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Research Report

DETERMINATION OF SUPERCONDUCTING TRANSITION TEMPERATURES FROM RESISTIVITY MEASUREMENTS

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DETERMINATION OF SUPERCONDUCTING TRANSITION TEMPERATURES FROM RESISTIVITY MEASUREMENTS

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ABSTRACT: Methods of measuring the resistivity of poly- or single-crystalline bulk and thin film samples are discussed with a view to determination of the transition temperature of superconducting materials. These techniques have been used successfully on a wide range of metallic materials including the recently discovered superconducting ceramics. Frequently encountered anomalies are described with a view towards their causes and possible remedies.

INTRODUCTION

The purpose of the paper is to describe in detail a technique to measure the resistivity and determine the superconducting transition temperature (Tc), the temperature at which the resistivity falls to zero in superconducting compounds. In addition, a section is dedicated to troubleshooting possible false readings and apparatus anomalies.

In a typical two-probe measurement, a current (either dc or ac) is passed between two contacts placed on the sample, and the potential developed across the same two contacts is measured using a voltmeter (for dc excitation) or a lock-in amplifier (for ac excitation). For this configuration, since the current passes through the voltage contacts, there will be, in addition to the voltage developed across the sample, voltages developed across any contact resistances, resulting from poor electrical contact between the probes and the sample. Large errors can arise when the resistance of the sample is small compared to the contact resistances. These potential errors can be eliminated by using separate voltage and current contacts in a four-probe measurement.

A common four-probe technique used at the ARC (Almaden Research Center) is a low-frequency, 4 in-line resistivity measurement. A typical configuration of the sample and contact geometry is shown in Figure 1. The voltage and current probes comprise fine gold wires, typically 0.001" to 0.010" diameter. These wires are attached to the sample using a small amount of gold or silver paint (i.e., a solution containing Au or Ag particles). It is important not to stress the sample by ensuring the wires are bent into position on the sample before applying the paint. The paint should be applied in a continuous line around the sample normal to the flow of current. Under these circumstances, the resistivity of the sample is given by the expression, $\rho = \frac{V}{I} \times w \frac{t}{l}$ where w and t are the width and thickness of the sample and l is the distance between the voltage contacts. V is the voltage developed across these contacts for the current I passed between the outer current contacts. Typically for an ac measurement, a low-frequency current excitation at a frequency of 100 Hz for currents in the range 1-100

μA is used. The potential developed across the voltage contacts is measured using a lock-in amplifier.

EQUIVALENT CIRCUIT

Figure 2 illustrates the low-frequency, 4 probe in-line resistivity apparatus equivalent circuit. An oscillator voltage source E and series resistor R_s simulate an AC current source. Z_I is the lead and contact impedance from the current source to the sample shown as R_I , R and R_I. The input, lead, and contact impedance of the lock-in amplifier is shown as R_m and Z_v. The lock-in amplifier we use is a Princeton Applied Research 124.

CONSTANT CURRENT SOURCE

A common practice is to use a large series resistor 100 K Ω or greater with an oscillator to simulate a constant current source as shown in Figure 2. This works well for samples with resistances of less than 1 K Ω. However, if with sample resistance is greater than 1 K Ω, large errors can occur as shown in Figure 3 and Table I. An actual ac constant current source is the best way to avoid potential problems, since they usually have overload indicators to signal high sample resistance or a bad current contacts.

CURRENT DENSITY

Current density is an important issue since a balance must be achieved between currents high enough to yield an appropriate signal-to-noise ratio, yet small enough as to not overheat the sample causing thermometry problems. If heating is suspected, verify that a change in current yields a proportional change in voltage. If not, the currents must be lowered. Heating problems are most likely to appear when measuring thin films and single crystals since the cross sections are very small. Typical resistivity measurements on ceramics at the ARC use 2 mm × 0.5 mm × 0.5 mm rectangular bars with currents from 1-100 μA.

COMMON AND DIFFERENTIAL MODE

The lock-in amplifier can be configured in either the common or differential mode. Differential mode is preferred because its 100 M Ω input impedance is isolated from ground which eliminates the possibility of ground loops. However, if common mode is desired a transformer should be used to help isolate the shield which is tied to ground through a 10 Ω resistor.

FREQUENCY DEPENDENCE

Operating at a modulating frequency of 100 Hz is desirable since it is low enough to avoid shunt capacitive effects, high enough to work well with the lock-in and is not a multiple of 60 Hz line noise. Figure 4 shows an approximation of the frequency dependence of our entire resistivity apparatus. The frequency roll off below 10 Hz is attributed to the lock-in Noise Contours, especially when working with small source resistances. The frequency roll off above 1 Khz is attributed to the capacitive effects of using twisted pairs, for the current and voltage leads, from the sample to the lock-in. Miniature coaxial cable is recommended for modulation frequencies above 1 Khz.

THERMOMETRY

Silicon diodes are small, rugged and can be accurate to 0.1 Kelvin if configured correctly. Temperature gradients between the sample and diode can cause large loops between warming and cooling resistivity curves, making it difficult to determine actual temperature transitions. The best way to limit temperature gradients is to mount the sample as close as possible to the diode. At the ARC, a diode is mounted to the cryostat with G.E. varnish on the bottom and a thin piece of paper varnished to the top. The varnish on the bottom keeps the diode in good thermal contact with the cryostat while the thin paper on top provides electrical isolation from the diode to the sample. The sample is placed on top of the diode and held in thermal contact with a thin layer of vacuum grease. Care should be taken that the sample is contained in a water vapor free thermal transfer gas environment. Otherwise one runs the risk of water vapor condensing on the sample and thermometer, thus altering their respective thermal contact and yielding large errors in the determination of the temperature transition.

SAMPLE CONTACTS

Silver paste electrodes are a simple and effective way of achieving low ohmic sample contacts provided the paste is properly mixed and applied. If too much solvent is used, the paste will tend to run over large areas of the sample possibly causing shorts between contacts; if too little solvent is used the paste will make bad contact to the sample since it does not fill the samples contours. Using too much paste on a contact will require a long drying time and may yield unstable measurements due to shifting values of ohmic contact resistance during a measurement.

ELECTROSTATIC CHARGING

High impedance voltage meters are susceptible to atmospheric static charge build up on their small but finite input capacitance. This can be a problem when measuring voltages in the high sensitivity ranges.

THERMOELECTRIC EFFECTS

Dissimilar metal junctions will generate +/- dc thermoelectric voltages which change with temperature. This voltage usually is in the low millivolt range. The lock-in technique circumvents this problem. In DC four probe measurements the polarity should be switched to check for this effect.

GROUND LOOPS

Improperly grounded equipment or cable shields will cause small amounts of current to flow from one point to another causing spurious voltages to appear. All equipment should be connected to a single common ground and shields should only be grounded at one end of the cable to eliminate any ground loops.

DC OFF-SETS

Most instrumentation does not have zeroing to ground potential, hence a small negative or positive offset potential is present. This value would have to be algebraically subtracted from the measured voltage for a true reading. This can be done by recording the voltmeter output on an X-Y recorder which provides zeroing.

NOISE

Noise is an important issue when making low voltage resistivity measurements. Good grounding, good quality cabling and quality instrumentation are essential for these measurements. At low frequencies, less then 1 KHz, a twisted pair shielded cable works satisfactorily. Coaxial cables are recommended at frequencies greater then 1 KHz.

ANOMALIES

High Sample Resistances

When measuring highly resistive materials($> 100\ K\ \Omega$) a sample will often increase in resistance ($> 1M\ \Omega$) until the lock-in overloads at its lowest sensitivity. However, these highly resistive samples can often yield a very different result which we refer to as saturation. In this case the in-phase signal will decrease while the out-of-phase signal increases. If only monitoring the in-phase signal, it might look quite similar to a superconducting transition as shown in Figure 5. There are many possible causes of saturation i.e. decreased current due to increased series resistance, phase shifts of the input signal due to capacitve effects from the sample and wire leads, or problems with ground potentials. In most cases the cause of the artifact saturation are difficult to determine. However, it is more important to simply verify that the transition is the saturation artifact. As a matter of practice one should always check the two probe contact resistance of each sample contact and verify that lock-in out-of-phase signal is zero.

Very Low Sample Resistances

Samples that are very conductive are difficult to measure since they develop small potentials across the voltage contacts, and hence small signal-to-noise ratios. Figure 6 illustrates the dominance of noise in a very conductive sample. This can be overcome by decreasing the cross-sectional area of the sample, increasing the length between the voltage contacts or increasing the current excitation. For extreme cases, all of the above may need to be exercised to produce a accurate measurement.

Cracks

Sample cracks have various misleading effects depending on their size and location. A crack between a current and voltage contact may appear to be a decreasing resistance transition, yet it is only a decrease in voltage proportional to the decrease in current through the sample. Cracks between two voltage contacts can show sharp jumps of increasing resistance as the crack grows as shown in Figure 7. Occasionally, some sample cracks close yielding sharp decreases in resistance.

Bad Contacts

Poor electrical contact to the sample electrodes can often yield misleading or noisy data. A short between a current and voltage contact can introduce noise to the measurement. An increase in the resistance of a current contact will proportionately decrease the measured voltage and appear to be a real transition. If a sample shows an unexpected transition or suddenly becomes very noisy, the contact resistances of the four electrodes should be systematically checked. Any sample contact that is more than five times higher then the others should be re-painted.

Inhomogeneous Samples

Deceiving results can often appear in inhomogeneous samples. For simplicity, we take inhomogeneous to include mixed phase, surface contaminated, oxidized materials, or a combination of the three. Part of the sample could be dropping in resistance or even superconducting while another part may be insulating. Figure 8 illustrates the result of an inhomogeneous resistive region at the current contact. The curve seems to indicate a superconducting transition, yet it is only a decrease in voltage proportional to the decrease in current caused by the resistive region at the current contact. The most common problem is an outside surface that is much more resistive than the inside bulk. This problem could cause bad measurements of samples that may actually be superconducting, as illustrated in Figure 9. The best remedy is to cleave the sample so that all four contacts are on a fresh new surface. Cleaning with a solvent or other reactive substances works sometimes but can possibly lead to further contamination.

CONCLUSION

To perform accurate resistivity and Tc measurements on superconducting compounds an ac-four probe technique is utilized to eliminate the effects of contact resistance and increase the signal to noise ratio. Placing the sample as close as possible to the temperature sensor will minimize temperature gradients and yield the most accurate temperature readings. Poor electrical contact to the sample and inhomogenous samples are the most common anomalies. Care should be taken to insure that electrical contacts are made to freshly cleaved surfaces and ohmic contacts between any two contacts on a sample do not vary by more than factor of 5.

TABLE I

Series Resistance Constant Current Sources

Source	Limiting Resistor	Current	Sample Resistance	Voltage	Error
1V	1M	1 μA	10 Ω	10 μV	
1V	1M	1 μA	1 KΩ	1 mV	0.1%
1V	1M	.99 μA	10 KΩ	9.9 mV	1%
1V	1M	.91 μA	100 kΩ	90.9 mV	9%
1V	100K	10 μA	10 Ω	100 μV	
1V	100K	9.9 μA	1 kΩ	9.9 mV	1%
1V	100K	9.1 μA	10 kΩ	91 μV	9%
1V	100K	5.0 μA	100 kΩ	500 mV	50%
1V	10K	100 μA	10 Ω	1 mV	
1V	10K	90.9 μA	1 KΩ	90.9 mV	9%
1V	10K	50 μA	10 kΩ	500 mV	50%
1V	10K	9.1 μA	100 KΩ	910 mV	90%

PART LIST

Lakeshore Silicon diode DT-470-11
Lakeshore Temperature Controller DRC-82C
Lakeshore Miniature Coaxial Cable
General Electric varnish #7031
General Electric varnish solvent #9424
Stanford Research Lock-in Amplifiers Model 510
Princeston Applied Research Lock-in Amplifiers Model 124
California Fine Wire (gold wire) 99.995 pure
Dupont conductor composition #4922 (Silver Paste)

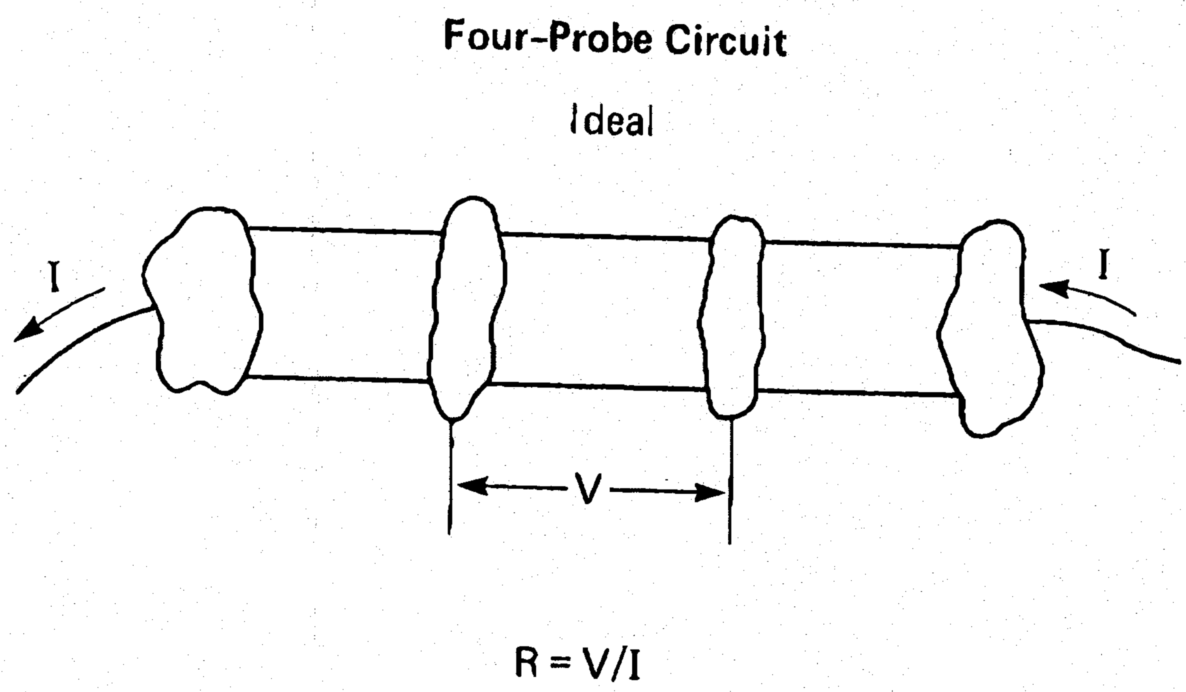
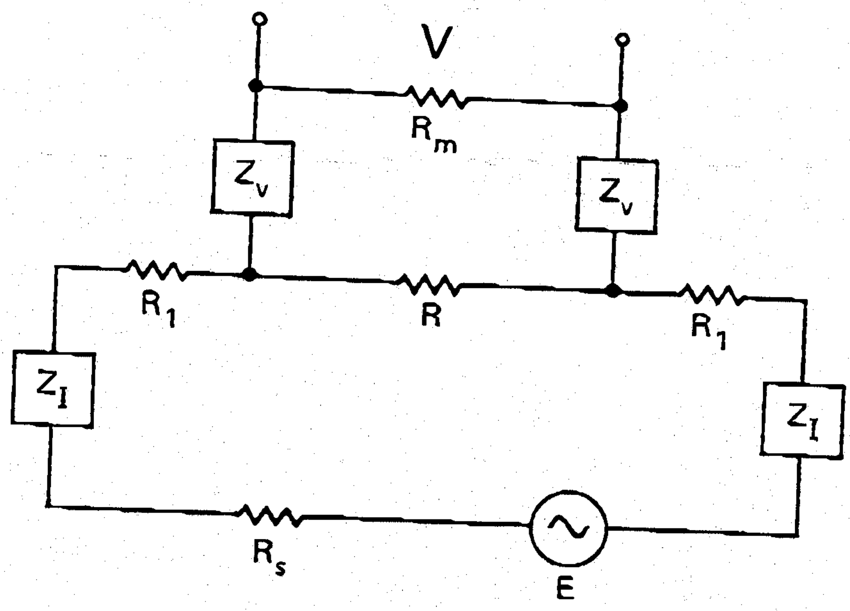


Figure 1. Configuration of the sample and contact geometry.

Four-Probe Circuit

Reality



$$V = \frac{E\,R\,R_m}{(R_s + 2Z_I + 2R_1 + R)\,(2Z_v + R_m + R) - R^2}$$

$$V = \frac{E}{R_s}\,R$$

If and only if:

$$\left.\begin{array}{l} R_s, R_m >> R, R_1, |Z_I|, |Z_v| \\ \phi(Z_I), \phi(Z_v) \approx 0 \end{array}\right\} \text{For all temperatures, currents and frequencies}$$

Figure 2. Four probe circuit schematic.

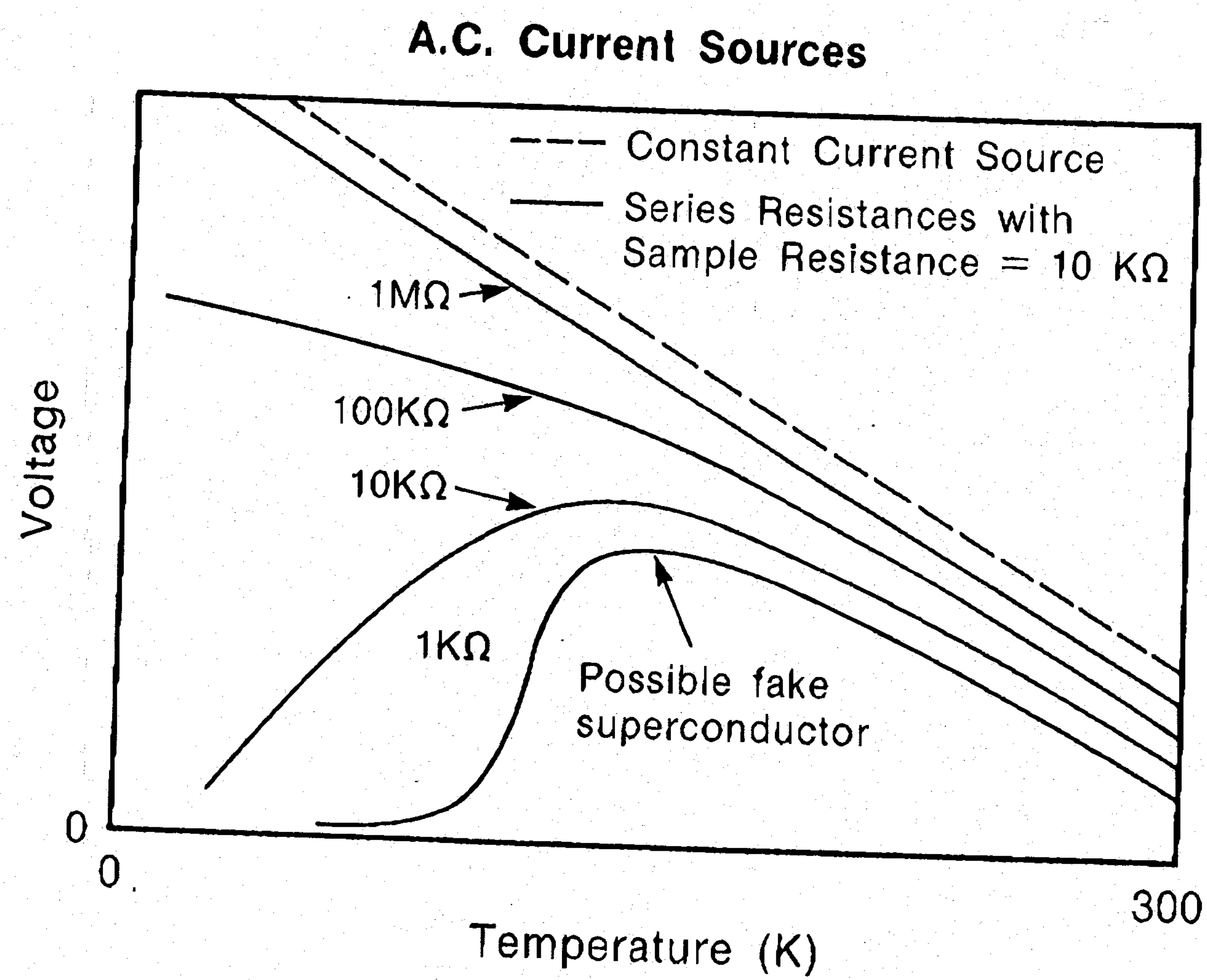


Figure 3. Actual vs. simulated constant current sources.

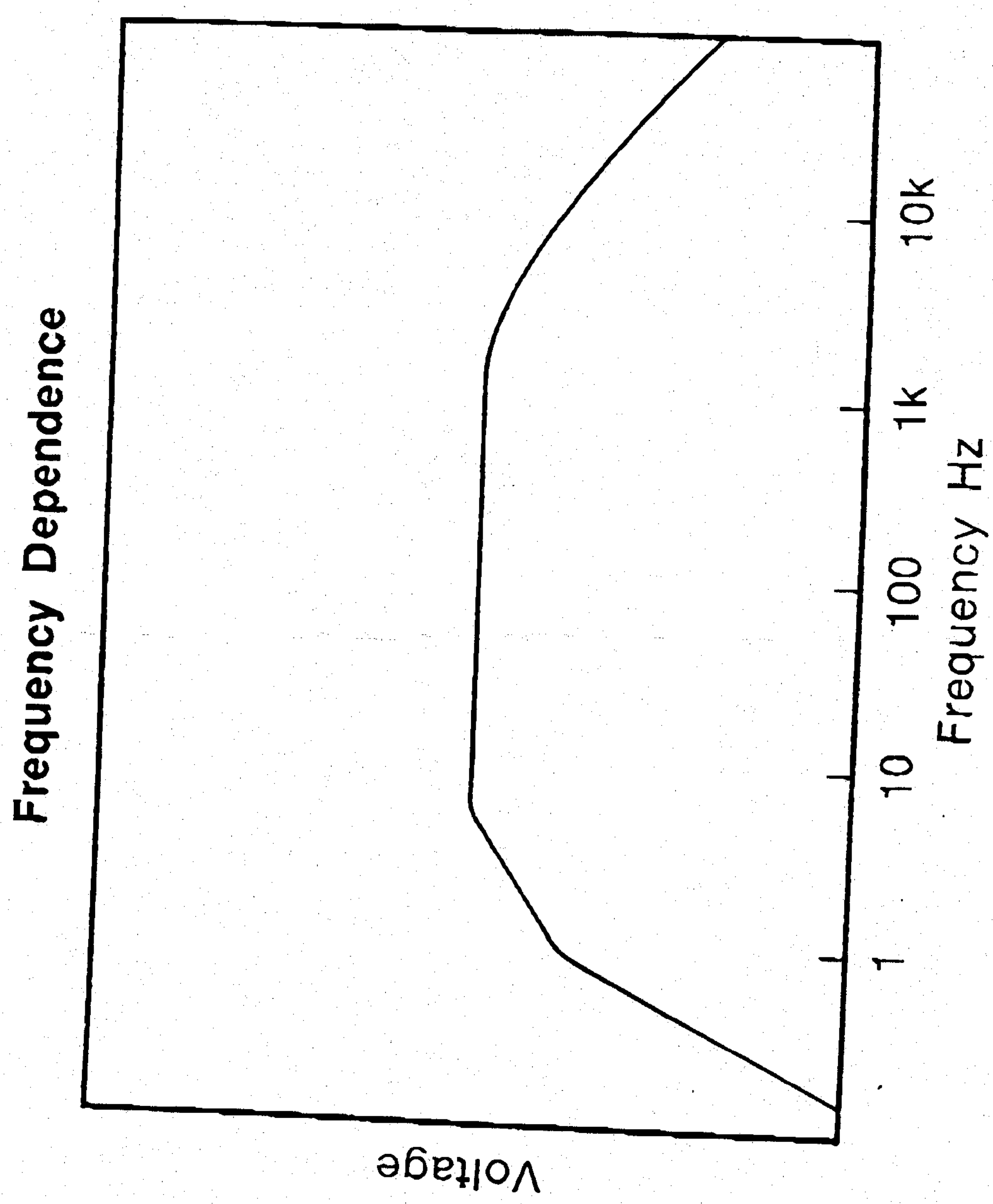


Figure 4. Frequncy dependence of system.

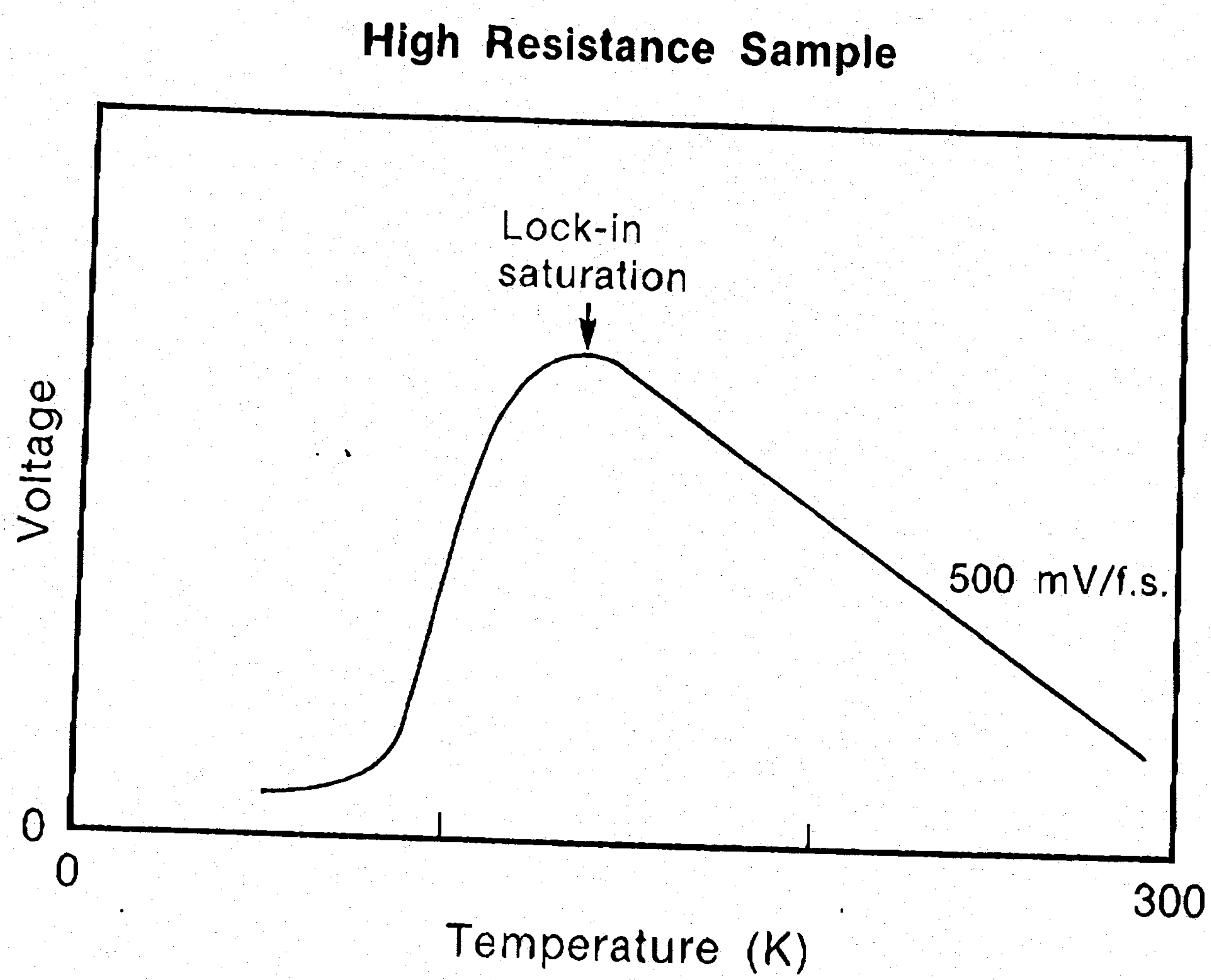


Figure 5. Typical high resistance sample.

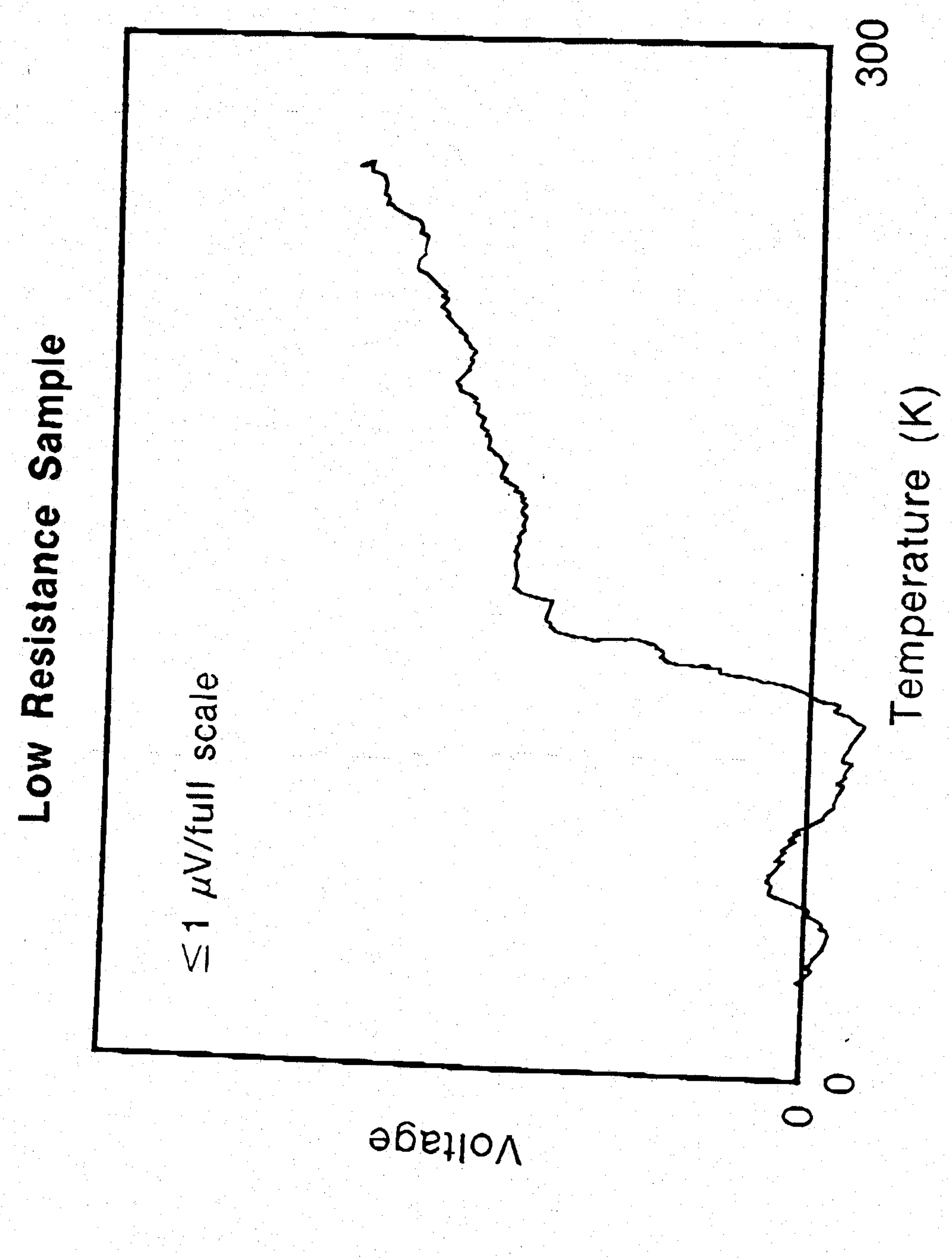


Figure 6. Typical low resistance sample.

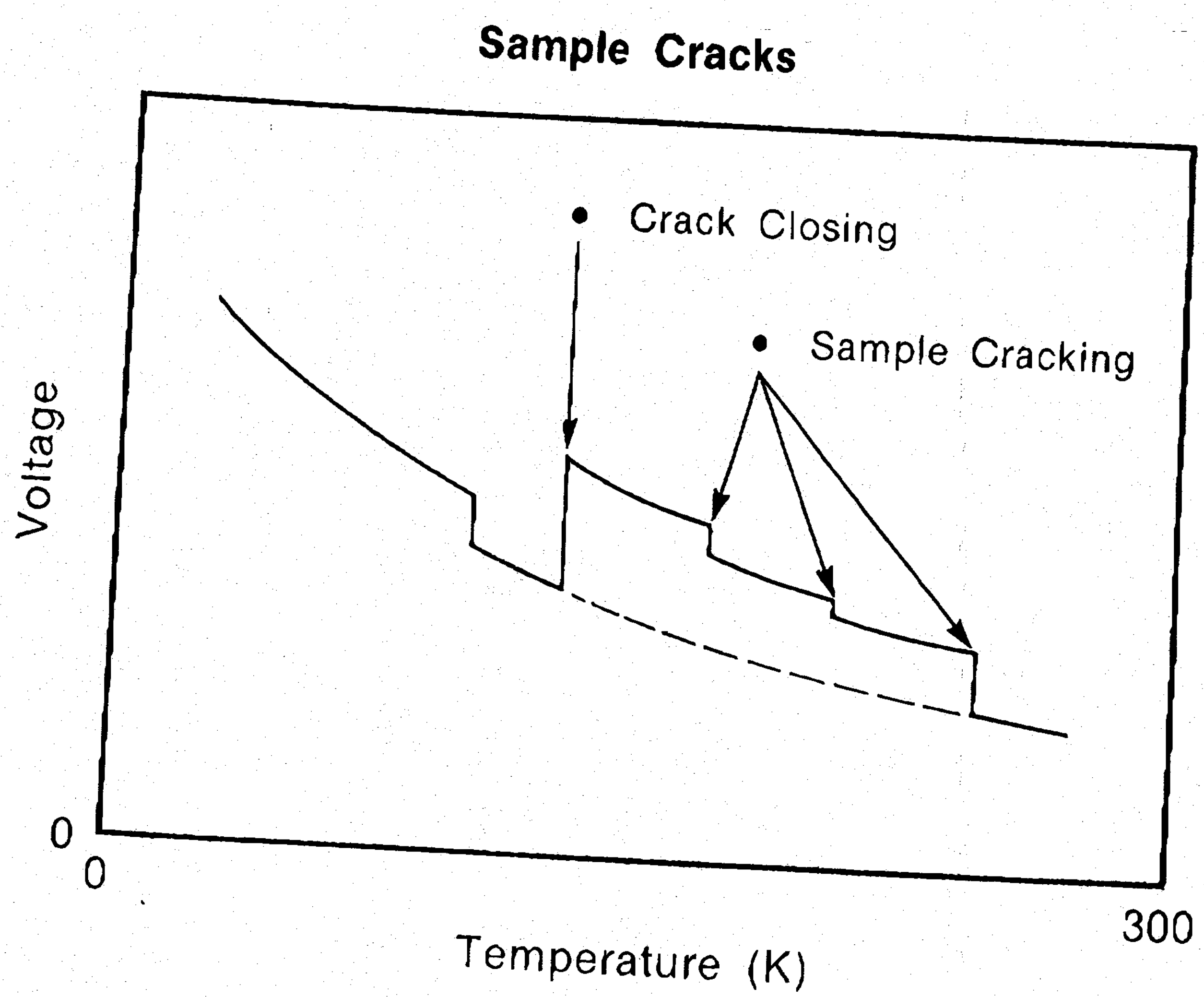


Figure 7. Effects of cracks in the sample.

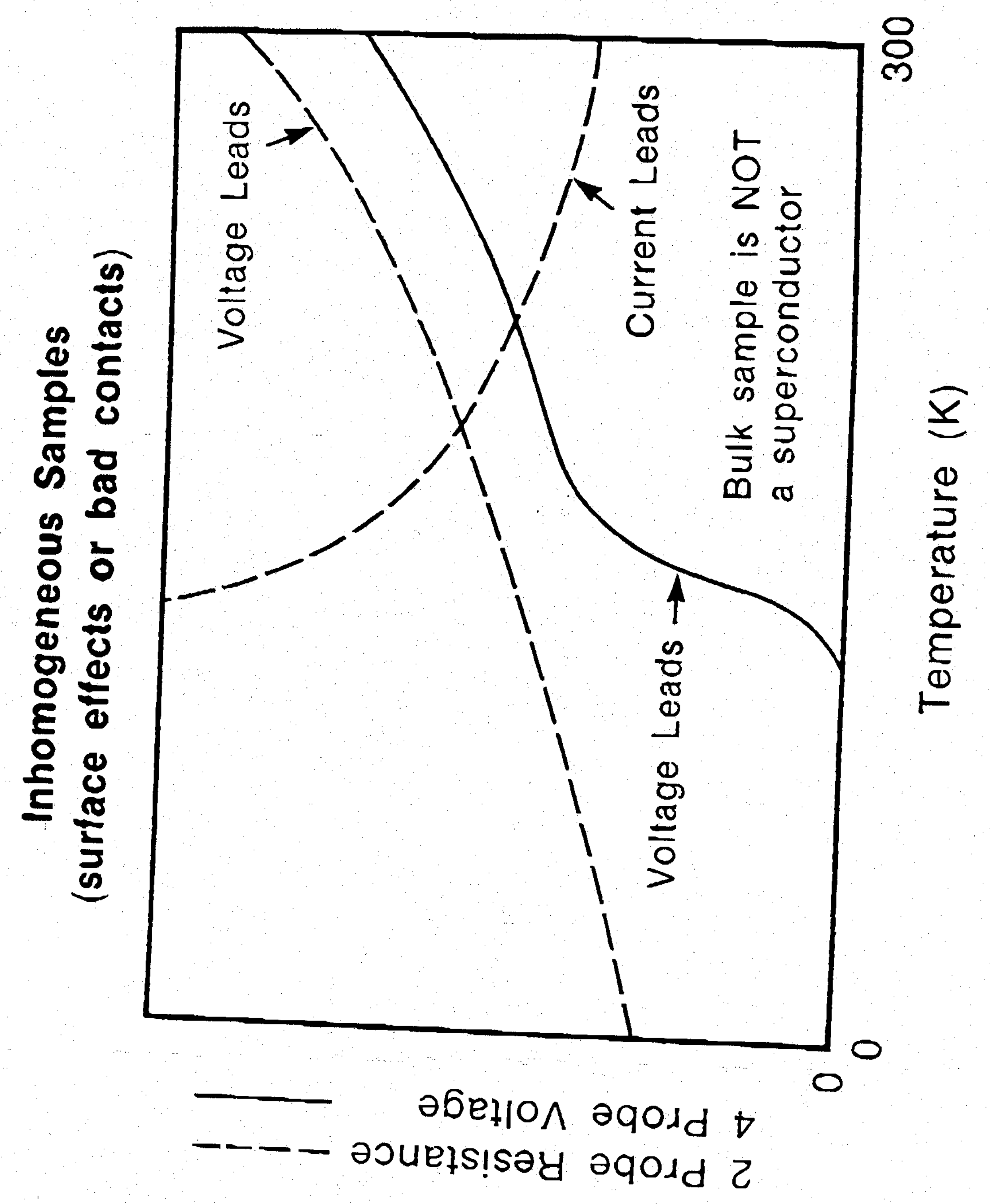


Figure 8. Anomalies from a non-superconducting inhomogeneous sample.

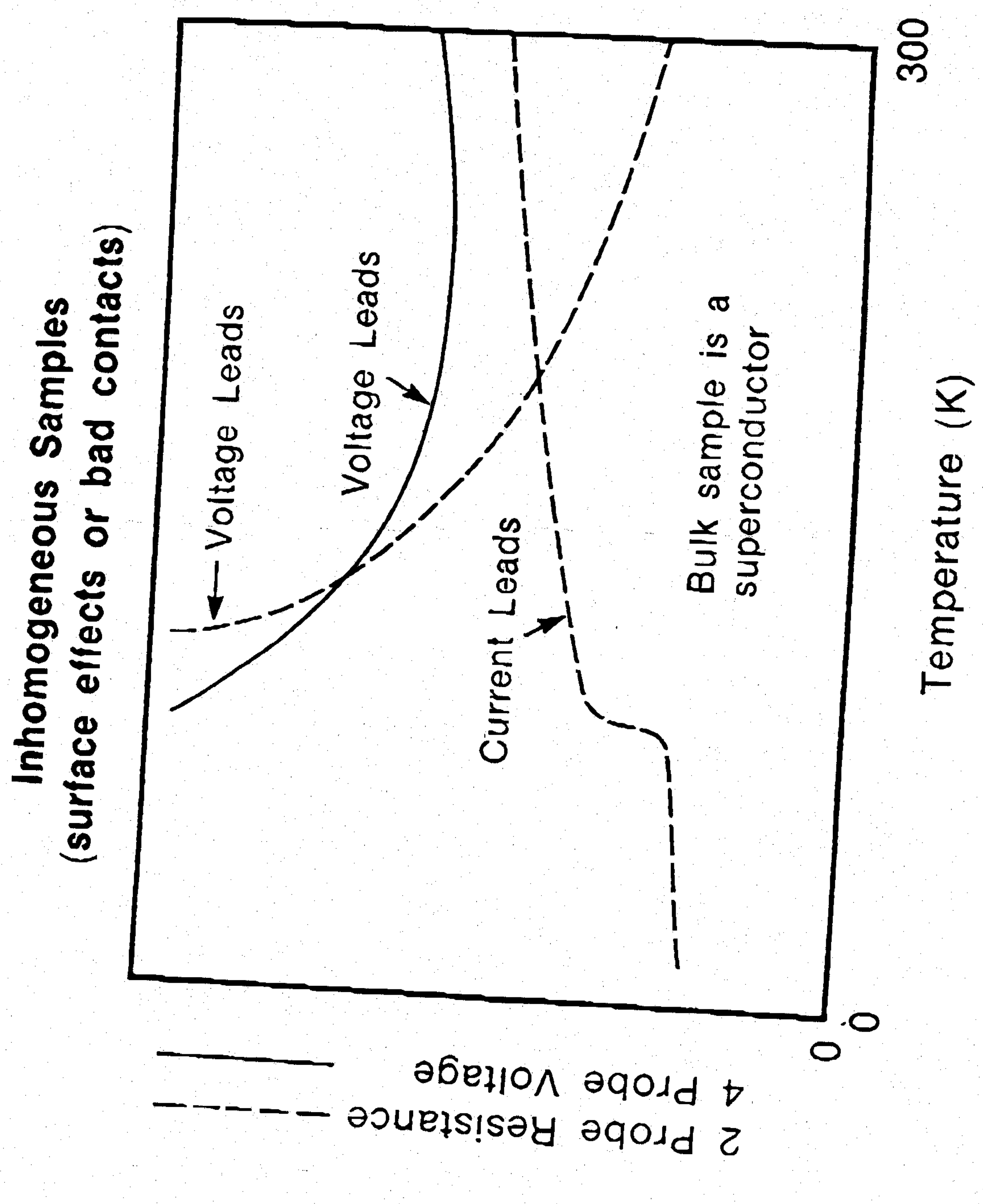


Figure 9. Anomalies from a superconducting inhomogeneous sample.