVF as compared with that in alloys $Cu_{99.5}Nb_{0.5}$ and $Cu_{98.5}Nb_{1.5}$. At about 9^0K a step-like increase in SVF has been observed for alloys $Cu_{100-x}Nb_x$, with $x = 1.5, 3$, and 5 . This corresponds to the resistivity drop at the same temperature as shown in Figs. 2 and 4. For a typical annealed $Cu_{97.0}Nb_{3.0}$, the initial increase of SVF is about 3%. At about 1.5^0K , the SVF of the same alloy increases to about 35%. It has been found that annealed samples generally exhibit a larger SVF than rolled ones.

4. The metallographic results as shown in Figs. 9a-9b, indicate that there are two distinct types of precipitates in the Cu matrix. The large precipitates (average size $\sim 10 \mu m$) randomly distributed in the alloy are probably formed at high temperature when the bulk of the alloy is still in the liquid state. The small precipitates that are visible under the magnification used (x750) appear to be discrete particles of average size $< 1 \mu m$. It is probable that there are even smaller size particles in between these relatively

small precipitates. It is to be noted that the smaller precipitates tend to form along grain boundaries and probably result from solid state precipitation. As shown in Fig. 9b, the effect of cold rolling the Cu_{99.5}Nb_{0.5} alloy is to align the precipitates in the rolling direction and the average inter-particle distance along a line is about 0.2 μ m. It has been found also that the large precipitates are more abundant in alloys containing more than 1.5 at. % Nb than in alloys containing less than 1.5 at. % is Nb, and the reverse is true for small precipitates.

IV. DISCUSSION

In interpreting the experimental results obtained in this investigation, it is necessary to know the phase diagram of the Cu-Nb alloys. The most complete investigation of this phase diagram was published by Popov and Shiryaeva³. Their paper contains more information than is shown in the diagram given in Ref. 4 which is somewhat confusing since the horizontal phase boundary line at 1550°C does not satisfy the phase rule. All the data points reported in Tables in Ref. 3 are shown in Fig. 10 and 11, and the phase boundaries have been traced in accordance with these data points. A two liquid phase field between about 20 and 33 at. % Nb has been included as suggested in Ref. 3, and by doing so the phase rule is satisfied. The copper-rich side of the diagram is rather well documented as shown in Fig. 10 and the solubility of Nb in Cu is less than 1 at. % just below 1100°C. This solubility decreases very fast with decreasing temperature, and the room temperature solubility is estimated to be about 0.10 at. %. In alloys cooled at rates in the range of those used in this investigation, the solubility is probably

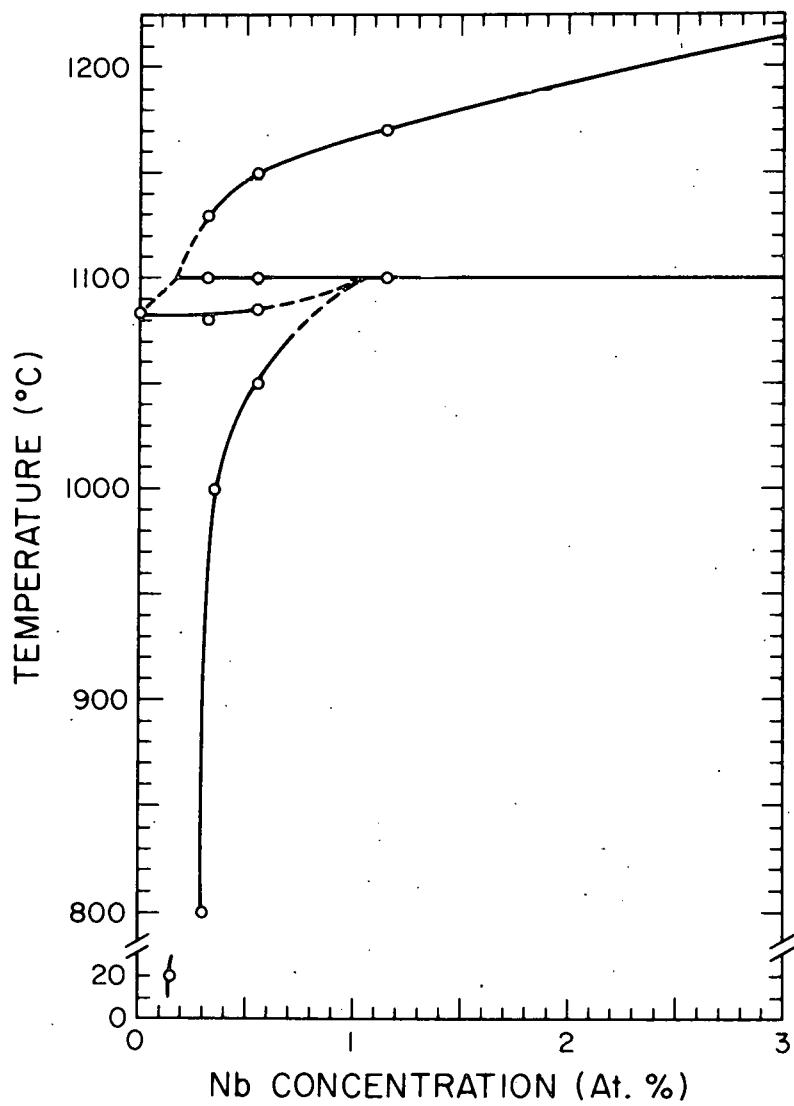


Fig. 10.

Copper rich portion of the Cu-Nb phase diagram.

The data points are from Ref. 3.

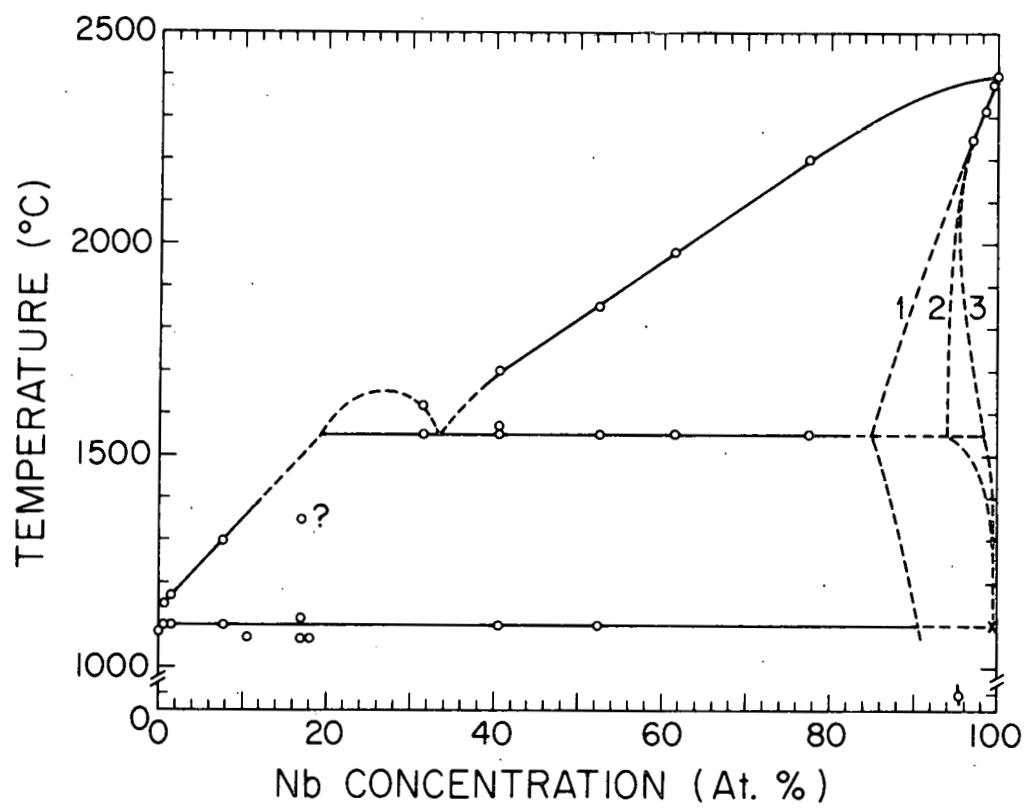


Fig. 11. Cu-Nb phase diagram. The data points shown by (0) are from Ref. 3. Three possible phase boundary lines are shown on the Nb rich side of the diagram and are explained in the text.

about 0.15 at. %.

The phase boundaries on the Nb rich side of the diagram are very poorly known. The boundaries shown in Ref. 3 and reproduced in Ref. 4 (curve 1 in Fig. 11) are not based on any data points. The solubility of Cu and Nb deduced from a microstructure examination⁵ and from electrical resistivity measurements⁶ would be 0.07 at. % at 1000°C. Possible phase boundaries consistent with this low solubility are shown by curves 2 and 3 in Fig. 11.

In summary, the data shown in the phase diagram indicate that at room temperature, the solubility of Nb in Cu(α solid solution) is limited to less than 0.10 at. % Nb and that Cu is almost insoluble in Nb. In equilibrium, the alloys containing more than 0.15 at. % Nb at room temperature should consist of two phases, Cu-rich α solid solution and Nb-rich solid solution containing less than 0.07 at. % Cu.

It is clear from the results presented in the previous section that any possible mechanism responsible for the superconducting properties observed in the Cu-Nb alloys, should account for the very large superconducting volume fraction for alloys containing less than 1.5 at. % Nb. In addition, the mechanism should also explain the disappearance of resistivity in $\text{Cu}_{99.8}\text{Nb}_{0.2}$ and $\text{Cu}_{99.5}\text{Nb}_{0.5}$ alloys below 3°K. Four possible mechanisms to explain these experimental results are discussed.

(1). The superconductivity observed may be due to the Nb dissolved in Cu(i.e. α solid solution). In view of the small solubility of Nb in Cu, it is unreasonable to expect this to be the cause of superconductivity. Furthermore, this mechanism cannot explain why an alloy like $\text{Cu}_{97.0}\text{Nb}_{3.0}$ would not be superconducting to at least the same extent as $\text{Cu}_{99.5}\text{Nb}_{0.5}$.

Another evidence which is against this mechanism is that the $\text{Cu}_{99.8}\text{Nb}_{0.2}$ alloy rapidly quenched from the liquid state⁷ at a rate of $\sim 10^5 \text{ }^\circ\text{C/sec}$ remains normal at 1.5°K .

(2). The niobium may form a layer on the surface of the copper-rich grains. To be superconducting at $\sim 4^\circ\text{K}$, the layer has to be about 100 \AA thick.^{8,9} If a typical grain size of $20 \mu\text{m}$ is assumed, then a simple calculation indicates that the amount of Nb needed to build such a layer is at least a few percents. In addition, part of the Nb is already present as precipitates and there is simply not enough Nb to form such a superconducting layer in the dilute alloys $\text{Cu}_{99.8}\text{Nb}_{0.2}$ and $\text{Cu}_{99.5}\text{Nb}_{0.5}$. The Nb layer formed on grains can then be ruled out as a mechanism for superconductivity.

(3). The Nb may form filaments and hence provides a continuous superconducting path. This is unlikely because first, there is no metallographic evidence for the existence of filaments, and second, the filaments mechanism would not explain the large superconducting volume observed.

(4). The proximity effect of the discrete Nb particles embedded in the Cu matrix gives rise to superconductivity observed. The metallographic results (as shown in Fig. 9b) definitely confirm the existence of discrete particles, and these particles can be identified as essentially Nb particles according to the phase diagram. It is reasonable to assume that there is a distribution of particle sizes ranging from the relatively large size visible in Figs. 9a and 9b (less than $1.0 \mu\text{m}$) to submicroscopic size not observed with light microscopy. In addition, there is a distribution of interparticle distances ranging from zero to few μm . In view of the probable distribution of the superconducting Nb particles just described, it is clear that the infinite conductivity observed in $\text{Cu}_{99.8}\text{Nb}_{0.2}$ and $\text{Cu}_{99.5}\text{Nb}_{0.5}$ alloys can

result from the leakage of Cooper pairs in Nb particles in the Cu-matrix.

The average interparticle distance must be comparable with the coherence length (of the order of 1000 Å) so that the Cooper pairs form a continuous path for superconductivity. The mechanism of proximity effect also explains the large superconducting volume as suggested by the inductance bridge measurements. The very wide superconducting transition shown in both the resistivity and the inductance measurements is consistent with the effect of a distribution of particle sizes as well as interparticle distances. The larger Nb particles contained in alloys Cu_{97.0}Nb_{3.0} and Cu_{95.0}Nb_{5.0} are typically 10 μm in diameter. It is expected that these Nb particles super conduct at about the same temperature as bulk Nb.^{8, 10} The interparticle distances (about 10 to 30 μm) are of the order of 100 times a typical coherence length. This definitely precludes the possibility of forming a superconducting path through the proximity effect of these particles. The effect of these superconducting particles (for T < 9°K) on the resistivity of the bulk alloy can be understood by considering the resistivity of an ideal system consisting of small, well-separated spheres of second phase (i.e. Nb) uniformly embedded in a metallic matrix (i.e. Cu). The resistivity of the alloy can be written approximately as¹¹:

$$\rho_{\text{alloy}} = \frac{\rho_{\text{Cu}} \left\{ 1 - f \left(\frac{\rho_{\text{Cu}} - \rho_{\text{Nb}}}{\rho_{\text{Cu}} + 2\rho_{\text{Nb}}} \right) \right\}}{1 + 2f \left(\frac{\rho_{\text{Cu}} - \rho_{\text{Nb}}}{\rho_{\text{Cu}} + 2\rho_{\text{Nb}}} \right)} \quad (1)$$

Where ρ_{Cu} and ρ_{Nb} are the resistivities of the matrix Cu and the second phase Nb, and f is the volume fraction of the second phase. In the limiting case, when the particles become superconducting below the transition temperature, i.e. $\rho_{\text{Nb}} = 0$ equation (1) can be approximated by the following

expression:

$$f_{\text{alloy}} \cong f_{\text{Cu}} \{ 1 - 3f \} \quad (2)$$

As shown in Fig. 8, the superconducting volume fraction of $\text{Cu}_{97.0}\text{Nb}_{3.0}$ near 9°K is about 3% (i.e. $f = 0.03$). Then, the resistivity at about 9°K would be reduced by a factor of $3f \approx 9\%$ which is about the right order of magnitude as indicated by the resistivity measurements (Fig. 4). Similarly for the case of $\text{Nb}_{5.0}\text{Cu}_{95.0}$, f is about 0.06 at 8.5°K , and the resistivity should decrease by $\sim 3f = 18\%$ according to equation (2). This is again approximately in agreement with the results of resistivity measurements (Fig. 8). In view of the approximations made in the above discussion, a quantitative agreement is not expected. This kind of analysis does indicate that if the superconducting particles are distributed far apart (i.e. interparticle distance is larger than the coherence length) the effect of the particles would reduce the resistivity according to equation (2). This conclusively demonstrates the need for a mechanism such as the proximity effect to explain the superconductivity of the alloys $\text{Cu}_{99.8}\text{Nb}_{0.2}$ and $\text{Cu}_{99.5}\text{Nb}_{0.5}$. In terms of this mechanism, the effect of annealing on the superconducting properties as shown in Figs. 3, 4, 7 and 8 can be understood as follows: Annealing at 800°C for ~ 2 days results in recrystallization, a relatively larger mean free path which can enhance the proximity effect. For alloys containing less than 1 at.% Nb, supersaturated α solid solution retained by cooling from the liquid state could precipitate more fine Nb particles during annealing. This effect also can lead to a sharper superconducting transition and a larger superconducting volume. On the other hand, it is possible that prolonged annealing at 800°C or higher

can cause the very fine Nb precipitation to coalesce and grow in size. This effect would tend to increase the superconducting transition temperature of the individual Nb particles. If the interparticle distances become significantly large as a result of coalescing, the proximity effect would be reduced. Diffusion between Nb and Cu during annealing could reduce the proximity effect. Judging from the results, this effect is not significant probably because of the near zero solubility of Cu and Nb at 800°C. From Figs. 9b and 9d, it can be seen that the size of the large Nb particles is reduced and the number of smaller Nb particles is increased after annealing. These smaller particles probably do not contribute significantly to the superconductivity because of their relatively large interparticle distances (typically $\sim 5000 \text{ \AA}$). The reduction in size of the larger Nb particles as a result of annealing is consistent with the observation that in the annealed samples the magnitude of the first resistivity drop at $\sim 9^{\circ}\text{K}$ is reduced.

Superconducting proximity effect has been studied in the form of superimposed films of a superconductor and a normal conductor¹². Previous work indicates that spurious effects can result from an insulating oxide layer or poor electrical contact between the superconducting and normal films. The present alloys should be free from these difficulties.

The magnetic properties of the Cu-Nb alloys have not been studied in this work. The magnetic properties of a superconductor film is greatly modified by the proximity effect of normal metal,¹² and similar effects can be expected in the present alloys. In these alloys, it should be of interest to find out how a distribution of superconducting particle sizes and interparticle distances will modify the magnetic properties. A measurement of critical field as a function of temperature should be particularly interesting

in view of a recent unusual prediction that some system consisting of superconducting spheres dispersed through a metal matrix may exhibit multiple transition temperatures.¹³ Such an effect, if it exists, should have been observed in the measurements of superconducting volume fraction by the inductance bridge technique. A close examination of the experimental results obtained in this investigation have failed to show any evidence of this effect.

Near the transition temperature, the specific heat of superconducting particles distributed in a metal is certainly affected by the proximity effect. As pointed out by Fulde and Moermann,¹⁴ the specific heat jump is a sensitive measure of the proximity effect. Therefore, a comparison between the specific heat of Cu-Nb alloys and that of bulk Nb should yield some valuable information concerning the proximity effect. A program of measuring the magnetic properties and the specific heat of Cu-Nb alloys is in progress.

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