Superconducting transition of electrodeposited technetium

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Complex-susceptibility measurements of the superconducting transition of Tc films prepared by electrodeposition and reduction (heat treatment) have been performed. In order to find the optimum experimental conditions for preparation of metallic Tc by the present method, several different conditions have been attempted. For the measurement of the complex susceptibility, a Hartshorn-type mutual-inductance bridge was constructed. The whole performance of the measuring system was examined by using Sn and Pb films. It has been revealed that the structural details (dislocation or homogeneity) of the samples are well reflected on the observed complex susceptibility and that the mean energy dissipation in the temperature region of the superconducting transition is a good probe for structural examination of the samples.

I. INTRODUCTION

Measurements of the superconducting transition temperature T_0 can be made by various methods, i.e., by means of resistivity, ac susceptibility (or complex susceptibility), dc magnetization, and specific heat. Among these, ac-susceptibility measurements are useful to obtain structural information on the specimens. In general, for a periodically varying magnetic field of frequency ω, the susceptibility of the materials can be approximately given by a complex expression,

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) \quad .$$

In the case of superconductors, changes in χ' with respect to temperature correspond to the occurrence of the Meissner effect. In addition, it is well known that χ'' is related to the energy dissipation in materials, $Q = (\frac{1}{2})\omega\chi'' H_0^2$, where Q is the mean energy dissipation per unit time per unit volume and H_0 is the amplitude of the external magnetic field.[1] These considerations suggest complex susceptibility measurement for obtaining structural information on superconductors.

A Hartshorn-type mutual-inductance bridge was constructed to measure the complex magnetic susceptibility of Tc films in the temperature range 1.54 – 10.1 K. A sample holder and an adiabatic cell were carefully designed so as to eliminate disturbances due to the susceptibility of surrounding materials. The whole performance of the device was checked by measuring the superconducting transition of Sn and Pb films.

Technetium is $4d$ transition metal with the second highest superconducting transition temperature of any pure metal at normal pressure. However, because of the absence of stable isotopes, investigations of this metal have so far been limited compared to other metals. We have developed a method to prepare metallic Tc by means of electrodeposition and reduction (heat treatment). Various samples prepared by this method were studied by measuring the ac susceptibility with the Hartshorn bridge. It has been revealed that the complex-susceptibility profile is affected sensitively by the experimental conditions for the preparations of metallic Tc and is a good probe to find the optimum conditions for obtaining homogeneous samples.

In this paper we give details of our experimental device and discuss the measurements with Tc samples. A discussion on the structure of the samples with respect to the profile of χ'' is also given.

II. EXPERIMENTAL

A. Sample preparation

Details of the sample preparation were previously reported in our relevant works.[2–6] For Tc, the deposition was carried out in several kinds of working solutions and onto different substrates. The sample thickness was estimated by measuring the activities of ^{99}Tc in the working solution before and after deposition, for which we used a liquid-scintillation counter. Table I lists the compositions of the working solutions, the electric currents for deposition, the deposition periods, the substrates, and the sample thicknesses.

The heat treatment for each sample listed in Table I is as follows: Tc-1 was annealed for 1 h at 1000 °C in a pure hydrogen atmosphere. Tc-2 and Tc-3 were used in three ways, i.e., as-electrodeposited and after two heat-treatment steps. The first heat treatment

TABLE I. Experimental conditions for electrodeposition of Tc. The temperature of the working solution is 40 °C.

Specimen	Working solution	Electric current (mA/cm^2)	Deposition period (h)	Substrate	Thickness (μm)
Tc-1	H_2SO_4 (20 ml, *p*H 1.0) NH_4F (50 mg) $NH_4{}^{99}TcO_4$ (12 μmole)	100	22	Nichrome	5.0
Tc-2	H_2SO_4 (24 ml, *p*H 1.0) NH_4F (50 mg) $NH_4{}^{99}TcO_4$ (26 μmole)	28	3.3	Cu	2.7
Tc-3	H_2SO_4 (24 ml, *p*H 0.7) NH_4F (50 mg) $NH_4{}^{99}TcO_4$ (26 μmole)	16	3	Cu	1.8
Tc-4	H_2SO_4 (24 ml, *p*H 1.0) NH_4F (50 mg) $NH_4{}^{99}TcO_4$ (26 μmole)	32	3	Pt	2.0

was carried out for 4 h at 900 °C, on samples Tc-2*a* and Tc-3*a*. Then the second heat treatment was carried out for 46 h at 900 °C, on Tc-2*b* and Tc-3*b*. Tc-4 was annealed for 2 h at 1100 °C and then a 150-h annealing was carried out at 1000 °C.

An x-ray diffraction study of Tc-2*b* and Tc-3*b* confirmed the hcp structure of metallic Tc ($a = 2.74$ Å and $c = 4.40$Å), and revealed that the *c* axis of Tc-3*b* is almost perfectly oriented with respect to the surface. Analysis by a scanning electron microscope showed that Tc-2 (2*a*, 2*b*) has a particle shape of about 2 μm in diameter, but Tc-3 (3*a*, 3*b*) has a mosaic structure.

As the standard samples, Sn and Pb were used. These samples were prepared by vacuum evaporation onto microscope cover glass. The pressure in the vacuum chamber at the initial stage of evaporation was 7.4×10^{-7} Torr for Sn and 5.0×10^{-6} Torr for Pb. The temperatures of the substrates and the deposition rates were 77 K, 90 Å/sec for Sn and 300 K, 30 Å/sec for Pb. The sample thicknesses of Sn and Pb were estimated to be 1.0 and 0.65 μm, respectively.

B. Measurements of $\chi'(\omega)$ and $\chi''(\omega)$

The Hartshorn-type mutual-inductance bridge was first introduced by Hartshorn,[7] and has been widely used in the field of low-temperature physics.[8]

The bridge essentially consists of two coils (cryostat coil M_1 and standard coil M_2) and a phase-shift potentiometer. In the present experiment, the cryostat coil M_1 (sample coil) consists of two coaxial cylindrical coils. The inner coil (primary) is 6970 turns (in seven layers) of Cu wire (0.14 mm in diameter) coated by polyvinyl formal (PVF). The outer coil (secondary) is divided into two sections. Each section is 2025 turns of PVF Cu wire in seven layers, wound in counter direction to each other. The mutual inductance of M_1 in the absence of the sample is less than 10 μH. The sensitivity of the variable standard coil M_2 is 0.01 μH. The phase-shift potentiometer is composed of manganin wire (1 mm in diameter and 1-m long) and of a slide contact.

The bridge was designed for the use of discrete frequencies of 20, 30, 71, 80, 85, and 90 Hz. The earthing line of the system was carefully designed to minimize the effect of the electrical noise. The bridge was usually drived by the primary current producing a magnetic field of 0.1 Oe at the sample position (see below). Under these conditions, the sensitivity of the present device is 0.05 μH for χ'.

As mentioned before, in a periodically varying magnetic field, the response of the materials manifests as a change in magnetization, and the susceptibility is approximately expressed in a complex form,

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) \ ,$$

where $\chi'(\omega)$ and $\chi''(\omega)$ correspond to the in-phase and out-of-phase response of the substance. In the

Hartshorn bridge, χ' is proportional to the change in the mutual inductance of M_2 when a sample is inserted in M_1. Similarly χ'' is proportional to the change in the readings of the phase-shift potentiometer.

C. Temperature control of specimens

Since the effect of surrounding materials on the measurement of the complex susceptibility may introduce serious errors, careful attention was paid to the constituent materials used in the sensitive region of the cryostat coil M_1. Especially, ferromagnetic and superconducting substances should be avoided. In addition, bulk materials having high electric conductivity are not desirable because of the eddy-current loss produced in an ac magnetic field.

Taking into consideration the problems mentioned above, the sample holder and the adiabatic cell were designed as shown in Fig. 1. The film sample was sandwiched between two glass ampoules filled with 1 atm He gas at room temperature. A small Cu block, in which a Ge thermometer was mounted, was attached to the upper glass ampoule. A coil-foil (a sheet made with 0.14-mm diam PVF Cu wires glued together with GE7031) was rolled around the Cu block and two glass ampoules, and was tightly bound by silk strings. The convenient features of the coil-foil are: First, because of the small cross section perpendicular to the external magnetic field, the eddy-current loss can be minimized; second, Cu wire is a good thermal conductor; and third, the sample holder is effectively shielded from thermal radiations. A better thermal contact between two sample-holder parts was achieved by using Apieson *N* grease. A manganin heater (0.08 mm in diameter and 1.5-m long) for temperature control was wound bifilarly and uniformly around the sample holder.

The sample holder was thermally insulated from the adiabatic cell by using silk strings. A holder thermal shield for radiation from topside was also set above the cell. A teflon weight placed at the bottom of the sample holder was hung by silk strings. The adiabatic cell was made of pyrex glass and was coated by aquadag for thermal shielding. All of the electric connections were made with 40-wt.%-Bi–60-wt.%-Cd solder, which is in the normal state above 1 K.

Temperature control for 4.2 – 10 K was achieved by using a manganin heater. In this case, the adiabatic cell was kept in high vacuum, less than 10^{-6} Torr at 300 K. To obtain temperatures below 4.2 K, the cell was filled with He exchange gas at a pressure of 1 Torr at 300 K, and then the He bath was pumped down. After having reached the lowest temperature (~1.3 K), the cell was evacuated and the manganin heater was used to get the necessary sample-holder temperature.

A Ge thermometer is located about 12 cm away from the specimen. However, T_0 of the Sn sample measured by setting the Ge thermometer in the Cu block (see Fig. 1) and in the vicinity of the sample gave only 16 mK difference, proving that the temperature gradient in the sample holder is quite small. This smallness is due to the good thermal conductivity of the coil-foil and also to the He exchange gas contained in the glass ampoules. The resistance of

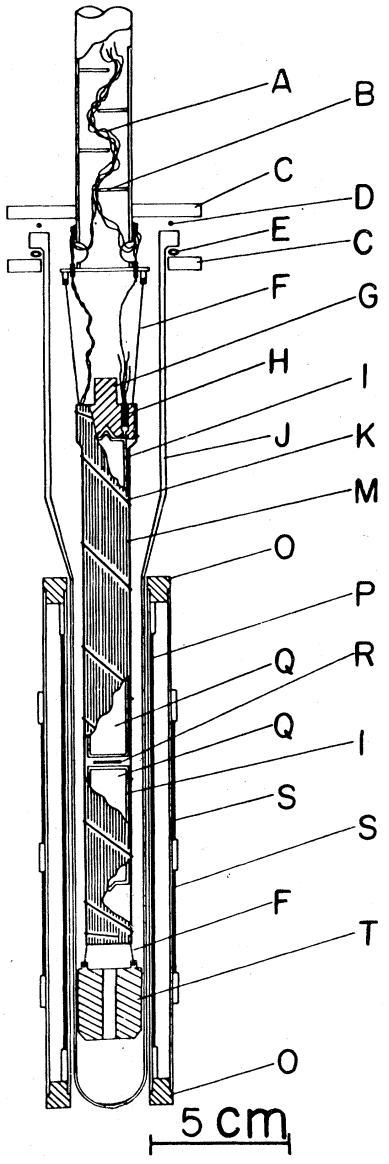

FIG. 1. Details of the sample holder and of the adiabatic cell. A: Electrical leads, B: Cu radiation shield, C: Brass flange, D: Indium seal, E: Teflon ring, F: Silk strings, G: Cu block, H: Ge thermometer, I: Glass ampoule, J: Adiabatic cell, K: Manganin heater, M: Coil-foil, O: Teflon support, P: Primary coil, Q: He gas, R: Specimen, S: Secondary coil, T: Teflon weight.

the Ge thermometer was measured by the conventional four-probe method, where a constant current of 10 μA was supplied within an error of 5×10^{-3}%. Calibrations of the Ge thermometer was previously made in the temperature range 1.54 − 10.1 K. The accuracy of the thermometer was estimated to be ±10 mK in absolute value and ±0.1 mK in relative value.

Susceptibility measurements without a sample have shown that both the sample holder and the adiabatic cell do not cause any appreciable disturbance in the measurement of the complex susceptibility in the temperature range to be studied.

III. RESULTS AND DISCUSSION

Since the geometrical demagnetization coefficient is generally large for film specimens,[9] the dependence of χ' on the amplitude H_0 of the ac magnetic field should be derived to obtain an optimum value of H_0. For this purpose, χ' of the Sn film placed perpendicular to the magnetic field was measured as a function of H_0 for various temperatures below T_0. As a typical result, in Fig. 2 is shown $\chi'(\omega)$ vs H_0 for $\omega = 71$ Hz, where $T = 2.979 - 3.892$ K. In the vicinity of T_0 (=3.79 K), χ' strongly depends on H_0. Especially, as seen in the figure, for $H_0 = 0.1 - 0.5$ Oe, χ' changes rapidly with respect to H_0. However, for $H_0 = 0.1$ Oe and less, the value of χ' near T_0 approaches those for other temperatures below T_0. In addition, comparisons of the results for different frequencies have proved that there is no appreciable dependence of χ' on frequency. Thus, the H_0 and ω used in the present experiment were reasonably chosen as 0.1 Oe and 80 Hz.

For confirmation of the reliability of the present device, two standard samples, Sn and Pb, were measured. In Fig. 3 are shown the observed χ' and χ'' curves for the Pb case. The value of T_0 taken as the midpoint of the transition curve of χ' is 7.28 K, which agrees well with the current value.

As seen in Fig. 3, χ' changes monotonically when the specimen subsequently goes from the normal state down to the superconducting state. On the contrary, χ'' has a peak at a temperature near T_0. This particular response of χ'' accompanied by the normal-superconducting transition was first observed by Maxwell and Strongin[10] for a cold-worked Sn specimen (99.9%, resistivity ratio 300). Their explanations for this response are the following: (a) When the temperature goes down, small filamentary inclusions which are in the superconducting state are produced in the sample. (b) This results in an increase of the average conductivity of the sample, but due to the smallness of the inclusions, there appears no Meissner effect at this stage. (c) Consequently, the energy dissipation due to the eddy current increases as the temperature goes down to T_0. (d) In the vi-

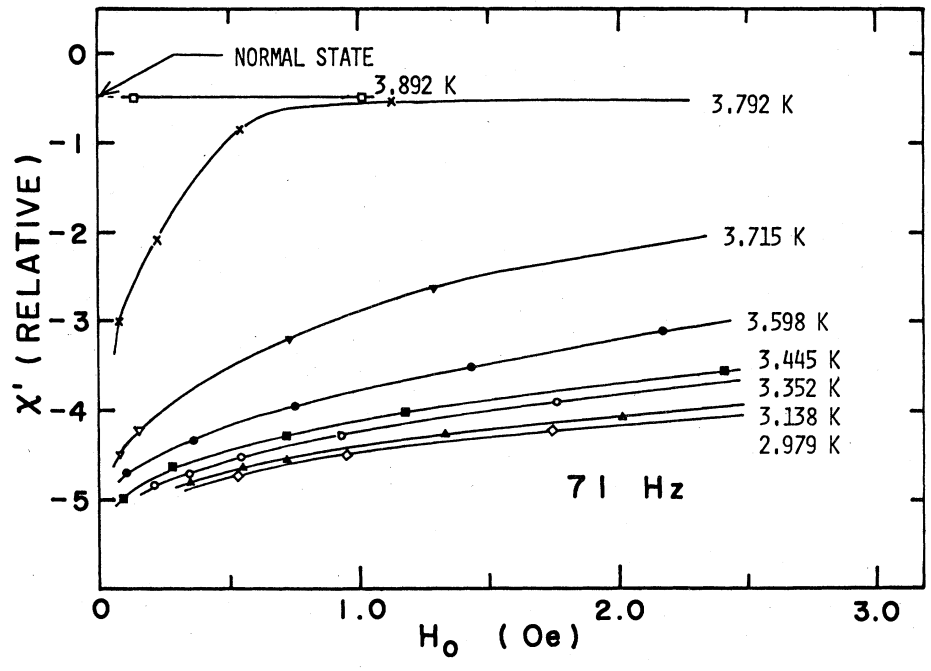

FIG. 2. χ' of Sn film specimen vs amplitude of ac magnetic field H_0 for various temperatures below T_0.

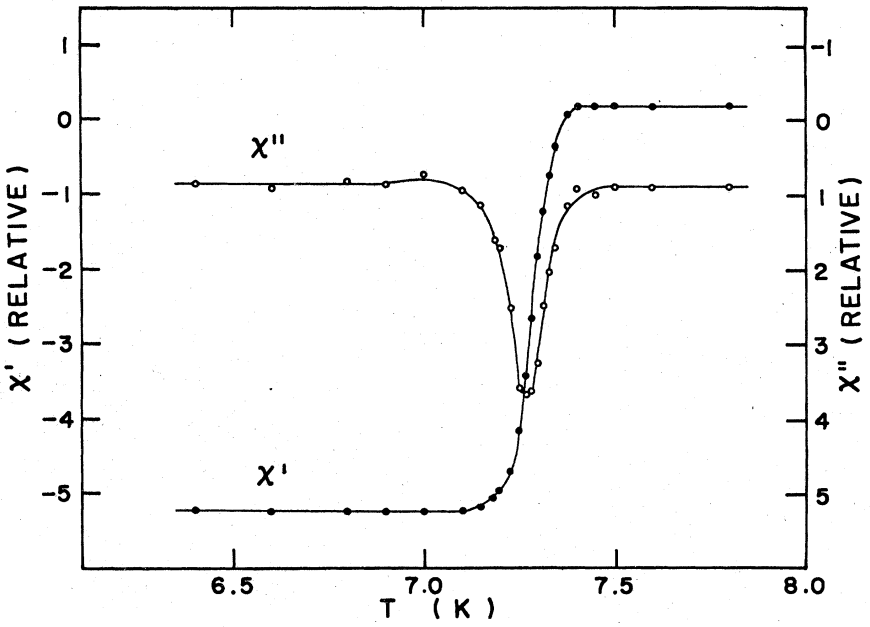

FIG. 3. Complex susceptibility of Pb film specimen vs temperature.

cinity of T_0, originally unconnected superconducting filamentary inclusions eventually join to form a multiply connected mesh. (e) As the temperature is lowered further, the eddy-current shielding becomes dominant and the energy dissipation in the specimen begins to decrease.

It should be noted that, with a purer cold-worked Sn specimen (99.999%, resistivity ratio 5000), Maxwell and Strongin[10] could not find any peak in the χ'' curve. The disappearance of the peak for the purer specimen was interpreted as this being a nonfilamentary superconductor in which the superconducting inclusions have much volume in the earlier stage of the transition. In this case, the conductivity increase for eddy current would not result in an increase of the average energy dissipation, because the effective fraction of normal metal would be lessened.

The above two cases reported by Maxwell and Strongin are really suggestive, i.e., it can be said that the complex susceptibility, especially χ'', is a sensitive probe of dislocations or homogeneity in samples. Based upon their observations as well as our present results with Sn and Pb samples, we examined Tc samples prepared by the method described before.

In Fig. 4 shows χ' versus temperature for Tc-1 (nichrome base) together with the resistive curve previously measured[2] with the same sample. As seen in the figure, the transition width of χ' is larger than that in the resistive curve, but the transition temperatures still agree well within experimental error, $T_0 = 7.42 \pm 0.05$ K and 7.46 ± 0.05 K, respectively. The difference in two curves reflects some inhomogeneity in this sample, which could not be found by the resistive method.

The sample Tc-2 was prepared on a Cu sheet in the working solution of $p\mathrm{H} = 1.0$. Because of the good conductivity of Cu, it was not possible to measure the resistive transition. By repeating the heat treatment, we obtained Tc-2*a* and Tc-2*b* for which the heat-treatment conditions were described before. The complex susceptibility versus temperature for Tc-2, 2*a*, and 2*b* are shown in Fig. 5.

In each stage of heat treatment, the annealing ef-

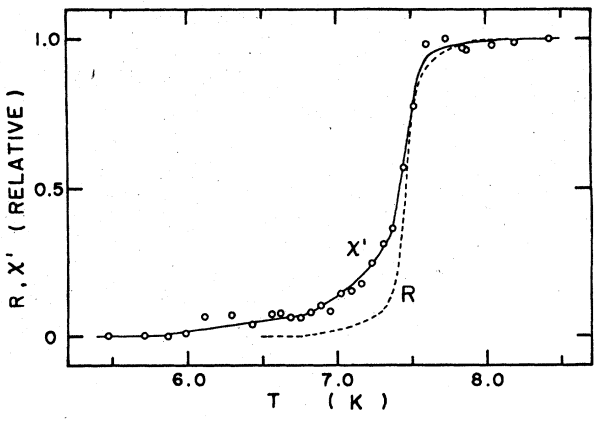

FIG. 4. χ' vs temperature for Tc-1 (see text). The dashed curve is the result obtained by the resistive method.

fect is reflected in χ' and χ''. For the as-electrodeposited sample Tc-2, the transition occurs in a broad temperature region. This broadness may be due not only to dislocation and ununiformity, but also to the coexistence of metal and Tc oxide in the sample. There are two peaks in the χ'' curve. As suggested by Strongin *et al.*,[11] multiple peaks in the χ'' curve probably correspond to separate transitions occurring in different parts of the specimen. In addition, at the earlier stage of the transition from normal to superconducting, the change in χ'' is more remarkable than in χ'. This can be explained by the average-conductivity model mentioned above, i.e., in Tc-2, the tiny filamentary inclusions are dominant at the beginning of the transition, and consequently the eddy-current loss increases in the temperature region where the Meissner effect is not so evident. It is interesting to point out that T_0 defined as the midpoint of the whole change in χ' is still near the maximum point in χ'', in spite of such a wide transition range.

Tc-2*a* shows an upward shift of T_0 and a decrease in transition width compared to Tc-2. Although the χ' curve shows much improvement in symmetry, the χ'' curve still has a similarity to that for Tc-2, i.e., two peaks are still there. From these curves, it is concluded that Tc-2*a* is physically not homogeneous yet.

For Tc-2*b*, annealing seems to be sufficient. No improvement in the transition curve can be expected as long as the purity of the sample ($\sim$99.9%) is not improved. The χ' and χ'' curves indicate that Tc-2*b* is a homogeneous and single-phase system. For comparisons, the transition temperature of this specimen is given in Table II together with those obtained

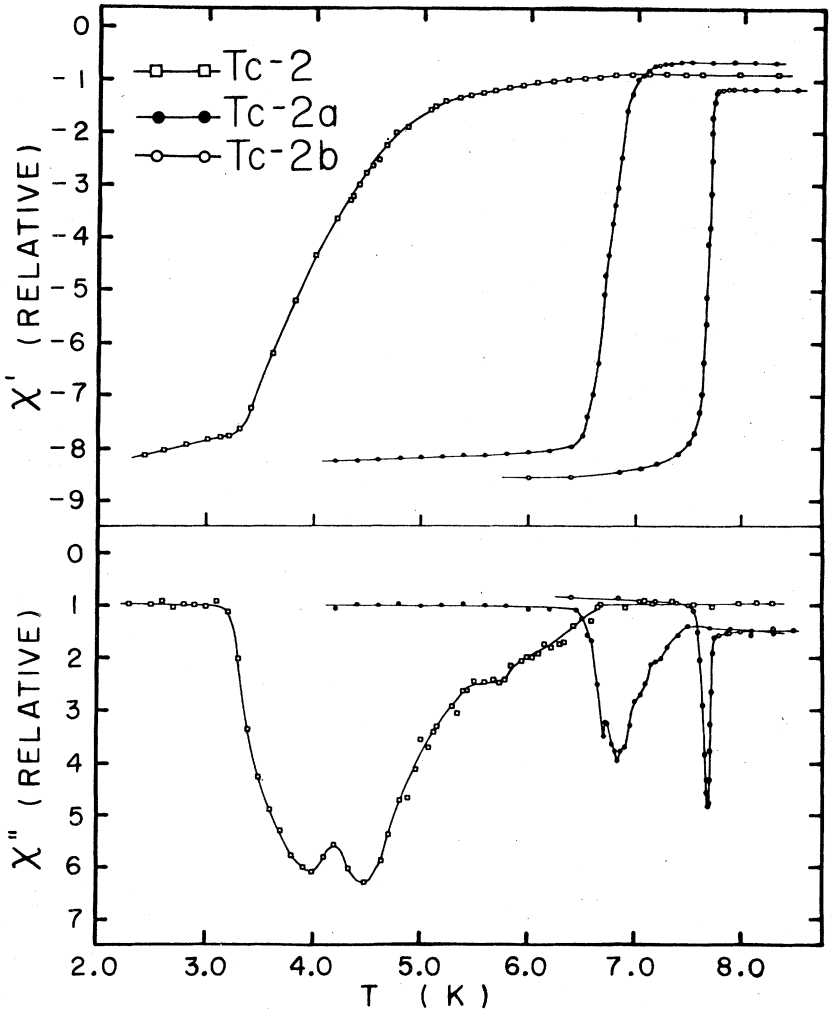

FIG. 5. Complex susceptibility vs temperature for Tc-2 (as-electrodeposited), Tc-2*a* (heat treatment for 4 h at 900 °C), and Tc-2*b* (heat treatment for 4 h at 900 °C and then for 46 h at 900 °C).

TABLE II. Transition temperature of Tc.

T_0 (K)	Method	Reference
8.22 ± 0.01	dc resistance	12
8.35	dc magnetization	13
7.77 ± 0.02	dc magnetization	14
7.73 ± 0.02	dc magnetization	14
8.00 ± 0.01		15
7.924 ± 0.01		15
7.46 ± 0.04	dc magnetization	16
7.82 ± 0.02	dc magnetization	17
7.70	resistance	18
7.85	ac susceptibility	19
7.86	specific heat	20
7.87	ac susceptibility	21
7.7	resistance	22
7.46 ± 0.05	ac resistance	2
7.67 ± 0.05	ac susceptibility	present

by other workers.[2,12–22]

It is interesting to note something more about the χ'' curves in Fig. 5. For Tc-2, the saturation values of χ'' in the superconducting and the normal state are nearly the same. However, for Tc-2*a* some difference between them appears, i.e., χ'' in the normal state is larger than in the superconducting state. The difference is more remarkable for Tc-2*b*. The possible explanations for this difference are: (a) In the superconducting state, the ac loss in the sample is negligibly small. On the contrary, in the normal state, the sample χ'' is approximately proportional to its electric conductivity, as long as the skin depth is large compared to the sample thickness.[1] (b) For Tc-2, the electron mean free path (electric conductivity) is considered to be small since the crystal is disordered and because of the coexistence of Tc oxide and metal. This indicates that ac loss in Tc-2 in the normal state is small, giving similar saturation values of χ'' in both states. (c) By heat treatment, the electric conductivity of the sample increases,

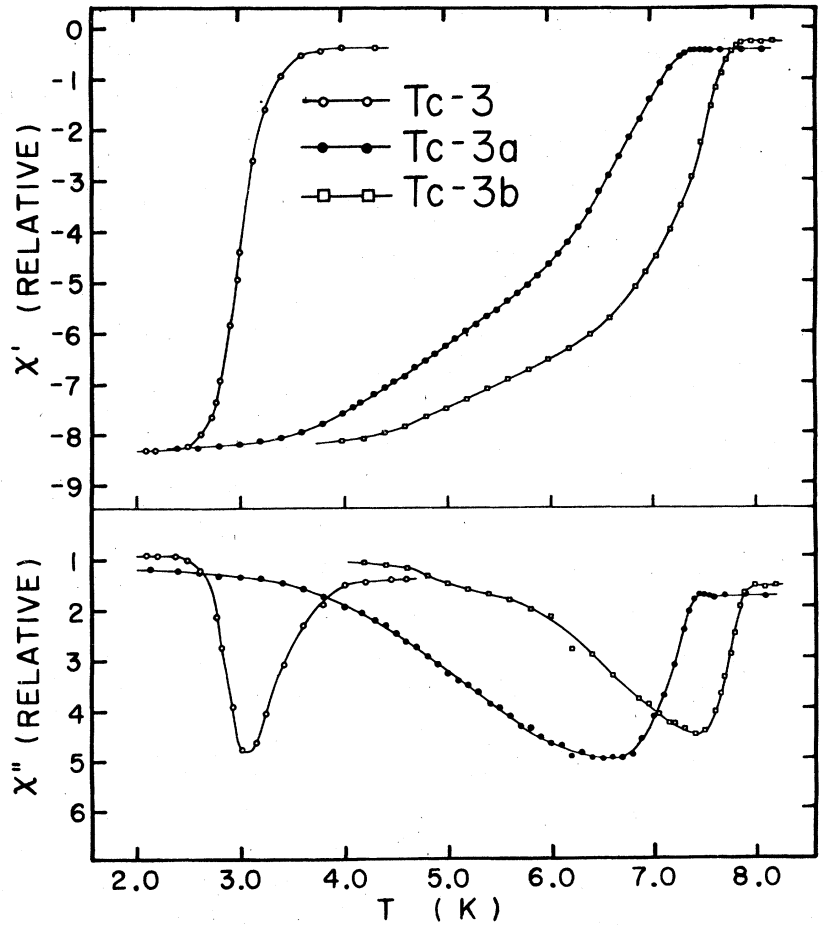

FIG. 6. Complex susceptibility vs temperature for Tc-3 (as-electrodeposited), Tc-3*a* (heat treatment for 4 h at 900 °C), and Tc-3*b* (heat treatment for 4 h at 900 °C and then for 46 h at 900 °C).

resulting in the increase in ac loss of the sample in the normal state.

It is known from the chemical properties of Tc that the chemical form of electrodeposited Tc depends on the pH of the working solution. To see the effect of the acidity, Tc-3 was prepared in the working solution of $p\mathrm{H}=0.7$. As shown in Fig. 6, T_0 of Tc-3, 3*a*, and 3*b* shows a subsequent upward shift, but the transition width becomes larger and appreciable improvement in the shape of the χ'' curves is not obtained by heat treatment. The reason for this enhancement in the transition width is not clear yet, but the effectiveness of the heat treatment evidently depends on the chemical nature of the working solution for electrodeposition. It should be noted, however, that the saturation values of χ'' for Tc-3 in the superconducting and in the normal state show some difference, as observed for Tc-2*a* and 2*b*. This indicates that Tc-3 prepared at $p\mathrm{H}=0.7$ has a better electric conductivity than Tc-2 prepared at $p\mathrm{H}=1.0$.

As mentioned before, an x-ray diffraction analysis of Tc-3*b* shows that the *c* axis for hcp structure is almost perfectly oriented perpendicular to the surface, but in Tc-2*b* the orientation is not so evident as in Tc-3*b*. The difference between Tc-2*b* and Tc-3*b* in their orientations suggests that the growth of the Tc crystal on the substrate depends sensitively on acid concentration in the working solution.

Measurements with Tc-4, prepared on a Pt substrate in the working solution of $p\mathrm{H}=1.0$, were inconclusive. In spite of heat treatment at more than 1000 °C, the complex susceptibility did not change in the temperature range 1.5 – 10 K. Further studies are needed with Tc-4.

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