Complex Susceptibility Measurements of Superconducting Transition of Electrodeposited Technetium

Takekazu Ishida and Hiromasa Mazaki*

The superconducting transition of electrodeposited Tc films was studied by measuring the complex susceptibility of specimens. The electrodeposition was carried out under several different conditions and the preparation of metallic Tc by this method was established. For the measurement of complex susceptibility, a Hartshorn-type mutual inductance bridge was constructed. The measuring system involving the bridge was examined by using Sn and Pb films, and was found to have the sensitivity of 0.05 μH. It has been revealed that the structural situation of specimens is well reflected in the observed complex susceptibility and that the information on dislocation and homogeneity in the sample can be obtained from the measurement. Some attempts to prepare Re samples were also performed by means of electrodeposition.

INTRODUCTION

Measurements of 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, the ac susceptibility measurement is useful to get information concerning the structure of specimen. In general, the response of magnetic materials for an external magnetic field varying in time appears as the change in magnetic moment. For periodically varying field of frequency w, the susceptibility can be approximately given by a complex expression, $\chi(w) = \chi'(w) - i\chi''(w)$. In the case of superconductors, changes in χ' with respect to temperature correspond to the Meissner effect, and χ'' is proportional to energy dissipation in the sample.[1] By this reason, applications of the ac susceptibility measurement for superconductors are useful to get structural information of specimens.

A Hartshorn-type mutual inductance bridge was constructed to measure the complex magnetic susceptibility of film specimen of Tc in the temperature range of 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 experimental procedure was checked by measuring superconducting transition of Sn and Pb, and was proved to be satisfactory.

Technetium is 4d transition metal with the second highest superconducting transition

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* 石田武和, 間崎啓匡 : Laboratory of Nuclear Radiation, Institute for Chemical Research, Kyoto University, Kyoto, Japan.

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 heat-treatment. Various samples prepared by this method were studied by measuring the ac susceptibility with the Hartshorn bridge. The results obtained were compared with those previously found by the resistive method.[2] It has been revealed that complex susceptibilities are more sensitive probe than electrical resistance for obtaining the information on dislocation and homogeneity in samples.

Rhenium is 5d transition metal superconductor. The sample was also prepared by electrodeposition. The sample thus prepared seems to be amorphous and the transition temperature found by the ac susceptibility method is appreciably higher than the current value of a bulk specimen.

In this paper, we present details of our experimental device and procedures mainly with Tc samples. Discussion on the structure of samples corresponding to the change in χ'' is also given.

EXPERIMENTAL

1. Sample Preparation

Details of 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 activities of ^{99}Tc in the working solution by a liquid scintillation counter before and after deposition. In Table I are listed the composition of working solution, electric current for deposition, deposition period, substrate, and sample thickness. For Re, the sample thickness was estimated from Re concentrations in the working solution before and after deposition, where the concen-

Table I. Experimental Conditions for Electrodeposition of Tc and Re.
The Temperature of Working Solution is 40°C

Specimen	Working solution	Electric current (mA/cm^2)	Deposition period (h)	Substrate	Thickness (μm)
Tc-1	H$_2$SO$_4$ (20 ml, pH 1.0) NH$_4$F (50 mg) NH$_4$ ^{99}TcO$_4$ (12 μmole)	100	22	Nichrome	5.0
Tc-2	H$_2$SO$_4$ (24 ml, pH 1.0) NH$_4$F (50 mg) NH$_4$ ^{99}TcO$_4$ (26 μmole)	28	3.3	Cu	2.7
Tc-3	H$_2$SO$_4$ (24 ml, pH 0.7) NH$_4$F (50 mg) NH$_4$ ^{99}TcO$_4$ (26 μmole)	16	3	Cu	1.8
Tc-4	H$_2$SO$_4$ (27 ml, pH 1.0) NH$_4$F (50 mg) NH$_4$ ^{99}TcO$_4$ (26 μmole)	32	3	Pt	2.0
Re	H$_2$SO$_4$ (24 ml, pH 0.7) NH$_4$F (50 mg) NH$_4$ReO$_4$ (25 μmole)	16	3	Cu	0.3

tration was measured by an atomic flame emission spectrophotometer. The experimental conditions for deposition of Re are also given in Table I.

Heat-treatment for each sample listed in Table I is as followings: Tc-1 was annealed for 1 h at 1000°C in pure hydrogen atmosphere. Tc-2 and Tc-3 were heat-treated in pure hydrogen atmosphere in two steps. First a 4-h annealing at 900°C was carried out, for which we signify as Tc-2a and Tc-3a. Then two samples were annealed for 46 h at 900°C, for which we signify as Tc-2b and Tc-3b. Tc-4 was annealed for 2 h at 1100°C and then a 150-h annealing was carried out at 1000°C.

As standard samples, Sn and Pb were used. These samples were prepared by vacuum evaporation onto a microscope cover glass. The initial pressure in the vacuum chamber was 7.4×10^{-7} torr for Sn and 5.0×10^{-6} torr for Pb. But, during evaporation, the inner pressure of the vacuum chamber was deteriorated by a factor of about 2. Temperatures of the substrates and 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 μm and 0.65 μm, respectively.

2. Measurements of χ' and χ'' by Mutual Inductance Bridge

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]

Schematic diagram of the mutual inductance bridge used in the present experiment is shown in Fig. 1. The bridge essentially consists of two coils, M_1 and M_2, and the phase-shift potentiometer R. The cryostat coil M_1 in which a sample is placed consists of two coaxial cylindrical coils. The inner coil (primary) is 6970 turns (in 7 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 7 layers in the counter direction to each other. The mutual inductance of M_1 without any sample is less than 10 μH. As a variable standard mutual inductance M_2, Tinsley type 4229 is used, of which the working range is 0.1 μH~1.111 mH with the sensitivity
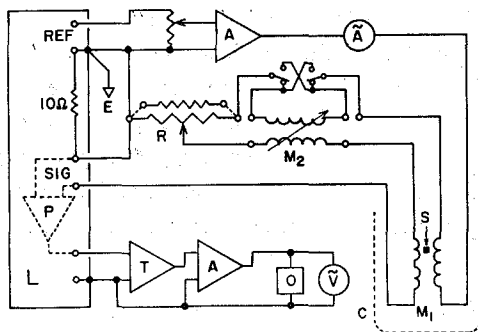

Fig. 1. Schematic diagram of the Hartshorn-type mutual inductance bridge. L) Lock-in amplifier, P) Tuned preamplifier, SIG) Signal input, REF) Reference signal, E) Earth line, A) Audio amplifier, Ã) ac digital currentmeter, R) Phase-shift potentiometer, M_2) Variable standard mutual inductance, T) Narrow band amplifier, O) Oscilloscope, Ṽ) ac analogue voltmeter, S) Specimen, M_1) Cryostat coil, C) Cryostat.

of 0.01 μH. The phase–shift potentiometer is composed of a manganin wire (1 mm in diameter and 1 m long) and of a slide contact. As an ac signal generator, the reference signal of a lock–in amplifier (NF LI–572A) is used. The output current fed into the bridge circuit is monitored by an ac digital multimeter. The voltage signal induced in the secondary circuit of the bridge is fed into a tuned preamplifier of the lock–in amplifier. The signal from the preamplifier is then fed into a narrow band amplifier which can be tuned to discrete frequencies of 20, 30, 71, 80, 85, and 90 Hz. The output of the narrow band amplifier is measured by an ac analog voltmeter, by which balancing of the bridge is achieved.

The earth line of the system was carefully designed to minimize the effect of electrical noise. The bridge was usually drived by the primary current which produced magnetic field of 0.1 Oe at the sample position. Under these conditions, the sensitivity of the present device is 0.05 μH.

As mentioned before, in a periodically varying magnetic field, the response of magnetic substance is expressed by the change in magnetization. In general, however, the response appears with a certain amount of time–delay as to the variation of applied magnetic field. Taking into consideration this time–delay, the susceptibility $\chi(w)$ for a magnetic field of small amplitude can be approximately expressed in a complex form, $\chi(w)=\chi'(w)-i\chi''(w)$, where $\chi'(w)$ and $\chi''(w)$ correspond to in–phase and off–phase response of the substance.

As is well known, two components of $\chi(w)$ are given by

$$\chi'(w) = -\frac{1}{m_{10}g}(m_{2x}-m_{20}),\tag{1}$$

$$\chi''(w) = -\frac{1}{wm_{10}g}(r_x-r_0),\tag{2}$$

where m_{10} and m_{20} are respectively the coefficient of mutual inductance of M_1 and M_2 without sample, m_{2x} denotes the coefficient of mutual inductance of M_2 with sample, r_0 and r_x are respectively the readings of the phase-shift potentiometer without and with sample, and g is a constant which depends on the geometrical condition. Using Eqs. (1) and (2), one can obtain relative values of χ' and χ'' by observing changes in m_2 and r.

It is of interest to note about the physical meaning of χ' and χ''. In the case of superconducting samples, it is evident that the sharp change in χ' with respect to temperature is caused by the Meissner effect indicating the phase transition between the superconducting and the normal state. Meanwhile, χ'' is proportional to energy dissipation of the sample in a periodically varying magnetic field. The reason of this is as followings: The time–averaged variation in free energy of a material located in a magnetic field is given by

$$Q=<-MdH/dt>_t,\tag{3}$$

where Q is the mean energy dissipation per unit time per unit volume, M is the magnetization, and H is a uniform external magnetic field. Substituting $H=H_0\exp(iwt)$ in Eq. (3), Q becomes

$$Q=-\frac{1}{2}\text{Re}[iwMH^*]=\frac{1}{2}w\text{Im}[MH^*].\tag{4}$$

Since magnetization is given as $M=[\chi'(w)-i\chi''(w)]H$, one gets

$$Q = \frac{1}{2} w \chi''(w) H_o^2. \tag{5}$$

As the energy dissipation in samples directly depends on the structure, the proportionality between Q and $\chi''(w)$ is useful for obtaining structural information of samples.

3. Temperature Control of Specimen

Since the effect of surrounding materials to the measurement of complex susceptibility should be eliminated, a careful attention was payed 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, a sample holder and an adiabatic cell were designed as shown in Fig. 2. 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 was rolled around the Cu block and two glass ampoules, and was tightly bound by silk strings. The coil-foil was prepared with PVF Cu wire (0.14 mm in diameter). 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 good thermal conductor: and third, the sample holder is effectively shielded from thermal radiations. A better thermal contact between two pieces of sample holder 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 thermal shield of the holder for radiations from upside was also set on the top
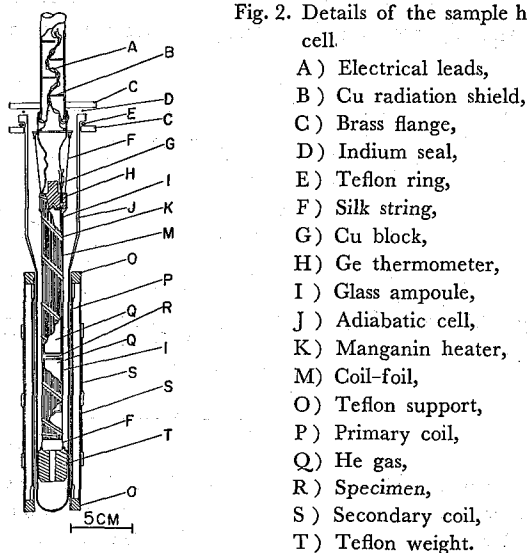

Fig. 2. Details of the sample holder and the adiabatic
    cell.
    A) Electrical leads,
    B) Cu radiation shield,
    C) Brass flange,
    D) Indium seal,
    E) Teflon ring,
    F) Silk string,
    G) Cu block,
    H) Ge thermometer,
    I) Glass ampoule,
    J) Adiabatic cell,
    K) Manganin heater,
    M) Coil-foil,
    O) Teflon support,
    P) Primary coil,
    Q) He gas,
    R) Specimen,
    S) Secondary coil,
    T) Teflon weight.

of the cell. A teflon weight used 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 shieldings. All of the electric connections were made with Bi40%-Cd60% solder, which is in the normal state above 1 K.

The temperature control for 4.2~10 K was made by using the manganin heater. In this case, the adiabatic cell was kept in high vacuum, less than 10^{-6} torr at 300 K. To achieve temperature 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 out. After having reached at the lowest temperature (~1.3 K), the cell was evacuated and the manganin heater was used to get necessary temperature of the sample holder.

A Ge thermometer is located about 12 cm apart from the specimen. However, the temperature gradient in the sample holder was confirmed to be quite small due to the good thermal conductivity of the coil-foil and also to the He exchange gas filled in the glass ampoules. The resistance of 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 of 1.54~10.1 K. The accuracy of measured temperatures was estimated to be ± 10 mK in absolute values and ± 0.1 mK in relative values.

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

RESULTS AND DISCUSSION

Since the geometrical demagnetization coefficient is generally large for film specimen,[9] it is necessary to find the dependence of χ' on the amplitude of ac magnetic field, H_0. For this purpose, with the Sn specimen placed perpendicular to the magnetic field, χ' was measured as a function of H_0 for various temperatures below T_0.

In Figs. 3 and 4 are shown the results obtained for frequencies of 71 Hz and 85 Hz, respectively. From the figures, we find that, in the vicinity of T_0, χ' strongly
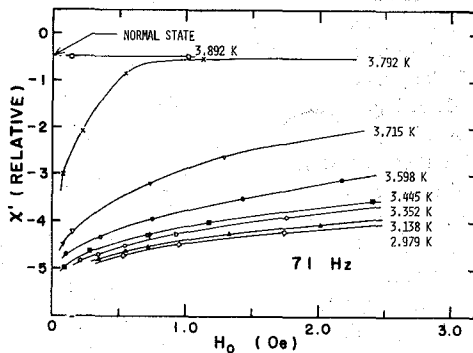

Fig. 3. χ' of Sn film specimen versus amplitude of ac (71 Hz) magnetic field, H_0, for various temperature below T_0.
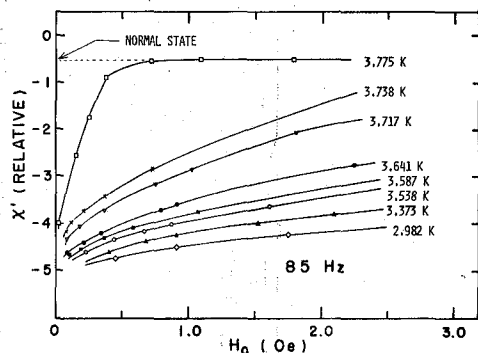
Fig. 4. χ' of Sn film specimen versus amplitude of ac (85 Hz) magnetic field, H_0, for various temperature below T_0.

depends on H_o. Especially for $H_o=0.1\sim0.5$ Oe, χ' changes rapidly with respect to H_o. However, for $H_o=0.1$ Oe or below, the value of χ' near T_o approaches to those for other temperature below T_o. Thus, H_o used in the present experiment was reasonably chosen as 0.1 Oe. Comparisons of the results for 71 Hz and 85 Hz have revealed that there is no appreciable dependence of χ' on frequency. Further measurements therefore were performed at 80 Hz.

For confirmation of reliability of the present device, two standard samples, Sn and Pb, were measured. As shown in Figs. 5 and 6, the observed curves of χ' are satisfactory for both cases. The values of T_o (3.79 K for Sn and 7.28 K for Pb) was taken as the midpoint of the transition. These values thus determined agree well with previous works (see Tables II and III) and prove the reliability of the present experimental device.

As seen in Figs. 5 and 6, χ' always changes monotonically when the specimen subsequently goes from the normal state down to the superconducting state. On the contrary, the curve of χ'' has a peak at temperature near T_o. This particular response of χ'' accompanied with the normal-superconducting transition was first observed by Maxwell and Strongin[22] for a cold-worked Sn specimen (99.9%, resistivity ratio is 300). Their explanations for this response are as followings: a) When temperature goes down, small

Table II. Transition Temperature of Sn

T_o(K)	Reference
3.752	10
3.726	11
3.742	12
3.722	13
3.712	14
3.79 ±0.01	present

Table III. Transition Temperature of Pb

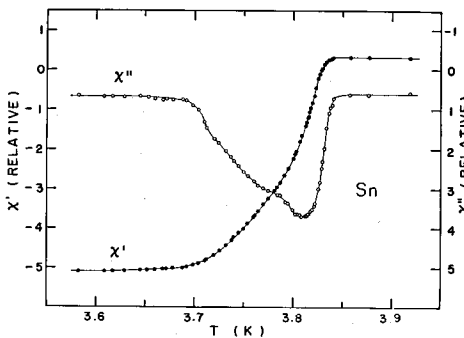| T_o(K)	Reference
7.22 ±0.03	15
7.24	16
7.20 ±0.01	17
7.22 ±0.04	18
7.175±0.005	19
7.193±0.005	20
7.155	21
7.25$_7$±0.01	2
7.28 ±0.01	present

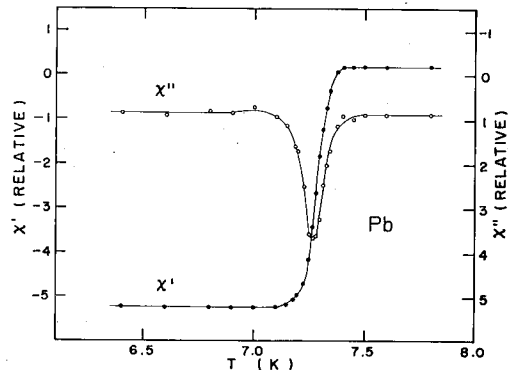Fig. 5. Complex susceptibility of Sn film specimen versus temperature.

Fig. 6. Complex susceptibility of Pb film specimen versus temperature.

filamentary inclusions which are in the superconducting state, are produced in the sample. b) This results in increasing 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 eddy current increases as temperature goes down to T_o. d) In the vicinity of T_o, 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 is 5000), Maxwell and Strongin[22] could not find any peak in the curve of χ''. The disappearance of the peak for the purer specimen was interpreted as a non-filamentary superconductor where the superconducting inclusions have much volume in earlier stage of transition. In this case, the increase of conductivity for eddy current would not result in the increase of the average energy dissipation, because the effective fraction for normal metal would be lessened.

Above two cases reported by Maxwell and Strongin are really suggestive, i.e., it can be said that complex susceptibility, especially χ'', is a sensitive probe for purity and dislocation in samples. Based upon the experimental results found with Sn and Pb samples as shown in Figs. 5 and 6, we examined Tc samples prepared by the method described before.

In Fig. 7 is shown 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, $T_o = 7.42 \pm 0.05$ K and 7.46 ± 0.05 K, respectively. The difference in two curves reflects some dislocations in this sample, which can not be observed by the resistive method, but can be by the measurement of χ'.

The sample Tc-2 was prepared on a Cu sheet in the working solution of pH $= 1.0$. Because of the high conductivity of Cu, it was not possible to measure the resistive transition. By repeating heat-treatment, we obtained Tc-2a and Tc-2b, of which the condi-
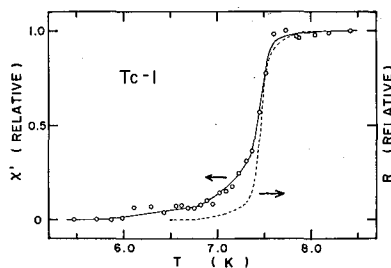
Fig. 7. χ' versus temperature for Tc-1 (see text). Scattered data are due to the smallness of the specimen. Dashed curve is the result obtained by the resistive method.
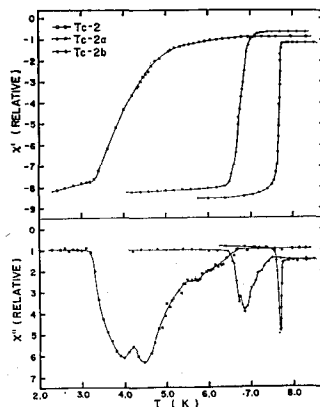
Fig. 8. Complex susceptibility versus temperature for Tc-2, 2a, and 2b (see text).

tions for heat-treatment were described before. The complex susceptibilities versus temperature for Tc-2, 2a, and 2b are shown in Fig. 8.

In each stage of heat-treatment, the annealing effect is reflected in χ' and χ''. For the as-electrodeposited sample Tc-2, the transition occurs in the broad temperature region. This broadness may be due not only to the dislocation and ununiformity, but also to the coexistence of metal and oxide of Tc in the sample. There are two peaks in the χ'' curve. As suggested by Strongin et al.,[23] multiple peaks in χ'' curve probably correspond to separate transitions occurring in different parts of the specimen. In addition, at the earlier stage of transition from normal to superconducting, the change in χ'' is more remarkable than in χ'. This can be explained by the average conductivity model, i.e., in Tc-2, the tiny filamentary inclusions are dominant at the beginning of 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 range of transition.

Tc-2a shows the upward shift of T_0 and the decrease in the 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-2a is physically not homogeneous yet.

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

It is known from chemical properties of Tc that the chemical form of electrodeposited Tc depends on pH of working solution. In an acid working solution, recovered Tc is expected to be metallic. Tc-3 was prepared in the working solution of pH=0.7. As

Table IV. Transition Temperature of Tc

T_0(K)	Method	Reference
7.77 ± 0.02	Magnetization	24
7.73 ± 0.02	Magnetization	24
7.46 ± 0.04	Magnetization	25
7.85	ac susceptibility	26
7.86	Specific heat	27
7.7	Resistance	28
8.22 ± 0.01	dc resistance	29
8.35	Magnetization	30
7.70	Resistance	31
7.82 ± 0.02	Magnetization	32
8.00 ± 0.01		33
7.924± 0.01		33
7.87	ac susceptibility	34
7.46 ± 0.05	Resistance	2
7.67 ± 0.05	ac susceptibility	present

shown in Fig. 9, T_o of Tc–3, 3a, and 3b shows subsequent upward shift, but the transition width becomes larger. The reason of this enhancement in the transition width is not clear yet, but the effectiveness of heat-treatment evidently depends on the chemical nature of working solution for electrodeposition.

As shown in Fig. 10, analyses of Tc–2 and Tc–3 by a scanning electron microscope analyzer show that the former has a particle shape of about 2 μm in diameter, but the latter has a structure like flat tiles. An X-ray diffraction analysis of Tc–3 shows that the c axis of hcp structure is almost perfectly oriented perpendicular to the surface. But in Tc–2, the orientation is not so evident as in Tc–3. Differences between Tc–2 and Tc–3 suggest that the development of Tc crystal on the substrate also depends on an acid concentration of working solution.

Measurements with Tc–4, prepared on a Pt substrate, did not give any conclusion, because the complex susceptibility did not change in the temperature range of 1.5∼10 K. Further studies are needed with Tc–4.

With an intention of developing a method to prepare a Re sample by means of electrodeposition, a similar procedure for deposition of Re was attempted with the working solution listed in Table I. An X-ray diffraction analysis shows a single broad line, suggesting that the Re sample is amorphous. The complex susceptibility measurement performed three days after sample preparation has revealed that the onset of superconductivity appears at 6.5 K when temperature goes down, and the transition is accom-
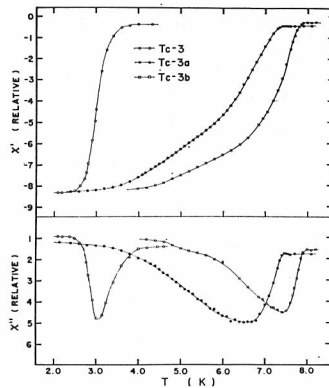

Fig. 9. Complex susceptibility versus temperature for Tc–3, 3a, and 3b (see text).
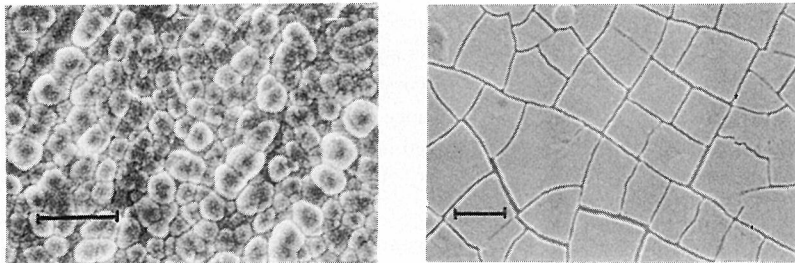

Fig. 10. Photographs of Tc–2 (particle shape) and Tc–3 (flat-tile shape) taken by a scanning electron microscope analyzer. The bar in each picture is 5 μm.

plished at 2.1 K. Another measurement repeated 13 days after sample preparation showed that the superconducting transition begins at 5.3 K, but the transition is not accomplished even at 1.5 K. Above two measurements indicate the instability of the present Re sample at room temperature. In addition, T_0 of the present sample is higher than that of a bulk specimen, but is much lower than 7.4 K found by Collver and Hammand[35] with a quench condensed Re onto a substrate at 4.2 K. Various attempts to achieve a reliable Re sample by means of electrodeposition are in progress.

ACKNOWLEDGMENT

REFERENCES

(1) L. D. Landau and E. M. Lifshitz, "Electrodynamics of Continuous Media", Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, (1960), Chap. 7.

(2) M. Kurakado, T. Takabatake, and H. Mazaki, *Bull. Inst. Chem. Res., Kyoto Univ.*, **55**, 38 (1977).

(3) T. Takabatake and H. Mazaki, *Phys. Rev. B*, in press.

(4) T. Takabatake, H. Mazaki, and T. Shinjo, *Phys. Rev. Letters*, **40**, 1051 (1978).

(5) H. Mazaki, S. Kakiuchi, and S. Shimizu, *Zeit. Phys. B*, **29**, 285 (1978).

(6) T. Takabatake and H. Mazaki, *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 45 (1979).

(7) L. Hartshorn, *J. Sci. Instr.*, **2**, 145 (1925).

(8) See for example, D. de Klerk and R. P. Hudson, *J. Res. Nat. Bur. Standards*, **53**, 173 (1954).

(9) A. L. Fetter and P. C. Hohenberg, "Superconductivity", 2, ed. R. D. Parks, Marcel Dekker, Inc., New York. (1969), p. 843.

(10) B. Serin, C. A. Reynolds, and C. Lohman, *Phys. Rev.*, **86**, 162 (1952).

(11) J. M. Lock, A. B. Pippard, and D. Shoenberg, *Proc. Cambridge Phil. Soc.*, **47**, 811 (1951).

(12) E. Maxwell, *Phys. Rev.*, **86**, 235 (1952) ; E. Maxwell and O. S. Lutes, *Phys. Rev.*, **95**, 333 (1954).

(13) W. S. Corak and C. B. Satterthwate, *Phys. Rev.*, **102**, 662 (1956).

(14) G. M. Androes and W. D. Knight, *Phys. Rev. Letters*, **2**, 386 (1959).

(15) J. G. Daunt, *Phil. Mag.*, **28**, 24 (1939).

(16) W. F. Brucksch, Jr. and W. T. Ziegler, *Phys. Rev.*, **62**, 348 (1942).

(17) W. T. Ziegler, W. F. Brucksch, Jr., and J. W. Hickman, *Phys. Rev.*, **62**, 354 (1942).

(18) H. A. Boorse, D. B. Cook, and M. W. Zemansky, *Phys. Rev.*, **78**, 635 (1950).

(19) W. B. Pearson and I. M. Templeton, *Phys. Rev.*, **109**, 1094 (1958).

(20) J. P. Franck and D. L. Martin, *Canadian J. Phys.*, **39**, 1320 (1961).

(21) T. Mizusaki and B. Serin, *Phys. Letters*, **48A**, 467 (1974).

(22) E. Maxwell and M. Strongin, *Phys. Rev. Letters*, **10**, 212 (1963).

(23) M. Strongin, E. Maxwell, and T. B. Reed, *Rev. Mod. Phys.*, **36**, 164 (1964).

(24) S. T. Sekula, R. H. Kernohan, and G. R. Love, *Phys. Rev.*, **155**, 364 (1967).

(25) G. Kostorz and S. Mihailovich, *Low Temp. Phys.*, *LT-12*, 341 (1971).

(26) C. C. Koch, W. E. Gardner, and M. J. Mortimer, *Low Temp. Phys.*, *LT-13*, **2**, 595 (1974).

(27) R. J. Trainor and M. B. Brodsky, *Phys. Rev. B*, **12**, 4867 (1975).

(28) A. A. Teplov, M. N. Mikheeva, and V. M. Golyanov, *Soviet phys. JETP*, **41**, 549 (1976).

(29) M. L. Picklesimer and S. T. Sekula, *Phys. Rev. Letters*, **9**, 254 (1962).

(30) E. Trojnar, C. Bazan, and J. Niemiec, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **13**, 481 (1965).

(31) V. M. Golanov, L. A. Elesin, and M. N. Mikheeva, *JETP Letters*, **18**, 335 (1973).

(32) G. Kostorz, L. L. Isaacs, R. L. Panosh, and C. C. Koch, *Phys. Rev. Letters*, **27**, 304 (1971).

(33) C. W. Chu, W. E. Gardner, and T. F. Smith, *Phys. Letters*, **26A**, 627 (1968).

(34) R. N. Shelton, T. F. Smith, C. C. Koch, and W. E. Gardner, *J. Phys. F*, **5**, 1916 (1975).

(35) M. M. Collver and R. H. Hammond, *Phys. Rev. Letters*, **30**, 92 (1973).