ELECTRICAL RESISTIVITY OF CARBON FILMS*

D. S. Kupperman, C. K. Chau and H. Weinstock
Department of Physics
Illinois Institute of Technology
Chicago, Illinois 60616

(Received 26 June 1972)

ABSTRACT

The electrical resistivity along 500 Å thick carbon films has been measured from 1.2 to 1100°K. The electrical resistivity measurements at high temperature indicate a change in the structure of the film beginning at about 670°K. In the theory of non-crystalline solids by Mott, the temperature dependence of the electrical conductivity σ, at low temperature, is given by $\ln \sigma = A - BT^{-1/4}$ where A and B are constants. Whereas previous investigators have shown general agreement with Mott's relation, the present result at low temperature shows deviation from the $\ln \sigma \propto T^{-1/4}$ relation.

* Supported by the U.S. Atomic Energy Commission

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

1. Introduction

Evaporated carbon films are particularly useful for studying electronic conduction in disordered systems because of their highly amorphous character. At high temperatures, electrons can be excited across the forbidden gap, thus exhibiting non-localized electronic conduction. At low temperatures conduction may occur by thermally assisted tunneling through potential barriers separating localized states.[1] The process of conduction in non-crystalline materials has been investigated by Mott.[2] He finds the temperature dependence of the electrical conductivity to be given by

$$\ln \sigma = A - BT^{-\frac{1}{4}} \qquad (1)$$

where A and B are constants. This behavior is most favorable at low temperature.

Experiments have previously been carried out on carbon films for temperatures as low as 5°K.[3,4] In those experiments, the electrical conduction has been found to follow Mott's relation. The purpose of the present study is to investigate the character of electronic conduction along carbon films at high temperatures and in the temperature region below 5°K.

2. Experimental Techniques

Carbon films prepared by arc-evaporation of highly pure graphite onto a glass substrate (vacuum $< 10^{-5}$ torr, growth rate on the order of 5 Å/sec, and temperature of glass during deposition about 300°K) were obtained from MicroMatter Co. Blue and Danielson[5] have reported non-reproducibility and a strong increase in resistivity for films less than 500 Å thick. Therefore, films with a nominal thickness of 500 Å were investigated. The carbon films used had a uniform brownish color with room temperature resistivity of the films varying from .02 ohm-cm to 1 ohm-cm. After high temperature heattreatment (750°C for 2 hours), all films had about the same room temperature resistivity (∿ 0.03Ω-cm). We attribute the differences in initial resistivity to differences in the amounts of gases trapped in the films during growth. Heat-treatment causes the gas molecules to diffuse out of the films leaving them with acceptor type regions which are a source of holes. Therefore, the resistivity decreases as the gas molecules are removed. A similar phenomenon is observed in bulk carbon.[6]

Measurements were taken on the low resistivity samples (∿ .02Ω-cm at room temperature) in a range 1.2 to 1100°K. Typical room temperature resistivity values for other investigators range from 0.1Ω-cm for 700 Å thick films[3] to about 2Ω-cm for 500 Å thick films.[5] Due to the geometry of the samples we have measured only planar resistivity.

A standard liquid helium cryostat was used for reaching temperatures down to 1.2°K while a Lindberg three zone furnace was employed for achieving temperatures as high as 1100°K. Temperatures below room temperature were measured with a calibrated carbon resistor and an a.c. bridge. Temperatures above room temperature were measured with a chromel-alumel thermocouple.

Low temperature measurements were made with the carbon film on the original glass substrate. Copper or gold foil strips, with a layer of uncured Epotek silver epoxy, were used to make electrical contact with the carbon films. To eliminate the effect of contact resistance, a four terminal method for measuring resistance was used. For high temperature measurements, the carbon films were floated off the glass substrates and transferred to a quartz plate. Gold foil strips coated with a thin layer of Aquadog were used for resistance measurements above room temperature, again with the four terminal technique employed.

In order to verify the amorphous structure of the carbon films, back reflection x-ray Laue photographs were taken of several films. The photographs indicated the absence of significant crystalline structure.

3. Results

3.1 High temperature

Figure 1 shows the change in resistance of a typical film (MS-17) without previous heattreatment, being heated rapidly from 300 to 1000°K. For this sample the room temperature value is 0.02Ω-cm. There is a change in resistivity by a factor of 10 in going from room temperature to 670°K. Above 670°K the change in resistivity is small. The log of the reduced resistivity of the same sample (MS-17) shown in Fig. 1 is plotted as a function of 1/T in Fig. 2. Below 550°K the slope of the curve varies with temperature. Between 550 and 650°K, however, the curve has a constant slope, (E_1). Above 670°K the slope has a different constant value, (E_2).

The above observations are interpreted in the following way. During evaporation of the carbon films, gas molecules are trapped inside the sample. As the film is heated, the gas molecules gradually diffuse out from the sample, resulting in the formation of free valence bonds with nothing to attach to and thereby becoming traps for electrons. This behavior, along with the influence of impurities in the sample, causes the initial increase in conductivity with temperature, and, correspondingly, a drop in resistivity from 300 to 550°K. From 550 to 670°K, the log of R/R_{300} vs. 1/T has a constant slope, (E_1). Above 670°K, the slope is smaller, (E_2). Initially, one might associate the regions of constant slope with an activation energy for the film. This apparent activation energy determined from the slope E_1 in the temperature range 550-650°K would have a value 0.34 ev. We note that Mizushima's optical data show a band gap for a 460 Å thick carbon film to be 0.69 ev, just twice the apparent activation energy. This interpretation may be suspect, however, since the material is being heattreated, thereby changing its structure and the constant slope in Fig. 2 may be due to the combined effects of some gas molecules migrating out of the specimen and the reordering of the crystallite structures. In the region above 670°K the carbon film begins to recrystallize, [illegible] A. Debenyl et al.[8] reported a change in structure of amorphous carbon films mainly between the temperatures of 500 and 700°K. They suggested that heating to these temperatures results in a transformation to a more ordered, polycrystalline type of state with ordering continuing up to 1575°K.

The effect of heattreatment of the carbon film is shown in Fig. 3. A sample (MS-21C) was held at the temperature of heattreatment indicated until there was no noticeable change in resistance (2 hours). The fractional change in room temperature resistance before (R_b) and after heattreatment (R_a) is indicated. The largest effect occurs between 500 and 700°K. At about 1100°K the heattreatment process is essentially completed.

3.2 Low Temperature

According to the theory of conduction in non-crystalline materials by Mott[2], the temperature dependence of the electrical conductivity σ should be of the form,

$$\ln \sigma = A - BT^{-1/4}$$

where A and B are constants. This relationship applies to the case where the localized states are overlapped sufficiently and the temperature is low enough to have tunneling between adjacent localized states. Resistivity measurements along carbon films for temperatures as low as 5°K have been taken by Morgan.[3] A linear relation between resistivity and $T^{-1/4}$ is observed between 5 and 7°K.

For higher temperatures and high fields, Hill[9] suggests a $T^{-1/3}$ dependence for $\ln\sigma$. A $T^{-1/3}$ dependence is reported by Morgan[3] in the temperature range 7 to 50°K. Electrical resistivity measurements along a carbon film 1600 Å thick are also reported by Adkins et al.[4] These latter authors find general agreement with the $T^{-1/4}$ dependence for electrical resistivity measurements between 10 and 25°K.

The resistance of two 500 Å thick films, one heated at 200°C for two hours, the other one not heated at all, has been measured as a function of temperature from 1.2 to 300°K. These low temperature data are reproducible if the samples have not been warmed above room temperature. Figure 4 shows the results of these measurements. In order to compare the data with Mott's theory, the log of reduced resistance is plotted as a function of $T^{-1/4}$ as shown in Fig. 5. A linear dependence is predicted at low temperatures and is observed in this plot between 20 and about 4°K, in general agreement with other investigators. Below 4°K the resistance is larger than the value predicted by Mott's relation, Eq. 1, for both samples before and after heattreatment. The deviation from Mott's relation begins at the same temperature for both samples.

The deviation observed cannot be explained in terms of leakage current or surface conduction as these effects cause the observed value of the resistance of the film to be lower than its actual value.

4. Summary

The electrical resistivity along 500 Å thick carbon films has been measured from 1.2 to 1100°K. A plot of the log of resistivity vs. T^{-1} indicates a structural change in the carbon films beginning at about 670°K. Although carbon films are not intrinsic semiconductors, the films behave in the temperature range 550-670°K like a semiconductor with an apparent activation energy of .34ev. Mott's theory of non-crystalline solids predicts that at low temperatures the temperature dependence of the electrical conductivity σ, to be given by $\ln \sigma = A - BT^{-\frac{1}{4}}$ where A and B are constants. In the region 20 to 4°K, this relation is verified by the present measurements but below 4°K there is a significant deviation from Mott's relation.

Acknowledgements

The authors would like to thank Professor J. Davis for many useful discussions, and Professor S. Mrozowski of State University of New York for his comments on this work.

References

1. H. Fritzsche, in Amorphous and Liquid Semiconductors (Edited by J. Tauc), Plenum Press, New York (to be published, 1972).

2. N. F. Mott, Phil. Mag. 19, 835 (1969).

3. M. Morgan, Thin Solid Films 7, 313 (1971).

4. C. J. Adkins, S. M. Freake and E. M. Hamilton, Phil. Mag. 22, 183 (1970).

5. M. D. Blue and G. C. Danielson, J. Appl. Phys. 28, 583 (1957).

6. S. Mrozowski, Phys. Rev. 85, 609 (1952). Errata, Phys. Rev. 86, 1056 (1952).

7. S. Mizushima and Y. Fijibayashi, Carbon 6, 123 (1968).

8. A. Debenyl, A. Gheorghin, A. Belu and G. Korony, Second Int. Conf. on Conduction in Low Mobility Materials, Eilat, Israel, 217 (1971).

9. R. M. Hill, Phil. Mag. 23, 59 (1971).

Figure Captions

Figure 1 - Reduced resistance versus temperature for rapid heating of a typical carbon film, sample MS - 17.

Figure 2 - Reduced resistance versus 1/T for a typical 500 Å thick carbon film, sample MS - 17.

Figure 3 - Fractional change in room temperature resistance versus heattreatment temperature for typical 500 Å thick carbon film, sample MS - 21 - C.

Figure 4 - Reduced resistance versus temperature for two typical 500 Å thick carbon films. Sample MS - 13 is heat treated at 200°C for 2 hours, and sample MS - 15 is not heat treated.

Figure 5 - Log of reduced resistance versus $T^{-1/4}$ for two typical 500 Å thick carbon films. Sample MS - 13 is heat treated at 200°C for two hours, and sample MS - 15 is not heat treated.

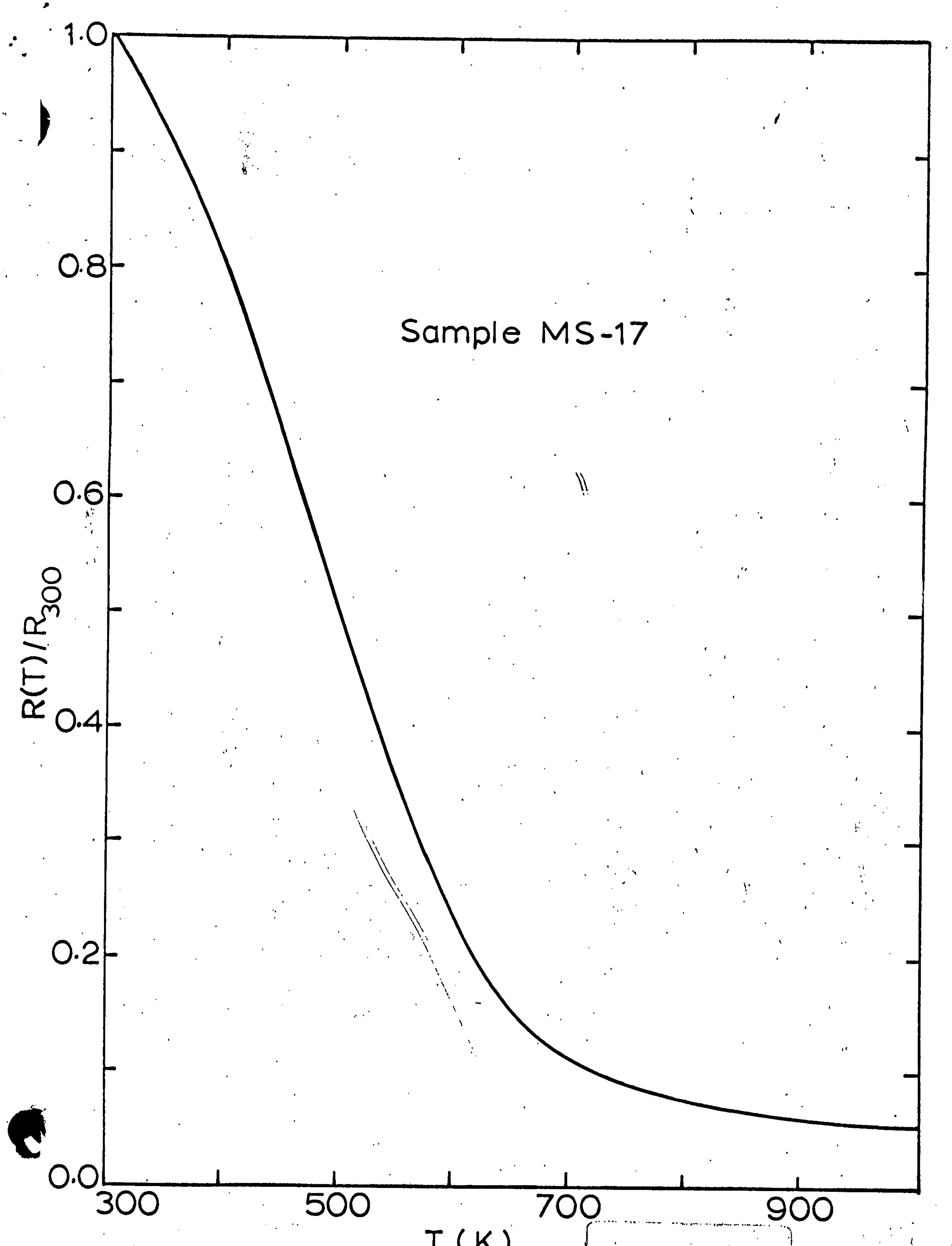


Fig. 1

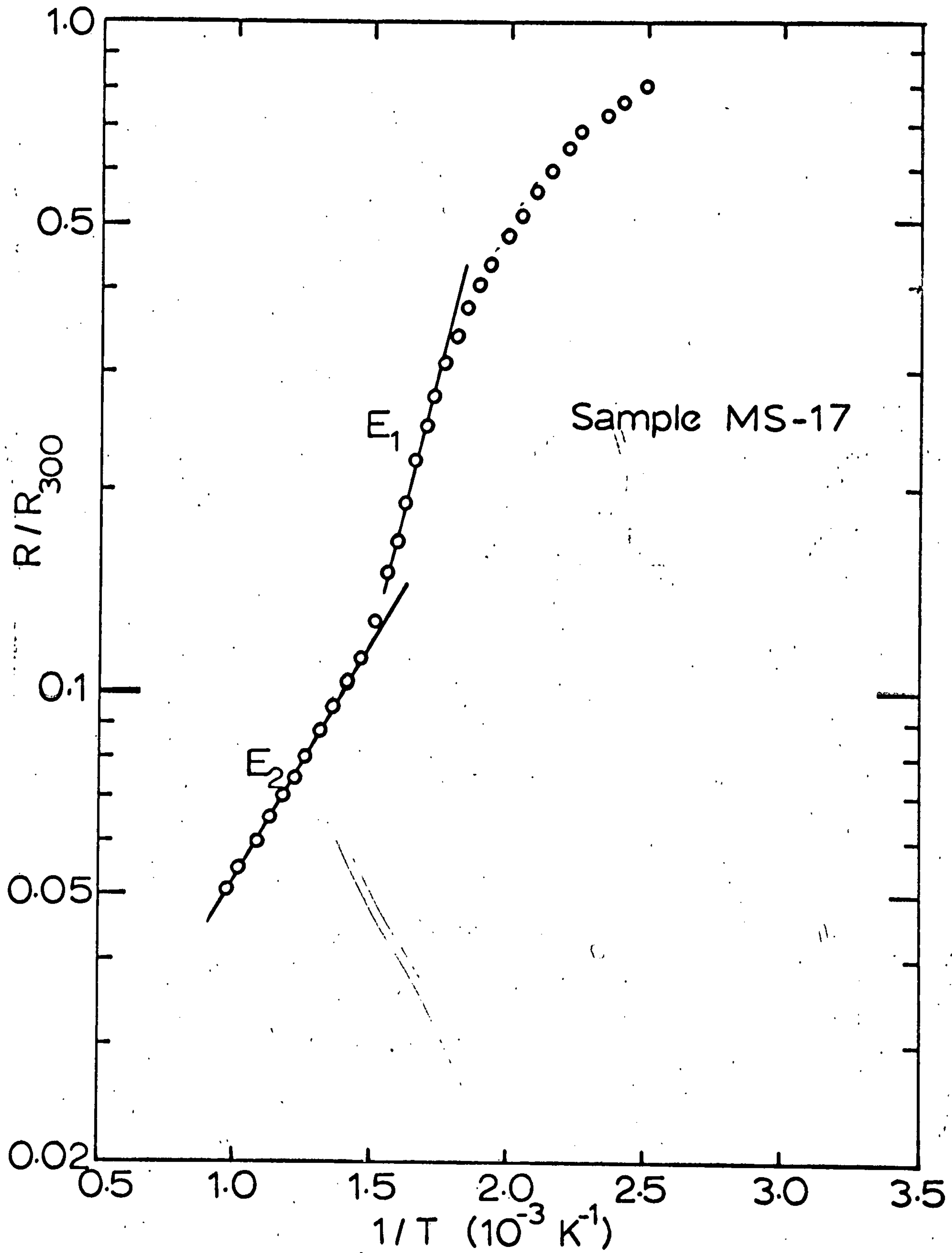

1.0
0.5
0.1
0.05
0.02
R / R300
E1
E2
Sample MS-17
0.5
1.0
1.5
2.0
2.5
3.0
3.5
1/ T (10-3 K-1)

Fig. 2

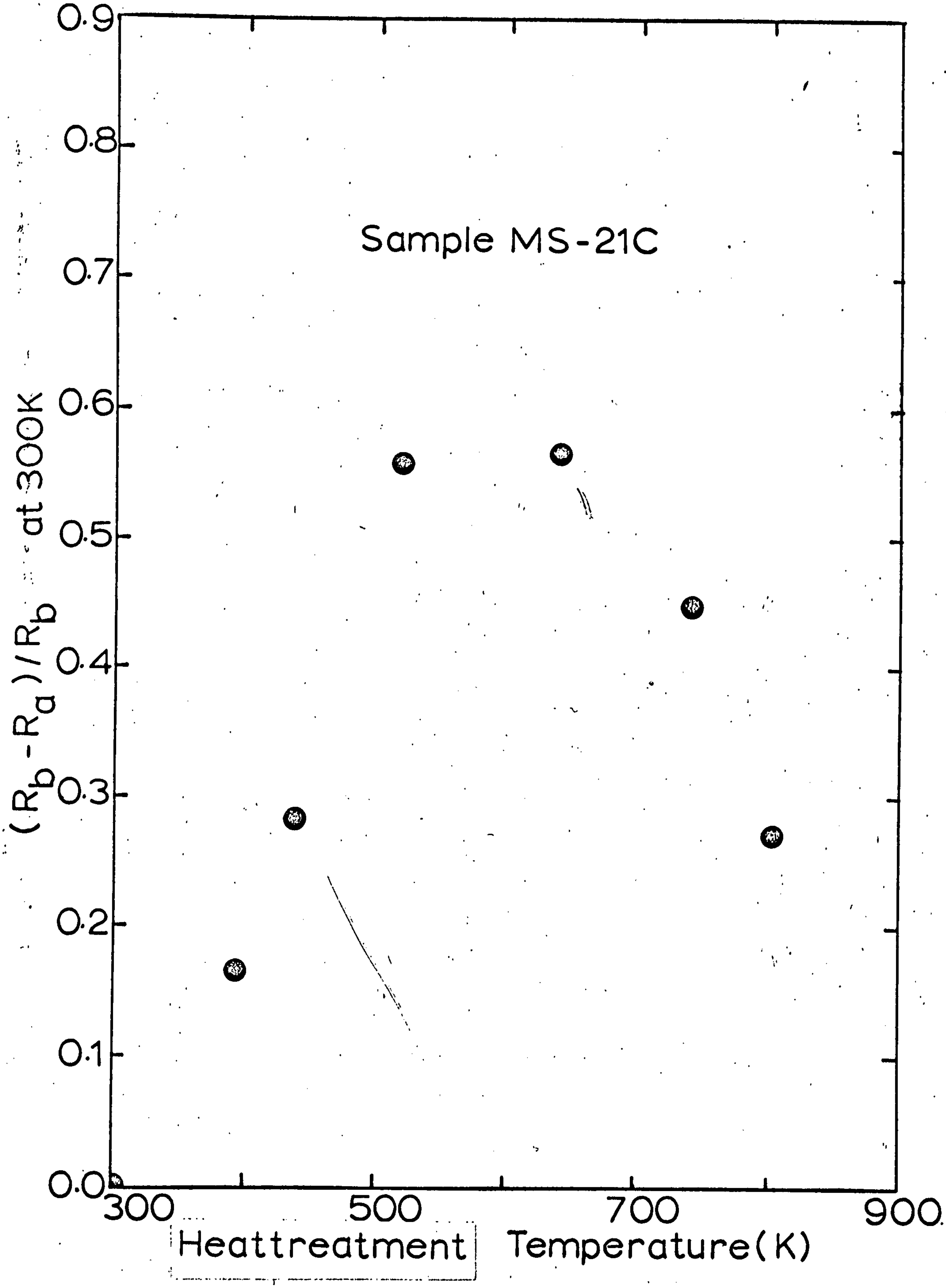
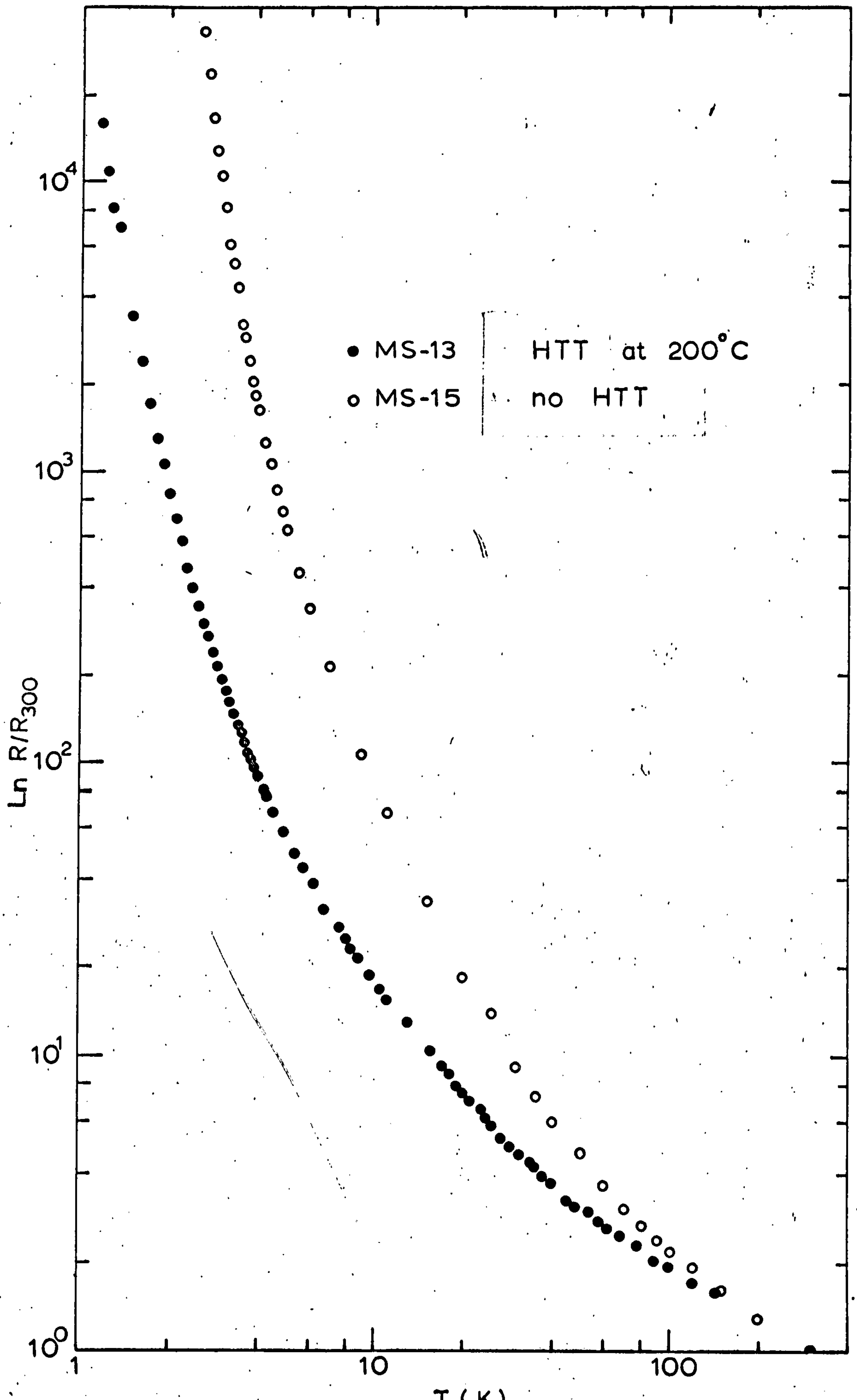

Sample MS-21C
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
300
500
700
900
$(R_b - R_a)/R_b$ at 300K
Heattreatment Temperature(K)

Fig. 3



MS-13 | HTT at 200°C
MS-15 | no HTT
Ln R/R300
T (K)
10^4
10^3
10^2
10^1
10^0
1
10
100

Fig. 4

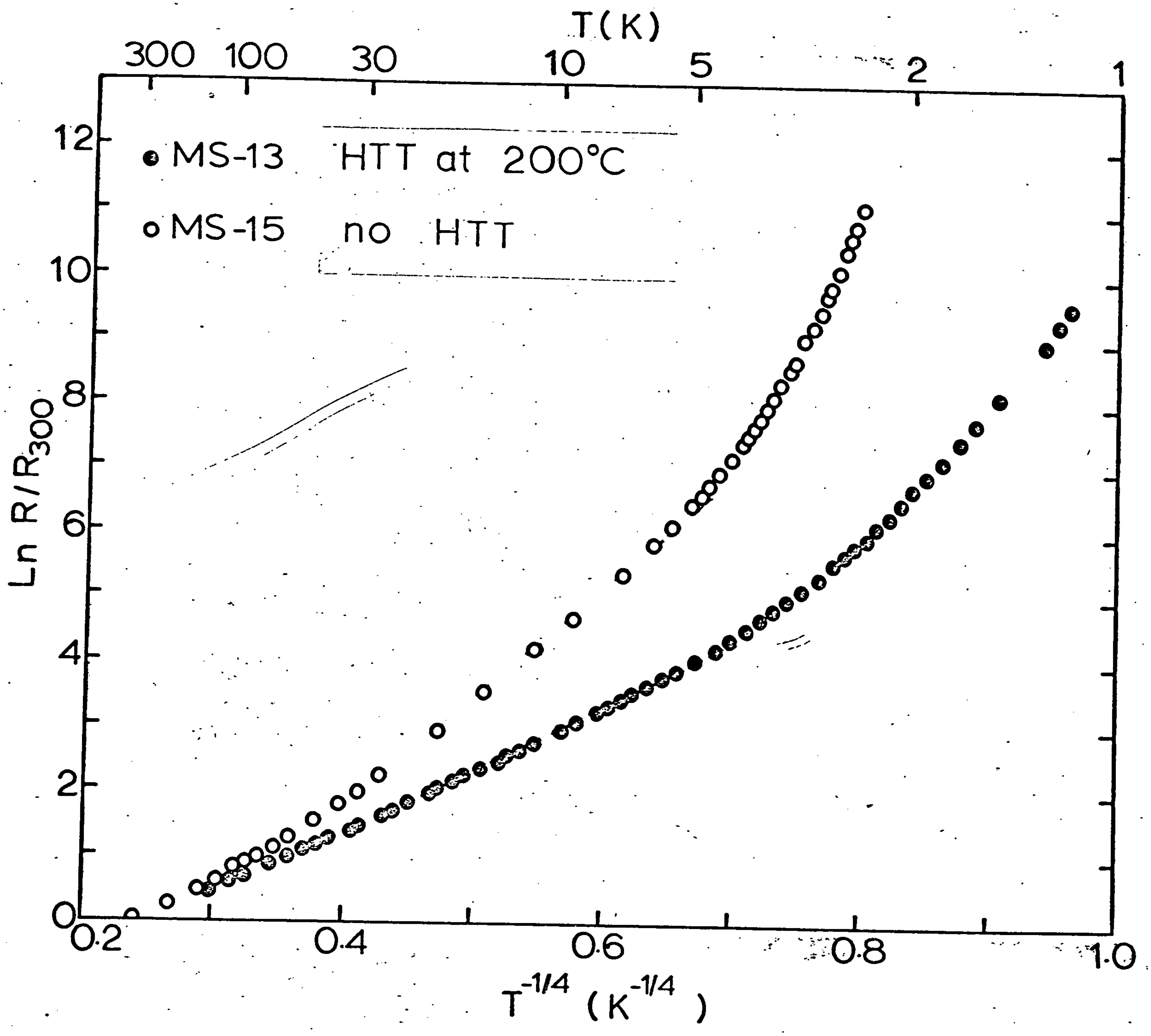

T(K)
300
100
30
10
5
2
1
MS-13 HTT at 200°C
MS-15 no HTT
Ln R/R300
12
10
8
6
4
2
0
0.2
0.4
0.6
0.8
1.0
T-1/4 (K-1/4)

Fig. 5