SUPERCONDUCTING TUNNELING AT HIGH MAGNETIC FIELDS AND POSSIBLE EVIDENCE FOR GINZBURG SURFACE SUPERCONDUCTIVITY*

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Behavior in the dV/dI-vs-V characteristics as a function of magnetic field and temperature in various Al-$\mathrm{Al}_x\mathrm{O}_y$-metal tunneling junctions has been found which may be evidence for Ginzburg[1] surface superconductivity. In particular, the striking characteristic of the curves of dV/dI vs V is that the superconducting-like behavior persists to magnetic fields of about 20 000-30 000 Oe,[2] which is orders of magnitude above the bulk critical field[3] of Al ($H_c \approx 30$ Oe) at temperatures of ≈1°K. These effects also persist to temperatures near 2°K.[4] Arguments and experiments are presented to show that these observations cannot simply be explained by strain effects.[5]

We have measured the dynamic resistance [$\rho = (dV/dI)(\text{superconducting density of states})^{-1}$] of a series of tunneling junctions. The ac and dc currents were fed from constant-current sources and the ac voltage on the junction was kept below 300 microvolts peak to peak. The junctions studied were made by oxidizing the initially deposited Al (about 1000 Å thick) and then depositing the second metal. The oxide was always in intimate contact with the Al. The films were deposited using standard techniques (i.e., in a vacuum of about 10^{-6} mm Hg on a glass substrate at room temperature). 2 to 60 minutes were allowed for the formation of the oxide layer.

Typical tunneling resistance-voltage curves in a magnetic field parallel to the junction surface are given in Fig. 1(a). The curves illustrate the last (gapless)[6] traces of superconductivity in Pb at 2.2°K as the field approaches the critical magnetic field. The width at the base of the resistance-voltage curves near the maximum field is still approximately the zero-field energy gap for Pb. While maintaining a field sufficient to suppress the superconductivity of Pb, the temperature was lowered. The resultant resistance-voltage curves are shown in Fig. 1(b). It is evident that at temperatures of 1.8°K and below, there appears superimposed upon the normal resistance-voltage curve an additional resistance. The small resistance increase (less than 1 % of the normal junction resistance) resembles the curves illustrating the last traces of superconductivity in Pb shown in Fig. 1(a), but the width of the resistance peak is appreciably less[7] than that of Pb. We note that there is a resistance dip before the resistance merges into the normal resistance. This is analogous to curves for superconductors in zero field, and further supports the superconducting nature of the additional resistance. Figure 2 illustrates the high-field persistence of the additional resistance. We see that the peak height decreases with increasing magnetic field, disappearing at about

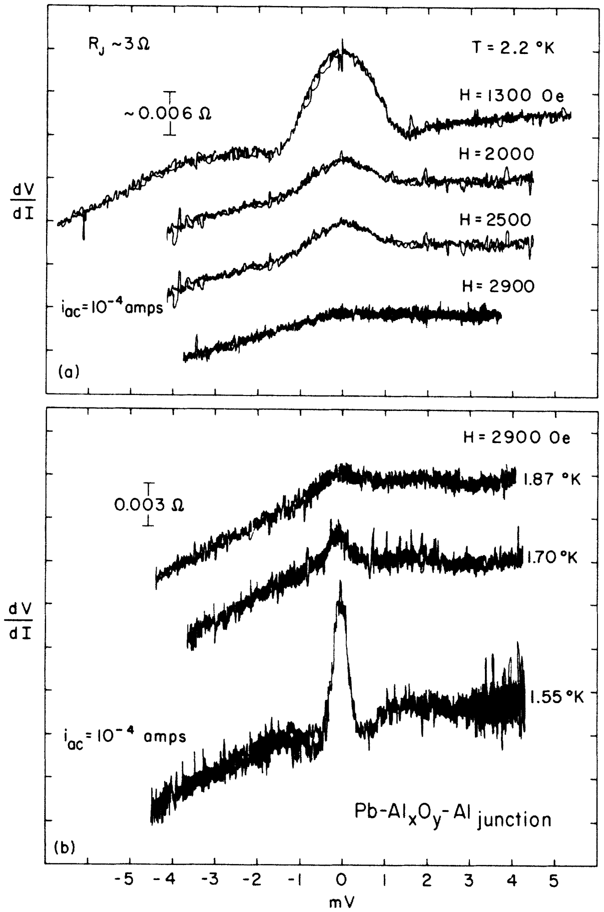

FIG. 1. (a) Last traces of lead gap in Pb-$\mathrm{Al}_x\mathrm{O}_y$-Al junction at 2.2°K. Thickness of Pb and Al is about 1000 Å each. (b) Emergence of high-field resistance peak below about 1.8°K for same junction. Magnetic field is 2900 Oe.

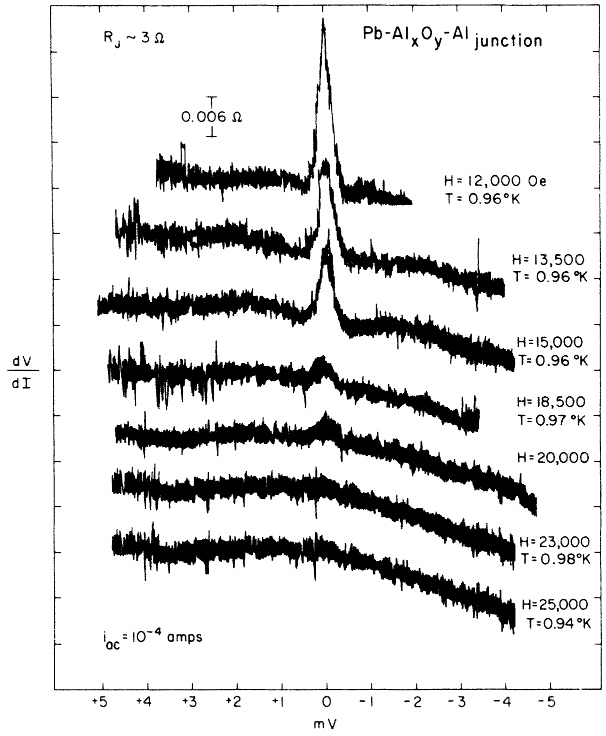

FIG. 2. Persistence of high-field resistance peak at a temperature below 1°K. Note that the x input to the recorder has been reversed thereby reversing the scale on the voltage abcissa, as compared to Fig. 1.

20 000 Oe at slightly under 1°K. It may further be noted that the peak width does not vary appreciably as the field is increased to the critical field. The maximum critical field also depends on the temperature; the critical field decreases as the temperature is increased. These effects have been observed in junctions with the second metal consisting of Al and Ni as well as the Pb used in the illustrations. The $Al\text{-}Al_xO_y\text{-}Al$ junctions were used to find the zero-field behavior of the additional resistance, since in this case a field does not have to be applied to remove the Pb gap. The zero-field data show that as the temperature is decreased, the resistance increase appears below $T \approx 1.8$°K. This junction also showed a sharp decrease in the peak width as T_c was approached. Ac resistivity measurements along the Al have shown that the full normal resistance is restored at 2°K, and higher in some junctions.

In summary, the main features in our observations suggest superconductivity whose major characteristics are a persistance to a $T_u \approx 1.8$°K, a maximum critical field $H_m \approx 20$ kOe at 1°K, and an equivalent thermodynamic bulk critical field H_c which would be $H_c \approx 200$ Oe (at 0°K). We first note that a superconductor should have a maximum critical field which does not exceed the limitation imposed by the energy gain from the paramagnetic energy of the normal state.[8] Using the Clogston estimate[8] for $H_m = 18.4T_c[1-(T/T_c)^2]$ kOe, we obtain 23 kOe, in agreement with our observed values[9] of 20-25 kOe for this junction. Two explanations for these high-field effects are that the superconducting regions may have a small dimension and thus have the upper critical field associated with thin film or filaments[3]; or that the regions giving rise to the superconductivity could have a large Ginzburg-Landau parameter K. In the first case, from the relationship for a thin film[3,10] [with $Kd/\lambda \ll 1$ $(H_m = 2\times 6^{1/2}\lambda/d)$ where λ is the actual penetration depth and d is the thickness of the superconducting region], we find that a dimension $d \sim 100$ Å or less would explain the data. In the second case, from the relationship for the type-II superconductor $\{H_{c2} = \sqrt{2}H_c[1-(T/T_c)^2]K$ or $H_{c3} = 1.7H_{c2}$, if the boundary conditions give further enhancement of the Saint-James–de Gennes type[11]$\}$, we find $K \approx 60\text{-}100$. Experiments in perpendicular fields, which showed only the normal tunneling behavior, suggest that the effects we are seeing are thin-film effects rather than due to high values for K. We have made some further effort to establish what regions are the source of the high-field effect and whether or not the effect is due to a Ginzburg surface layer at the superconductor-dielectric interface rather than a very thin film of highly strained Al. We have been able to show by separate resistivity measurements and additional measurements on junctions with trimmed edges that it appears that these effects are probably associated with the edges of the evaporated film, which are known to be much thinner than the main part of the film. Having established that the edges are probably the origin of the high-field effect, the question remains of establishing whether the observed upper temperature of $T_u \sim 1.8\text{-}2.0$°K$> T_c = 1.2$ (for bulk Al) can reasonably be attributed to highly strained Al rather than a special property of the Al-dielectric interface. Estimating the increase of critical temperature due to stresses arising from the different contraction between the Al and the substrate, we obtain a rise of no more than 0.4°K using a value of 10^{-4} °K/atm for dT_c/dp. The rise in T_c is due to the fact that Al contracts more than the soft glass substrate. A more conclusive demonstration that our observed $T = 1.8$-2.0°K is not due to the differential contraction is illustrated by depositing films on Teflon. Under these conditions the substrate contracts more than the Al, thereby giving a compressive stress which should result in a lowering of T_c. In this case we find that the main part of the evaporated film is not fully superconducting at 1.0°K. However, there is still evidence of superconducting regions that persist until 1.75°K. Thus, we conclude that there are effects which cannot simply be attributed to stresses arising from the different rates of contraction between the Al and substrate. We therefore suggest that the rise in T_c and the high fields are possibly due to Ginzburg surface superconductivity originating in the superconductor-dielectric interface in the film edges. Ginzburg has suggested that a metal dielectric surface would cause an additional attractive interaction energy between electrons in the vicinity of the surface. The configuration of a dielectric layer on a superconductor is exactly the configuration used in electron-tunneling measurements where a dielectric layer of the order of 20 Å is used to separate a superconductor from a metal.[12] These surface effects may also appear in sensitive bulk resistivity measurements in a magnetic field, if there is an oxide layer. This could explain the resistance tail up to at least $3H_{c2}$ observed by Rosenblum, Autler, and Gooen[13] in Nb.

We thank Professor David H. Douglass for his discussion of thin-film problems, and in particular for suggesting that the high-field effects we have observed could be associated with the edges of the junction. We also thank Dr. Arnold M. Toxen for a helpful discussion on the effect of strains in thin films and other thin-films problems.

Note added in proof. –Since submission of our paper, Hannay et al.[14] also have submitted a paper presenting possible evidence for two-dimensional superconductivity in graphite lamellar compounds. The possibility of general two-dimensional superconductivity has been discussed by Ginzburg and Kirzhnits.[15] In a later paper Ginzburg then discussed some possible types of two-dimensional superconductivity which could arise on the surface. Hence, both the data of Hannay et al.[14] and our own make it very probable that two-dimensional superconductivity exists and is observable in special situations.

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[1] V. L. Ginzburg, Phys. Letters 13, 101 (1964).

[2] In zero magnetic field we observe the usual I-V curves which have been observed by many authors. See, for example, D. H. Douglass, Jr., and R. Meservey, Phys. Rev. 135, A19 (1964), and I. Giaver and K. Megerle, Phys. Rev. 122, 119 (1961). In our Pb-$\mathrm{Al}_x\mathrm{O}_y$-Al junctions we see the usual Pb gap, with the Al gap "opening up" at about 1.3°K. At about 1°K we observe the disappearance of the bulk Al gap in a few hundred gauss, again in good agreement with the above authors. The effects described in this paper are too small to be seen when there is a Pb gap, and they only appear in fields large enough to destroy both the bulk Al and Pb gaps.

[3] E. A. Lynton, Superconductivity (John Wiley & Sons, Inc., New York, 1962).

[4] Other authors have observed a rise in T_c with decreased film thickness in Al. See especially reference 2 and see I. S. Khukhareva, Zh. Eksperim. i Teor. Fiz 41, 1728 (1961) [translation: Soviet Phys.–JETP 16, 828 (1962). We wish to point out, however, that for room-temperature deposition no sharp rise in T_c is seen. For instance Douglass and Meservey[2] give $T_c = 1.25$°K for a 1200Å film and they attribute this rise to stresses in the film. In this paper it is shown that the effects which we have observed in 1000Å films are probably not associated with stresses. Khukhareva also mentions that he and others have found a sharp rise in T_c (up to 3°K) when the films are deposited on low-temperature substrates. However, this is a different effect from the one we are describing and is probably due to the very small mean free path in this type of film.

[5] See A. M. Toxen, Phys. Rev. 123, 442 (1961), and 124, 1018 (1961), for a good discussion of stresses in films.

[6] In tunneling experiments with fields $>H_c$ no gap is observed, and hence these measurements are evidence for gapless superconductivity [see, for example, P. Fulde and R. A. Ferrell, Phys. Rev. 135, A550 (1964); and Y. Goldstein, Phys. Letters 12, 169 (1964)].

[7] The distance between minima or the width of the resistance peak is about two times the BCS value of $3.5kT_c$ with $T_c \approx 1.8$°K. This seems quite reasonable in that as $T \rightarrow T_c$, I. Giaever [Superconductors, edited by M. Tannenbaum and V. Wright (Interscience Publishers, Inc., New York, 1962), p. 14] finds that the dI/dV peaks or the dV/dI minima get broadened and shifted to values greater than the BCS value. For temperatures about $T_c/2$ Giaever finds the "width" of the resistance peak for Sn is about 1.5 times the BCS value.

[8] A. M. Clogston, Phys. Rev. Letters 9, 266 (1962); B. S. Chandrasekhar, Appl. Phys. Letters 1, 7 (1962).

[9] In the Al-Al$_x$O$_y$-Al junction at $T \approx 1.2$°K we observe a field about 30% higher than the Clogston paramagnetic criterion. This is still within the error that Clogston assigns to his estimate because of uncertainties in the estimate of the paramagnetic susceptibility.

[10] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. 47, 720 (1964).

[11] D. Saint-James and P. G. de Gennes, Phys. Letters 7, 306 (1963). Saint-James and de Gennes calculate the enhancement of the critical field arising from the vacuum boundary condition on a bulk sample. Abrikosov[10] has recently extended the treatment to cover the case of vacuum surface enhancement of a thin film. As our estimates of the properties of the region giving rise to dielectric enhanced superconductivity are meant to be correct only to order of magnitude, no attempt has been made to include combined thin-film and Saint-James–de Gennes surface superconductivity effect.

[12] The edges of the thin film are an ideal place for the observation of this effect since most of the edge region is not in contact with thick normal regions which would be expected to lower T_c.

[13] E. S. Rosenblum, S. H. Autler, and K. H. Gooen, Rev. Mod. Phys. 36, 77 (1964).

[14] N. B. Hannay, T. H. Geballe, B. T. Matthias, K. Andres, P. Schmidt, and D. MacNair, Phys. Rev. Letters 14, 225 (1965).

[15] V. L. Ginzburg and D. A. Kirzhnits, Zh. Eksperim. i Teor. Fiz. 46, 307 (1964) [translation: Soviet Phys.–JETP 19, 269 (1964)].

HYPERFINE STRUCTURE OF THE 14.4-keV γ RAY OF ^{57}Fe IN HYDRATED FERRIC AMMONIUM SULFATE AS A FUNCTION OF THE MAGNETIZATION OF THE SALT*

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The hyperfine-structure (hfs) spectra of the 14.4-keV γ ray of the nucleus ^{57}Fe in the paramagnetic salt hydrated ferric ammonium sulfate have been measured through the use of the Mössbauer effect. These measurements were performed at an absolute temperature T in the liquid helium region in zero applied magnetic field, and also in the presence of applied magnetic fields H large enough to produce a substantial polarization of the unpaired electron spins of the Fe^{+++} ions. The behavior of the Mössbauer linewidths, shapes, and spacings of the hfs spectra observed here differ from the hfs spectra found for either magnetically dense of exceedingly dilute magnetic materials.

In previous recoilless radiation studies where the magnetic materials have had a high density of magnetic ions, for example metallic iron[1] or α-Fe$_2$O$_3$,[2,3] it has been found experimentally that the individual gamma-ray lines of the hfs multiplet may show widths which are very close to $\hbar/\tau_N$ where τ_N is the nuclear γ-decay lifetime,[4] and that the line spacings may be very well described[1-3] by an approximate Hamiltonian which for either the nuclear excited or ground state has the form

$$\mathcal{H}_1 = AMI_z/g\beta + g_n\beta_n HI_z \tag{1a}$$

$$= g_n\beta_n(H_{\mathrm{eff}} + H)I_z, \tag{1b}$$

where

$$H_{\mathrm{eff}} = AM/g\beta g_n\beta_n. \tag{1c}$$

In Eqs. (1), g_n is a nuclear gyromagentic ratio, β_n is the nuclear magneton, A is an hfs coupling constant, I_z is the z component of the nuclear spin operator $\vec{I}$, g is the electron gyromagnetic ratio, and β is the Bohr magneton. The quantity M, the electron spin magnetization or sublattice magnetization in the case of an antiferromagnet, is the thermal average of S_z, the z component of the electron spin operator $\vec{S}$, and H_{eff} is an effective magnetic field. Recoilless radiation studies have also been made on dilute magnetic materials, for example by Wertheim and Remeika[5] on very dilute solutions of Fe$_2$O$_3$ in Al$_2$O$_3$. For zero applied magnetic field, Wertheim and Remeika observed a resolved hfs spectrum in which the lines of the multiplet, as above, showed widths close to $\hbar/\tau_N$ and where the line spacings were well described by $A\vec{I}\cdot\vec{S}$ plus a small crystal-field term. Measurements have not been reported, but it may be expected that if this magnetically dilute material were placed in a strong magnetic field ($g\beta H \gg A$),