

Additional rf Resistance due to Hydrogen Motion in NbH_x

Shigeru Isagawa

KEK, National Laboratory for High Energy Physics

1-1 Oho, Tsukuba-shi, Ibaraki-ken, 305 Japan

The effect of the forced hydrogen motion on the residual surface resistance of niobium has been considered. The temperature dependence of the additional loss due to the direct acoustic generation has been estimated for a system of NbH_x dilute solution using the Pippard and BCS kernels together with the two fluid model. The calculation has been carried out at 6.5 GHz. As compared with the hydride phase, the α solid solution of NbH_x shows only a weak dependence of superconducting transition temperature T_c on hydrogen concentration. The detrimental effect of hydrogen in α phase is neither so severe nor so straightforward as in the hydride one. It can, however, become a limiting factor which determines the lowest obtainable value of residual resistance in most purified niobium surfaces which are very easy to be contaminated with hydrogen.

*Proceedings of the 5th Workshop on RF Superconductivity,
August 19 - 23, 1991, DESY, Hamburg, Germany.*

The rf surface resistance of a superconductor shows a higher value and a much smaller temperature dependence than predicted by BCS theory. When extrapolated to zero temperature it approaches to a constant, nonzero value referred to as the residual surface resistance. In addition to the residual loss caused by the scattering of quasiparticles on impurity atoms, several kinds of loss mechanism, e.g. frozen-in magnetic flux^{1,2}, direct electromagnetic generation of phonons at fissures³ and oxide⁴ or hydride⁵ precipitation on surface have been proposed.

Amongst them, the direct excitation of acoustic waves by electromagnetic fields incident on a metal gives the lowest obtainable limit of the intrinsic loss, and has been most extensively studied from both experimental and theoretical points of view. Such a mechanism has been originally observed in Al by P. K. Larsen and K. Saermark⁶, and in Ag, Al and PbTe independently by J. R. Houck et al⁷, and in Al, Nb, Sn and Cu by A. G. Betjemann et al⁸ at relatively lower frequencies, 4-40 MHz, in the presence of a dc magnetic field. On the other hand, direct excitation of transverse acoustic waves by microwaves⁹ and its converse effect, the direct excitation of electromagnetic fields by microwave phonons, have been also found to occur in superconducting indium films in the absence of a magnetic field^{10,11}.

Based on these studies, the residual rf resistance of superconducting cavity surfaces in GHz region has been discussed at zero temperature, and comparison with experimental results has been done by J. Halbritter,^{12,13} C. Passow¹⁴, A. A. Golub¹⁵, E. P. Kartheuser and Sergio Rodriguez¹⁶, and K. Scharnberg¹⁷. Amongst them Kartheuser and Rodriguez have expanded their theory to a finite temperature and calculated the anomalous surface resistance of pure niobium, using the two fluid model, together with Pippard and BCS kernels¹⁸. According to their theory, the average momentum of the normal electrons can be transferred to the positive ions of the material. Niobium ions are forced to move by the combined effect of the rf electric field and the collision-drag force.

On the other hand, there has been a sufficient experimental evidence that hydrogen exists as a screened proton even in the purest currently prepared niobium. Especially, after activation process like UHV firing and surface etching, hydrogen can be uptaken to niobium surface even under UHV conditions¹⁹. It is, of course, absorbed in niobium in great quantities by exposure to atmosphere containing hydrogen and immersion in hydrogen-rich etchant^{5,20}. Hydrogen first enters into niobium interstitially and then forms several hydride phases. It shows a detrimental effect on

rf superconductivity of niobium by precipitating near its surface as ϵ -hydride phase (poor or non superconductor). The extent of precipitation can be suppressed by controlling the way especially the speed of cooling and the quantity of impurities like oxygen or nitrogen which work as the trap centers against hydrogen diffusion²⁰⁻²³. Hydrogen in this case, however, is left solved in bulk niobium locally in high quantity as a dilute solution (α phase) and can play as a positive proton. As it is the lightest atom and has the largest diffusivity even at low temperature, it must play the important role rather than niobium atom itself in the above mentioned mechanism of rf dissipation. In this note a possibility of the additional loss due to the ionic motion of protons dissolved in Nb surface is proposed, and a rough estimate of the rf residual resistance is given, following the method of Kartheuser and Rodriguez.

According to their theory at finite temperature, the surface impedance which is determined as

$$Z = \frac{4\pi i \omega}{c^2} \frac{E(+0)}{E'(+0)} \quad (1)$$

can be written as the following integral

$$Z = -\frac{8i\omega}{c^2} \int_0^\infty \frac{dq}{F(q,\omega)} \quad (2)$$

where ω is the angular frequency of electromagnetic wave to

impinge normally on the plane $z=0$ which separates the superconductor ($z > 0$) from the empty space ($z < 0$). The value $F(q, \omega)$ is the ratio

$$F(q, \omega) = - \left(\frac{2}{\pi} \right)^{1/2} \frac{E'(+0)}{E(q)}, \quad (3)$$

and, neglecting the displacement current ($(\omega/c)^2 \ll q^2$), can be expressed as follows,

$$F(q, \omega) = q^2 + \left(1 - \frac{n_N}{n} \right) K(q, \omega) - \frac{4\pi i \omega}{c^2} \left(\frac{n_N}{n} \right) \sigma_0 G(q, \omega) - \left(\frac{\Omega \omega}{s c} \right)^2 \psi(q), \quad (4)$$

and

$$\psi(q) = \left[1 - \left(\frac{n_N}{n} \right) G \right]^2 \left\{ q^2 - \left(\frac{\omega^2}{s^2} \right) \left[1 + \frac{i}{\omega \tau} \left(\frac{\Omega}{\omega_p} \right)^2 \frac{n_N}{n} (1 - G) \right] \right\}^{-1}, \quad (5)$$

where n_N/n is the fraction of normal electrons which equals to $(T/T_c)^4$ in the two fluid model, σ_0 is the dc conductivity if all electrons were normal, which is expressed as

$$\sigma_0 = ne^2 \tau / m, \quad (6)$$

s is the velocity of shear acoustic waves, and the quantities Ω and $\omega_p = (4\pi ne^2/m)^{1/2}$ are the ion and electron plasma frequencies, respectively. In equation (6) τ is the relaxation time between successive collisions of an electron, effective mass of which is m .

Furthermore, in the above formula, $G(q, \omega)$ is given, as in

references^{18,24}, as

$$G(q, \omega) = \frac{3}{4} \int_0^\pi \frac{\sin^3 \theta d\theta}{1 - i\omega\tau + iql \cos \theta} \quad (7)$$

which is reduced to

$$G(q, \omega) = -\frac{3}{2\beta^2} (1 - i\alpha) + \frac{3}{4\beta^3} \left[\beta^2 + (1 - i\alpha)^2 \right] \\ \times \left(\arctan(\beta - \alpha) + \arctan(\beta + \alpha) - \frac{i}{2} \ln \frac{1 + (\beta - \alpha)^2}{1 + (\beta + \alpha)^2} \right) \quad (8)$$

where α and β can be written as $\alpha = \omega\tau$ and $\beta = ql$. Here we define the electron mean free path l by the equation

$$\tau = l / v_F, \quad (9)$$

where v_F is the electron Fermi velocity. In equation (4), $K(q, \omega)$ is the kernel which relates the superconducting current $I_{es}(q)$ to the electric field $E(q)$ as

$$I_{es}(q) = (ic^2 / 4\pi\omega)(1 - n_N/n) K(q, \omega) E(q), \quad (10)$$

In order to take the protonic motion into account, a composite ion plasma frequency Ω_{12} instead of $\Omega = (4\pi n\gamma e^2 / M)^{1/2}$ is used in the calculation. Namely,

$$\Omega_{12}^2 = 4\pi \left(\frac{n_1 \gamma_1 e^2}{M_1} + \frac{n_2 \gamma_2 e^2}{M_2} \right) \quad (11)$$

with

$$n_1 + n_2 = n \quad (12)$$

The value n_1 / n shows the atomic fraction of hydrogen in niobium samples. In equation (11) the subscripts 1 and 2 correspond to

hydrogen and niobium, respectively. The quantities γ_1 and γ_2 are the number of conduction electrons per each atom and are assumed to be $\gamma_1 = \gamma_2 = 1$ for simplicity. Owing to the lack of the information on the interaction between H and Nb at low temperatures the modification is only made by replacing the velocity of sound in a pure niobium by that for a hydrogenated niobium. The velocity of sound is obtained by a relation $s = (c_{44}/\rho)^{1/2}$, where ρ is the density and c_{44} is the elastic shear modulus which increases with increasing dissolved H²⁵.

Figure 1 shows the results of a rough estimate of the surface resistance of Nb-H systems at 6.5 GHz (C- band) with the hydrogen concentration as a parameter. The calculations have been carried out by performing the numerical integration of eq. (2) with the aid of the semiempirical frequency-independent kernel proposed by Pippard²⁶

$$K(q,0) = (1/\Lambda^3 q) f_P(q, \xi_0) \quad (13)$$

with

$$f_P(q, \xi_0) = \frac{2}{\pi} \left(\frac{1+r_0^2 q^2}{r_0^2 q^2} \arctan(r_0 q) - \frac{1}{r_0 q} \right) \quad (14)$$

where $r_0 = \xi_0 / (\xi_0 + 1)$, and $\Lambda = (4\lambda_L^2 \xi_0 / 3\pi)^{1/3}$ are characteristic lengths. In the calculations the following material parameters have been used: coherence length $\xi_0 = 387 \text{ \AA}$; London penetration

depth $\lambda_L = 225 \text{ \AA}$; electron mean free path $l = 10000 \text{ \AA}$;

$T_c = 9.25 \text{ K}$; $n = 5.55 \times 10^{22} \text{ cm}^{-3}$ and $v_F = 2.6 \times 10^7 \text{ cm sec}^{-1}$.

Assuming the estimate $l(\text{\AA}) \approx 40 \text{ RRR}^{27}$, RRR of this material equals about 250.

Similar results can be obtained as shown in Fig. 2, by using the BCS kernel which can be written as²⁸

$$K(q,0) = (1/\Lambda^3 |q|) f_{\text{BCS}}(q, \xi_0) \quad (15)$$

$$f_{\text{BCS}}(q, \xi_0) = 1 - \left(\frac{4}{\pi^3 \xi_0 |q|} \right) \int_0^\infty \frac{g(x) dx}{x [x^2 + (2/\pi q \xi_0)^2]^{1/2}} \quad (16)$$

where

$$g(x) = 2x + (1 - x^2) \ln |(1+x)/(1-x)|. \quad (17)$$

In both figures results for $\Omega = 0$ ($\Omega = (4\pi n_2 e^2 / M_2)^{1/2}$)

correspond to the surface resistance without any ionic motions and those for $H/\text{Nb} = 0$ correspond to the original calculation by Kartheuser and Rodriguez without protonic motions. In the above discussions the mean free path l is assumed to be independent of hydrogen concentration in order to simplify the problem. In a real superconducting dilute alloy as Nb-H, such a quantity as l is certainly decreased with H concentration. The decrease in l increases the collision drag effects which have been neglected in the original calculation by Kartheuser and Rodriguez and in this work, too.

As K. Scharnberg has indicated¹⁷, these effects decrease the rf surface resistance and may become important when the mean free path l becomes so small as the order of or less than a coherence length. While, there are other evidences that hydrogen becomes immobile, forming H-O or H-N cluster in the presence of oxygen or nitrogen²², and that it precipitates in limited regions of grain boundary after sufficient annealing process. In case of Nb-H system of high H concentration, the additional loss effect due to the precipitation of poor or non superconducting hydride phase may be larger than that of protonic motion.

In most purified niobium with very high RRR, however, electron mean free path l is large, hydrogen mobility is large and then the contamination with hydrogen from the bulk as well as from the inner surface can easily occur unless the effective passivating pretreatment has been taken. In higher frequencies above 11GHz, in particular, which is to be used for future high gradient accelerators, the decrease of the surface resistance owing to the phonon drag mechanism is relatively small and on the contrary the increase of it due to the direct phonon generation especially due to the hydrogen motion must get more and more important. Forced hydrogen motion by rf can become a limiting factor which determines the lowest obtainable value of residual resistance, that is, the highest obtainable accelerating field in most purified UHV

fired niobium cavity structures.

The precipitation of hydrogen near the surface layer of niobium can be controlled by adjusting the way especially the speed of cooling. Diffusivity of hydrogen in niobium is very high. Hydrogen atom remains mobile even at low temperatures due to quantum mechanical tunneling processes. On the other hand, hydrogen absorption in Nb is an exothermal process. As hydrogen is more stable at lower temperatures, it diffuses to lower temperature parts along the temperature gradient. It suggests that one can obtain the hydrogen free surface by locally heating up the surface and then rapidly quenching down. In case of accelerating cavities, temperature gradient can be made by continuously feeding the microwave power (on assumption that a sufficient coupling is made), feeding the laser or the infrared ray power, or by beam loading itself from the initial stage of cooling down process. As an example, change of normal conducting Q after such an rf conditioning process is shown in Fig. 3²⁹. The normal conducting Q was measured by a decrement method³⁰. Feeding power was only about 2.2 W. The resistivity ratio may be recovered near the surface within the penetration depth, due to the emigration of hydrogen from the region near surface into the bulk.

For the use of high purity niobium with $RRR > 1000$ in future, however, the absolute quantity of hydrogen in the bulk must be

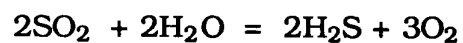
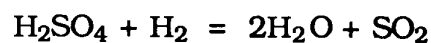
diminished and kept all the time as small as possible. In order to get high RRR, UHV firing in a good vacuum furnace having a high pumping speed for especially hydrogen (wrapping Nb with Ti foil³², use of Ti sublimation pump with a liquid nitrogen cold panel⁵, use of high speed cryopump etc. ---) is indispensable.

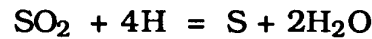
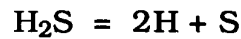
The solubility of hydrogen in niobium at temperature above 1000 °C is very small. In addition the diffusivity of H in niobium is very rapid. Consequently hydrogen removal should not provide any difficulties in the high temperature vacuum outgassing process. The main problem is to avoid the reocclusion of appreciable amounts of hydrogen at lower temperatures, when the cavity is cooled down after the annealing process. As the niobium surface which is annealed at high temperature under UHV conditions is very clean, no barriers such as niobium oxides oppose the penetration of hydrogen. Hydrogen can be absorbed in niobium not only from the inner vacuum, but also from the outer atmosphere while the cavity is being prepared and evacuated.

Oxygen pretreatment which consists of the introduction of small amount of oxygen (1×10^{-4} Pa, 2 min) before opening the furnace was effective to protect niobium surface from hydrogen entering^{5,19}. However surface oxide (NbO) layer which has been intentionally formed in such a way is also a bad superconductor ($T_c \approx 1.38\text{K}$) and increases the rf loss of the cavity. In order to solve this dilemma

two different ways can be considered. One is to make the oxide layer thinner, and another is to anodize the oxide layer to form a dielectric pentoxide, Nb₂O₅. The thick Nb₂O₅ has, however, the porous structure and cannot completely protect the Nb surface from hydrogen entering. A stable and dense Nb₂O₅ layer of about 30A without NbO + NbO₂ transition layers is reported to be formed by rinsing in H₂O₂ solution after electropolishing^{31,32}.

According to our experiences in C- band cavities, light electropolishing of only one or two cycles at lower temperature (-10 ~ -20°C) could thin the NbO layer and remarkably improve the rf properties of Nb cavities^{5,20}. Electropolishing seemed superior to chemical polishing as a final treatment. One reason may probably be the ease of hydrogen entering during the latter process. In case of palladium (Pd) for example, during the electrolysis of the sulfuric acid, it is well known that sulfur as well as pure nascent hydrogen separates at the cathode and the sulfur forms a film over the negative electrode. This film is believed to retard the occlusion of the freed hydrogen³³. It might be expected that hydrogen acting on sulfuric acid would set free sulfurous anhydride as





In case of KEK cavities for TRISTAN, sulfur is also often detected on niobium surfaces^{32,34}. Sulfur, as well as impurities like oxygen or nitrogen, which can be left on niobium surface after electropolishing in a bath containing sulfuric acid can form a film retarding the occlusion of the freed nascent hydrogen. Generally speaking, surface contamination by sulfur or carbon must be avoided, but from the view point of the hydrogen attack they must play some key role to protect niobium from hydrogen entering³³.

The computations in this work have been carried out by using the HITAC computer system at KEK.

¹M. Rabinowitz, Appl. Phys. Lett. 19, 73 (1971).

²J. M. Pierce, J. Appl. Phys. 44, 1342 (1973).

³J. Halbritter, J. Appl. Phys. 42, 82 (1971).

⁴C. C. Koch, J. O. Scarbrough, and D. M. Kroeger,
Phys. Rev. B9, 888 (1974).

⁵S. Isagawa, J. Appl. Phys. 51, 6010 (1980).

⁶P. K. Larsen and K. Saermark, Phys. Lett. 24A, 374 (1967).

⁷J. R. Houck, H. V. Bohm, B. W. Maxfield and J. W. Wilkins,
Phys. Rev. Lett. 19, 224 (1967).

- ⁸A. G. Betjemann, H. V. Bohm, D. J. Meredith, and F. R. Dobbs,
Phys. Lett. 25A, 753 (1967).
- ⁹R. C. Alig, Phys. Rev. B7, 1188 (1973).
- ¹⁰B. Abeles, Phys. Rev. Lett. 19, 1181 (1967).
- ¹¹G. S. Weisbarth, Phys. Lett. 27A, 230 (1968).
- ¹²J. Halbritter, Phys. Lett. 49A, 379 (1974).
- ¹³J. Halbritter, IEEE Trans. Magn. MAG11, 427 (1972).
- ¹⁴C. Passow, Phys. Rev. Lett. 28, 427 (1972).
- ¹⁵A. A. Golub, Fiz. Tverd. Tela. 15, 1468 (1973)
[Sov. Phys. - Solid State 15, 988 (1973)].
- ¹⁶E. Kartheuser and S. Rodriguez, J. Appl. Phys. 47, 700 (1976).
- ¹⁷K. Scharnberg, J. Appl. Phys. 48, 3462 (1977).
- ¹⁸E. Kartheuser and S. Rodriguez, J. Appl. Phys. 47, 3651 (1976).
- ¹⁹K. Faber and H. Schultz, Scripta Met. 6, 1065 (1972).
- ²⁰S. Isagawa, 2nd JIM Int. Symposium on Hydrogen in Metals,
Minakami Spa, Nov 1979, Supplement to Trans. Japan
Institute of Metals 21, 369 (1980); S. Isagawa, J. Appl. Phys. 51,
4460 (1980).
- ²¹G. Pfeiffer and H. Wipf, J. Phys. F6, 167 (1967).
- ²²C. C. Baker and H. K. Birnbaum, Acta Met. 21, 865 (1973).
- ²³K. W. Kehr, D. Richter, and K. Schroeder, Proc. of a Symposium

on Neutron Inelastic Scattering, Vienna (IAEA, Vienna, 1978)

Vol. 2, p399.

- ²⁴T. Kjeldaas, Jr., Phys. Rev. 113, 1473 (1959).
- ²⁵E. S. Fisher, D. G. Westlake, and S. T. Ockers,
Phys. Stat. Sol. (a) 28, 591 (1975).
- ²⁶A. B. Pippard, Proc. R. Soc. London, A216, 547 (1953).
- ²⁷E. Martinez and H. Padamsee, SRF 841201-EX.
- ²⁸J. Bardeen, L. N. Cooper, and J. R. Schrieffer,
Phys. Rev. 108, 1175 (1957).
- ²⁹S. Isagawa, Doctor Thesis, Tokyo University, Japan (1979).
- ³⁰S. Isagawa, IEEE Trans., IM-26, 329 (1977).
- ³¹K. Asano, T. Furuya, Y. Kojima, S. Mitsunobu, H. Nakai,
S. Noguchi, K. Saito, T. Tajima, M. Tosa, and K. Yoshihara,
KEK Report 88-2, 1988.
- ³²K. Saito, Y. Kojima, T. Furuya, S. Mitsunobu, S. Noguchi,
K. Hosoyama, T. Nakazato, T. Tajima, K. Asano, K. Inoue, Y. Iino,
H. Nomura, and K. Takeuchi, Proc. 4th Workshop on RF
Superconductivity, KEK (Aug 1989) pp635-694.
- ³³A. B. Antoniazzi, A. A. Haasz, and P. C. Stangeby, J. Nucl. Mater.
162-164, 1065 (1989).
- ³⁴Y. Kanda, and T. Furuya, private communication.

Figure captions

- Fig. 1. Surface resistance of NbH_x at 6.5 GHz as a function of T_c/T for several values of x . The calculations were carried out using the Pippard kernel. The value for $\Omega = 0$ corresponds to the pure electronic part of the surface resistance. In the calculations the following material parameters have been used: coherence length $\xi_0 = 387 \text{ \AA}$; London penetration depth $\lambda_L = 225 \text{ \AA}$; electron mean free path $l = 10000 \text{ \AA}$; $T_c = 9.25 \text{ K}$; $n = 5.55 \times 10^{22} \text{ cm}^{-3}$ and $v_F = 2.6 \times 10^7 \text{ cm s}^{-1}$.
- Fig. 2. Same calculations as Fig. 1 with the BCS kernel of Eq. (15).
- Fig. 3. The change of normal conducting Q of a niobium cavity at room temperature after rf conditioning process.

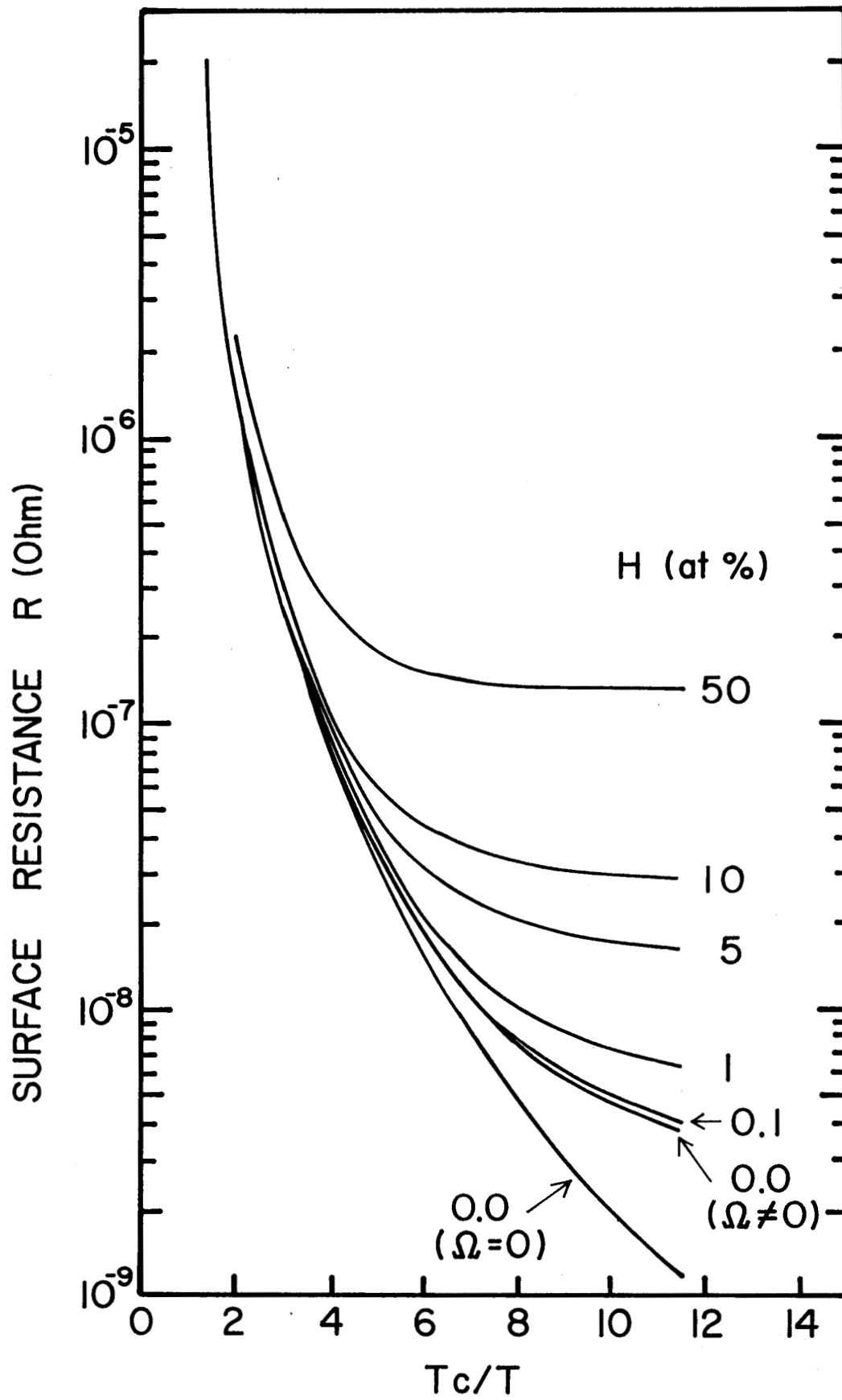


Fig. 1.

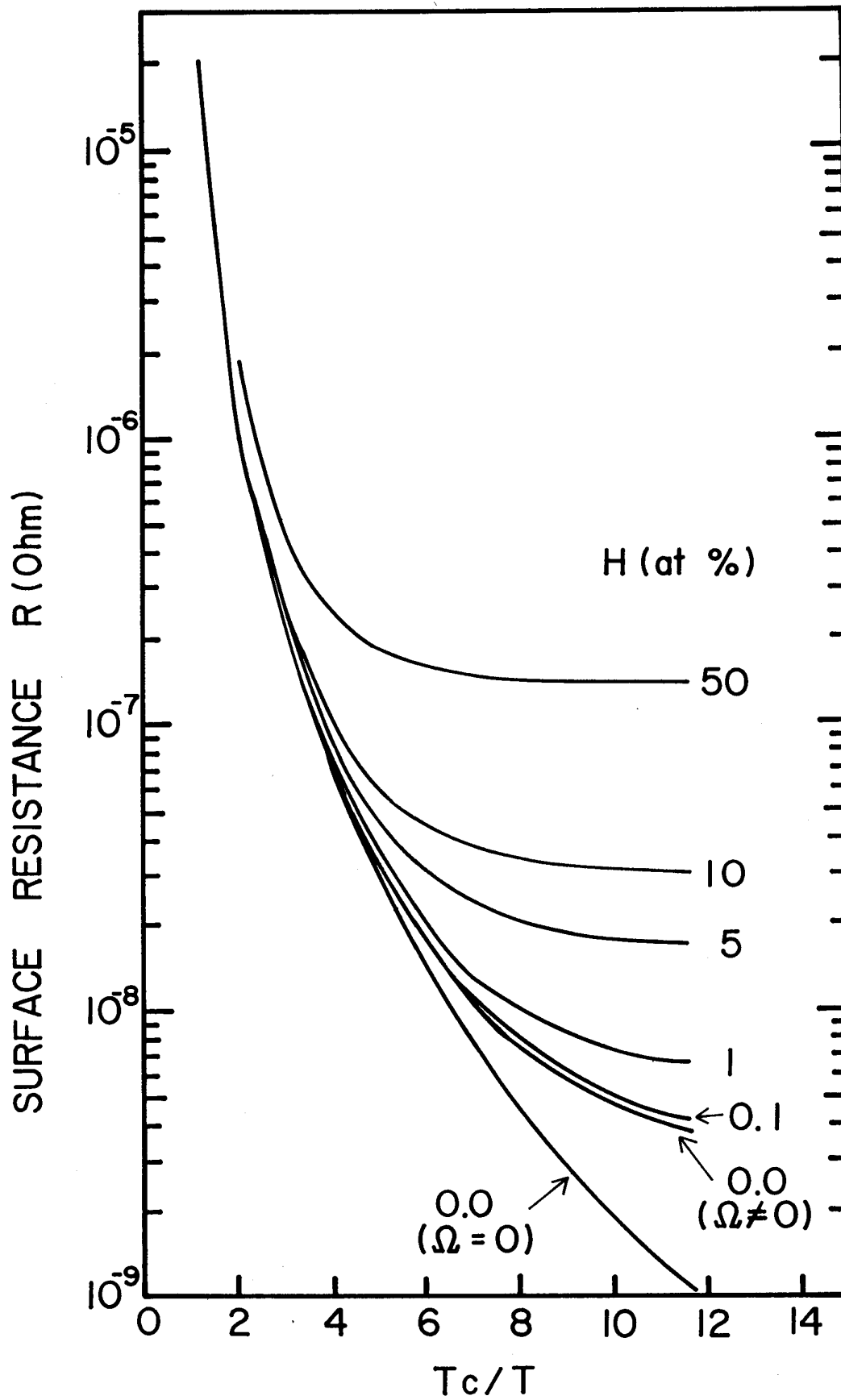


Fig. 2.

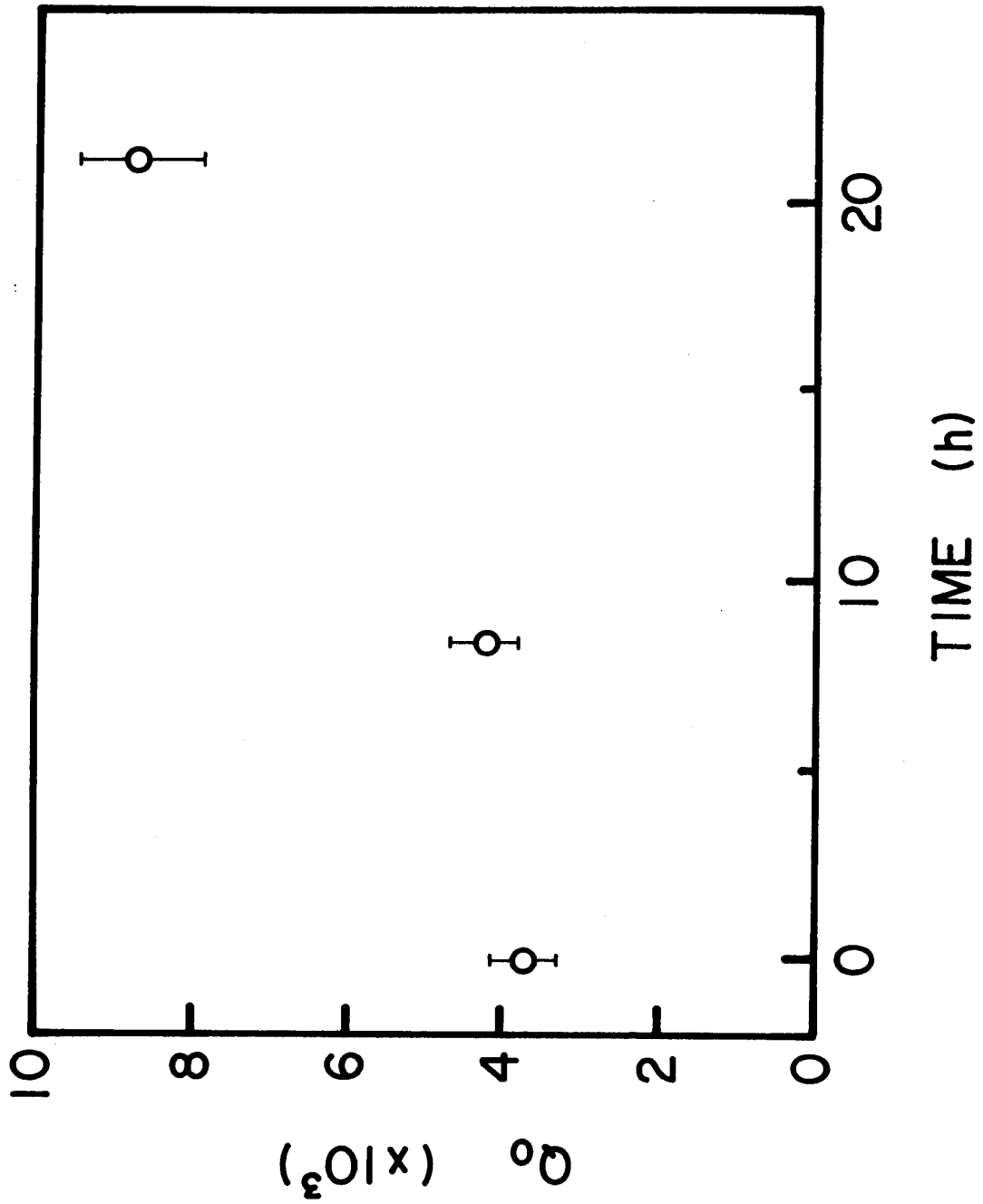


Fig. 3.