

Concerning Proposed Superconducting Fluctuations in the Electrical Resistivity of Bulk Aluminum

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Bulk superconducting fluctuation contributions to rounding of the electrical resistivity of Al just above T_c are demonstrated to be at least 5 to 10 times smaller than claimed recently by Sinvani, Levy, and Greenfield. Metallurgical artifacts provide a more plausible explanation for all of the measured rounding.

In a recent Letter,¹ Sinvani, Levy, and Greenfield (SLG) reported resistivity measurements on aluminum (Al) that showed rounding of the superconducting transition significantly above the transition temperature T_c of 1.17 K. They attributed this rounding to bulk superconducting fluctuations some two to three orders of magnitude larger² than expected from currently accepted theory.³ They did not, however, rule out completely the possibility of more mundane causes, such as sample inhomogeneity.

We present here measurements which bracket the regime examined by SLG. We find rounding effects that are at least five to ten times smaller than theirs. This means that their results cannot be predominantly intrinsic, so that bulk superconducting fluctuations cannot be nearly as large as they claimed. We suggest alternative explanations for this irreproducible rounding of the resistive superconducting transition.

Our measurements were made using a SQUID resistance bridge^{4,5} having very high resolution resistances as small as 10^{-5} to 10^{-8} Ω . A comparison of experimental conditions between our measurements and those of SLG (see Table I) shows that our conditions were at least as favorable as theirs to the observation of any fluctuation effects, and in most respects more favorable. The residual-resistance ratios [RRR= $R(300\text{ K})/R(4.2\text{ K})$] of our two samples (RRR=580 and 23) deliberately bracketed those of their four samples (RRR=380 to 62), so as to test for fluctuation effects over a wider range of RRR than they

did.

Our purer samples (RRR=580) was a single crystal grown from Johnson Matthey "Specpure" material. This RRR is distinctly low for a "pure" sample, but is consonant with the claimed level of impurities. Our other sample was an Al-0.045% Li alloy (RRR=23) fabricated by the Istituto Sperimentale Metalli Leggeri, Novara, Italy; its composition is well within the solubility limit ($\approx 5\%$) of Li in Al.⁶ This alloy was reported to contain also 20 ppm Fe and 50 ppm Si. Both samples were spark cut to the tuning-fork configuration⁵ that eliminates difficulties associated with electrical and thermal contact, and then annealed at 500 °C for several hours.

In order to make as clear a comparison as possible, we analyze our data in the same way as stated by SLG. They wrote the total resistivity as

$$\rho(T) = \rho_0 + AT^2 - \alpha [T_c / (T - T_c)]^n \rho_0^2, \quad (1)$$

where ρ_0 comes from residual defect and impurity scattering, the quadratic term is probably associated with electron-electron scattering, and the final term is modelled on an additional *conductivity* expected to arise from superconducting fluctuations.³ Other recent experiments,^{7,8} mostly on samples of considerably higher purity than those presently under consideration, agree on the presence of a dominant T^2 term in Al between T_c and 2 or 3 K (the most accurate experiments imply⁸ that there are discernible deviations from T^2 behavior, but these are not important here) with

TABLE I. Comparison of experimental conditions between the present study and Ref. 1.

	Experimental resolution	Sample length (cm)	Sample cross section (cm ²)	Measuring current (A)	Magnetic field at sample surface (G)	Ambient magnetic field (G)	Temperature uniformity of sample (K)
Ref. 1	$\sim 10^{-6}$	10 ²	10 ⁻²	0.2-0.9	1-4	?	?
Present study	$\sim 10^{-6}$	10	10 ⁻¹	0.01-0.09	0.01-0.1	10 ⁻²	10 ⁻⁶

values of the coefficient A in the range of $(3-5) \times 10^{-13} \Omega \text{ cm}/\text{K}^2$. Theoretical values³ for the coefficients α and n in Eq. (1) are $0.17 (\Omega \text{ cm})^{-1}$ and $\frac{1}{2}$, respectively; SLG fitted their data with $\alpha = 70 (\Omega \text{ cm})^{-1}$ and $n = 0.73$.

Following SLG, we define T_c (which, since it shifts with impurity content, must be determined independently for each sample), as the temperature of the midpoint of the resistive transition. The absolute uncertainties in our temperature scale are several millidegrees Kelvin, but the relevant small temperature differences from T_c should be accurate to better than 1 mK.

We begin with our "pure" sample, on which the measurements were made some time ago,⁴ before

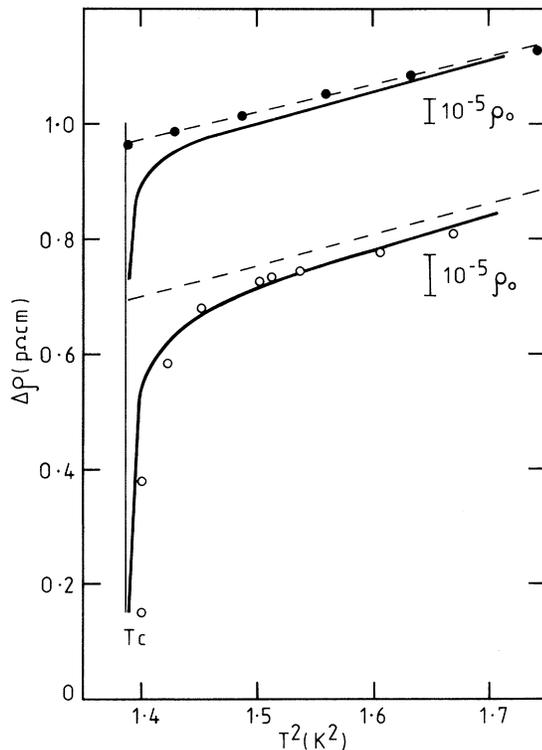


FIG. 1. Raw data of resistivity change $\Delta\rho$ vs T^2 below 1.3 K for the purest samples. Closed circles, our single crystal, RRR=580, $T_c = 1.177_5$ K; each datum point represents the average of two independent measurements differing by less than 1 ppm. Open circles, sample S-380 (RRR=380) from Ref. 1, in which the large changes below about $T^2 = 1.43$ were attributed to normal broadening of the transition, apparently caused primarily by their high measuring current. The broken lines represent T^2 behavior fitted to higher-temperature data. The solid curves are Eq. (1) with the T^2 term shown together with the fluctuation parameters $\alpha = 70 (\Omega \text{ cm})^{-1}$ and $n = 0.73$ specified in Ref. 1. The positions of the ordinate origins are arbitrary.

we had cause to examine the superconducting transition in great detail. Figure 1 shows the raw data near to T_c for this sample. Between 1.179 K and about 2 K it showed *no* significant deviation from T^2 behavior ($A = 4.8 \times 10^{-13} \Omega \text{ cm}/\text{K}^2$); at 1.176 K the sample was fully superconducting. We were thus able to approach within about 2 mK of T_c without seeing any hint of the divergent behavior (solid curve) expected from SLG's interpretation of their data. In contrast, the data for the purest sample (S-380) of SLG show, within about 10 to 20 mK of T_c (i.e., up to about $T^2 = 1.43 \text{ K}^2$), an ordinary smearing of the transition caused primarily by their large measuring current, which certainly obscures the possible presence of any smaller fluctuation effects. Taking into account the uncertainties in form and magnitude of the ordinary temperature dependence of the resistivity, for our "pure" sample

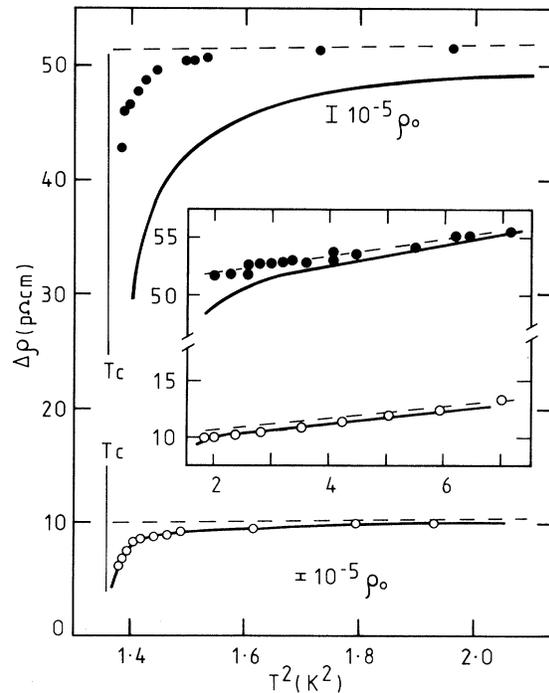


FIG. 2. Raw data of resistivity change $\Delta\rho$ vs T^2 below 1.4 K for the least pure samples. Closed circles, our Al-0.045at.%Li alloy. RRR=23; $T_c = 1.165$ K. The lowest datum point shown here is at 10 mK above T_c ; at 5 mK above T_c , $\Delta\rho$ is about two orders of magnitude greater. Open circles, sample S-62 (RRR=62) from Ref. 1. The lowest datum point shown is about 10 mK above T_c . The broken lines and solid curves are as described in the caption to Fig. 1. The inset shows how the data continue up to 2.5 K. The positions of the ordinate origins are arbitrary.

we can exclude the presence of a "fluctuation" term close to T_c larger than about one-tenth of SLG's claim.

Measurements on our alloy and SLG's most resistive sample (S-62) are shown in Fig. 2; again the solid lines correspond to Eq. (1) with use of their fluctuation parameters. The dashed line through our data corresponds to $A = 7.8 \times 10^{-13} \Omega \text{ cm/K}^2$; that through their data to $A = 5.2 \times 10^{-13} \Omega \text{ cm/K}^2$. On our sample we do see some rounding above the transition, but close to T_c we can be sure that it is at least a factor of 5 smaller than predicted by Eq. (1) with SLG's values of α and n .

Taken together, our two sets of data allow us to set an upper bound on any intrinsic anomalous bulk behavior close to T_c that is 5 to 10 times smaller than claimed by SLG. Because our sample RRR's bracketed theirs, this conclusion is independent of any weak dependence on ρ_0 , caused, for example, by associated changes in coherence length, additional to that given by Eq. (1).

In trying to account for the rounding of the resistive transition, it is important to recognize that more than a few millidegrees Kelvin from T_c the rounding is quite small. By 10 to 20 mK above T_c , it could be produced by a volume fraction of order 10^{-4} – 10^{-5} remaining superconducting. This fraction is equal to or smaller than the estimated impurity concentrations in the various samples. Two of the mechanisms by which small regions can become superconducting are the following: Firstly, by precipitation of an intermetallic phase that has a T_c higher than Al; Al_{10}V [$T_c = 1.6 \text{ K}$ (Ref. 9)] is a possible candidate for SLG's samples. Secondly, by increases in T_c due to strain fields, caused by cold work, or induced by thermal contraction around inclusions and precipitates.¹⁰ Al is particularly prone to enhancement of T_c by perturbations,¹¹ including strains.¹² For example, Joiner¹² has shown that even in high-purity Al heavy cold work followed by annealing can leave several percent of the sample superconducting at temperatures above the bulk T_c for Al. From the form of his data, it appears that a superconducting fraction of 10^{-4} to 10^{-5} could easily survive to tenths of a degree above the bulk T_c , and so account for the rounding seen by SLG in their heavily cold-worked samples. Small regions of higher T_c will, of course, be sensitive to magnetic field and current density, in accord with SLG observations. We note in passing that the heat treatment they attempted on their sample S-62 was at too low a temperature, 240 °C,

and for too short a time, 2 h, to anneal out more than a fraction of the cold work to which the sample had been subjected (see Table I of Ref. 12). Consequently it is not surprising that the heat treatment produced little change in behavior. We have examined metallographically both of our samples and find apparent inclusions (probably oxide) at a level of $\sim 1 \times 10^{-3}$ volume fraction in the alloy and $\sim 2 \times 10^{-4}$ in the "pure" sample. Because the elastic limit increases with the solute content, which in turn scales with ρ_0 , the amount of unrelieved strain caused by differential thermal contraction between the matrix and any inclusions should be correlated with ρ_0 . We therefore expect the size of the high-temperature tail to increase with increasing ρ_0 . This accounts qualitatively for the rounding and tails seen by Keesom nearly fifty years ago in very dirty Al,¹³ by SLG, and in our alloy sample.

In conclusion, we have demonstrated that any bulk superconducting fluctuation effects just above T_c in Al must be at least 5 to 10 times smaller than claimed by Sinvani, Levy, and Greenfield and we have indicated how the rounding seen in their samples and in our alloy could easily be caused by metallurgical artifacts alone. Any assertion that existing theories of resistive fluctuations effects are inadequate is thus clearly premature. We note, however, that existing technology is sufficiently sensitive^{5,14} to allow a quantitative test of prevailing theory, provided that the difficult metallurgical problems indicated above can be overcome.

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Identification of an Adsorbed Hydroxyl Species on the Pt(111) Surface

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The electronic structure and vibrations of an adsorbed hydroxyl (OH) species are identified and characterized for the first time on a transition-metal surface. In this study of water's interaction with clean Pt(111) in ultrahigh vacuum, water adsorbed at 100 K desorbs at 180 K without appreciable dissociation. However, in the presence of adsorbed atomic oxygen, water dissociates above 150 K to form adsorbed hydroxyl species. The O-H axis appears to be bent relative to the surface normal.

We report in this Letter the first evidence, supported by a combination of spectroscopies, for the existence of an adsorbed hydroxyl species on a single-crystal transition-metal surface. This finding has particular significance, since the direct observation of intermediate steps in catalytic reactions has proven very difficult even with many advances in our understanding of adsorbed atoms and molecules from a number of spectroscopies. Despite considerable study since the time of Faraday,¹ even the simplest oxidation reaction, that of hydrogen oxidation over Pt to form water ($2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$), has not had its mechanism elucidated over its entire temperature range. A wide range of mechanisms has been discussed for this reaction, including the reaction of adsorbed hydroxyl species with adsorbed hydrogen to form water.² However, at room temperature and above where the research is usually done, the reaction has more recently been discussed as a Langmuir-Hinshelwood proc-

ess, in which an adsorbed dihydrogen species reacts with adsorbed oxygen to form water which then desorbs.³ As part of a study of this reaction in ultrahigh vacuum over single-crystal Pt(111), we have identified and characterized for the first time the electronic structure and vibrations of an adsorbed hydroxyl or OH species by means of ultraviolet photoemission spectroscopy (UPS), x-ray photoemission spectroscopy (XPS), and high-resolution (65 cm^{-1} or 8 meV) electron energy-loss spectroscopy (EELS). The hydroxyl appears to exist at temperatures which relate to the water formation reaction.

During a study of water desorption from⁴ Pt(111) it was found that water's desorption behavior is quite different from clean Pt(111) than from a surface with oxygen present. Figure 1 shows the rate of water desorption from Pt(111) after a constant exposure of 0.3 L (coverage less than a monolayer) to surfaces which are clean and pre-exposed to small amounts of oxygen (1 L = 1 lang-