critical field H_{c2}, extrapolated from our measurements, of the order of 25-30 kG.

Measurements on several samples of the dihydride and the dideuteride indicate clearly that these compounds are not superconducting, consistent with an earlier report.[4]

Most of the results presented here have been corroborated by work done at Los Alamos.[7] Their transition temperatures differ by 0.5° to 1° from ours for the higher hydrides and deuterides, probably due to differences in composition.

The apparent absence of an isotope effect is puzzling and deserves more careful study, but on present evidence one would infer that the high-frequency lattice modes simply do not participate in the superconducting interaction.

We wish to acknowledge the help of Professor A. A. Beck, Mr. Richard Novak, Mr. Rick Anderson, and the analytical group at the Materials Research Laboratory in characterizing the materials. We also thank B. Keith Moore for continued help and enthusiasm, and Professor M. B. Salamon for helpful discussions. Thanks also go to Mr. R. W. Sullivan and Dr. C. B. Magee of Denver Research Institute and Dr. D. T. Peterson at Ames Laboratory for sharing with us their knowledge of the metal hydrides.

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*Research supported in part by the Advanced Research Projects Agency under Grant No. HC 15-67-C-0221.

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EXPERIMENTAL DETERMINATION OF THE PAIR SUSCEPTIBILITY OF A SUPERCONDUCTOR*

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(Received 29 July 1970)

An excess tunneling current due to order-parameter fluctuations has been found in tin-tin oxide–lead junctions just above the transition temperature of tin. Details of the variation of the excess current with voltage, magnetic field, and temperature are in agreement with a calculation by Scalapino in which the excess-current voltage characteristic is a direct measure of the frequency– and wave-number–dependent pair susceptibility characteristic of the superconducting transition. Estimates of the pair relaxation frequency in tin based on the data are 50% greater than theoretical predictions.

In a second-order phase transition, the coupling of the order parameter to an external field may be used to determine the susceptibility associated with the onset of the ordered phase. The susceptibility in turn is a quantity possessing clear theoretical significance which may be compared directly with the results of calculations of the fluctuations associated with the transition. In a recent Letter Scalapino[1] showed that the relevant susceptibility for the superconducting phase transition, the pair susceptibility, could be determined in a simple dc tunneling experiment. Ferrell[2] originally suggested that the pair susceptibility could be obtained by measuring the frequency-dependent conductivity of a Josephson junction. In the experiment proposed by Scalapino, the pair susceptibility of a metal just above its transition temperature is obtained from measurements of an excess current in the dc I-V characteristic of a tunneling junction in which one side of the junction is the metal of interest, near its transition temperature, while the other side is a superconductor well below its transition temperature. In this Letter we report measurements on tin–tin oxide–lead junctions which exhibit an excess current whose behavior is consistent in detail with Scalapino's calculation. The data indicate that dc tunneling measurements are a direct probe of the frequency– and wave-number–dependent pair susceptibility of a superconductor. Earlier studies of electrical conductivity,[3,4] magnetic susceptibility,[5] and quasiparticle tunneling[6] involve convolutions of the pair susceptibility and are thus indirect.

In the determination of the pair susceptibility of a superconductor by dc electron tunneling, the order parameter or pair field of the higher transition-temperature superconductor provides the necessary field to probe the fluctuating order parameter of the second metal. The central feature of the theory is the prediction that an excess pair-tunneling current due to fluctuations flows between a superconductor below its transition temperature and one above its transition temperature. This current is possible despite the fact that the average value of the order parameter is zero in the metal which is above T_c. It is a consequence of the instantaneous value of the order parameter in the normal metal. The predicted current is proportional to the imaginary part of the frequency- and wave-number-dependent complex pair susceptibility of the normal metal, where the frequency is related to the dc bias voltage V across the junction through the Josephson relation and the wave number is determined by a small magnetic field applied parallel to the junction, through a simple phase condition which will be given later. Ferrell,[2] Kulik,[7] and Tsuzuki[8] have each treated aspects of the pair-tunneling current due to fluctuations. Ferrell[2] calculated the conductivity associated with it in the limit of zero voltage. Experiments in qualitative agreement with his calculations have been reported by several groups.[9,10]

Using the connection between the fluctuation pair current and the susceptibility, and employing a mean-field[11] form for the susceptibility, Scalapino[1] obtained an expression for the pair current which can be written as

$$\frac{I_1(V,H)}{I_N(V)} = \frac{\ln^2|4T_c'/T_c|}{\ln(4\Delta'/\Delta)}\,\frac{E_1}{U\epsilon^2}\left|[1+\xi^2(T)q^2]^2+\left(\frac{\omega}{\Gamma_0}\right)^2\right|^{-1}. \quad (1)$$

This equation is normalized to the current which would flow at a bias voltage V if both metals were normal. Primed quantities refer to the superconducting side of the junction and unprimed to the normal. The equation is valid when $\Delta' > \Delta$ and in the semiclassical approximation[1] which holds when

$$(2eH/\hbar c)d^2 \ll 1. \quad (2)$$

In the above equations Δ and Δ' are energy gap parameters, T_c and T_c' are the transition temperatures, and $\epsilon = (T-T_c)/T_c$. E_1 is the low-temperature Josephson coupling strength and U is the condensation energy of a volume Ad of the unprimed side. This quantity is given by $\frac{1}{2}N(0)\Delta^2 Ad$ where $N(0)$ is the single-spin density of states, A is the area of the junction normal to the direction of current flow, and d is the thickness of the unprimed film. The wave vector q and the frequency are given by $q = (2e/\hbar c)H(\lambda' + d/2)$ and $\omega = 2eV/\hbar$, respectively. In these relations λ' is a penetration depth and H is a magnetic field applied parallel to the junction. The quantity Γ_0 is the pair relaxation frequency,

$$\Gamma_0 = (8/\pi)(k_B T_c/\hbar)\epsilon, \quad (3)$$

and the coherence length $\xi(T)$ is

$$\xi(T) = 0.74\xi_0\epsilon^{-1/2} \text{ [clean limit, } l \gg \xi_0\text{]}, \quad (4a)$$

$$= 0.85(\xi_0 l)^{1/2}\epsilon^{-1/2} \text{ [dirty limit, } l \ll \xi_0\text{]}. \quad (4b)$$

The quantity ξ_0 is the BCS coherence length.

Here we report a comparison of the magnetic-field and temperature dependence of the I-V characteristics of two junctions, at temperatures above and in the vicinity of the transition temperature of tin, with calculations based on Eq. (1). Measurements of the resistive transition of the tin film, the temperature and magnetic-field dependence of the maximum zero-voltage current, and the I-V characteristics of the junction below the transition temperature of tin were carried out for the purpose of characterizing the junctions. In these measurements careful attention was paid to rf and magnetic shielding and temperature control. The details of the apparatus are identical to those presented in an earlier publication.[12]

In any study of crossed film oxide junctions in the vicinity of a superconducting transition there are certain experimental difficulties. Deposited tin films possess edges which are under strain and are granular. Edges have a higher transition temperature than the center of a film and produce an upward broadening of the resistive transition. When these edges are incorporated in a Josephson junction a confusing high-temperature tail in the zero-voltage Josephson current is observed. To avoid this difficulty we have excluded the edges in our experiment by using evaporated insulating masking. A second complication is the possible presence of small metallic bridges across the oxide layer in junctions exhibiting almost ideal I-V characteristics. Measurements on structures of this type may exhibit supercurrents above T_c which look like the pair tunneling current. Matisoo[13] has shown that when small bridges are present the low-temperature I-V characteristic possesses zero-magnetic-field steps. We have excluded those junctions possessing zero-field steps. A third difficulty is the possible confusion of an I-V characteristic exhibiting a fluctuation-rounded[12,14] dc Josephson current with the characteristic of a junction exhibiting an excess current due to fluctuations. A distinction between the two regimes may be made by a careful study of the magnetic-field dependences of the I-V characteristics in the vicinity of T_c. Below T_c, in the fluctuation-rounded regime the I-V characteristic is periodic in the field in the usual way.[15] Above T_c the pair current due to fluctuations is a monotonic function of applied field according to Eq. (1). This qualitative difference can be used to establish T_c for the junction. The results are in reasonable agreement with extrapolations of the low-temperature zero-voltage current-temperature curve and with the values of T_c obtained from analyses of the properties of the excess current above T_c. Measurements of the resistive transition of the tin film in a junction are not independent of film edges and are thus considerably broadened (10-20 mK). However, temperatures corresponding to the onset of resistance were consistent to within a few millikelvins, with values of T_c obtained using various other methods which excluded the edges. The excess tunneling current was observed at temperatures well into the range in which the tin films were resistive. A fourth difficulty is the possibility of a distortion of the I-V characteristic because of the finite resistance of the tin films.[16] Junction resistances were always substantially larger than film resistances. Consequently this correction was always insignificant.

In analyzing the data we obtained the excess current-voltage characteristic by subtracting the quasiparticle current from the total current-voltage characteristic. Quasiparticle currents were estimated using a linear extrapolation from voltages at which the excess current was negligible. In Fig. 1(a) we display typical excess current-voltage characteristics at several temperatures. In Fig. 1(b) a typical curve is compared with the results of calculations of the excess current based on Eq. (1) where parameters have been adjusted to bring experiment and theory into agreement at the peak current. For voltages greater than the voltage at the peak current the experimental curve falls more rapidly with increasing voltage than is predicted by Eq. (1).

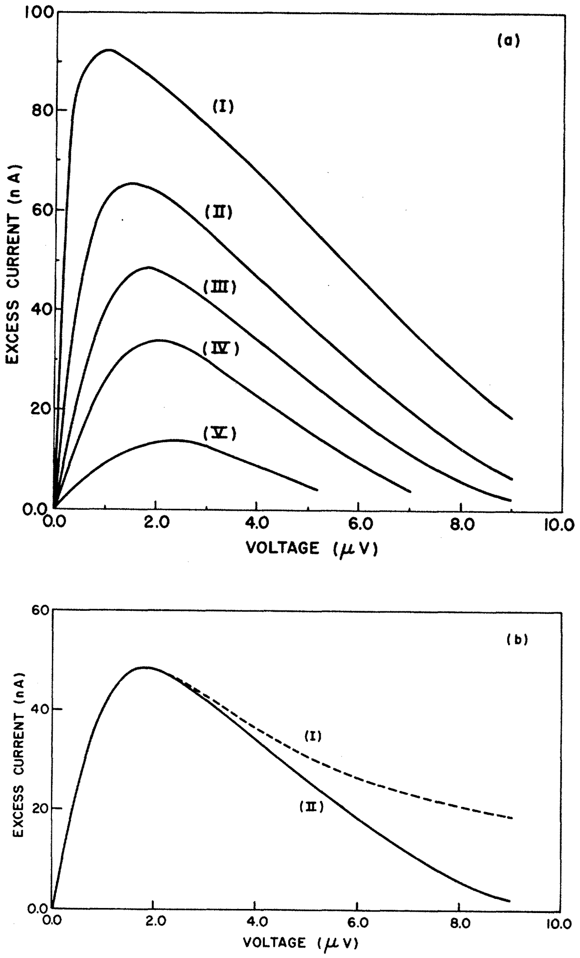

FIG. 1. (a) Excess current-voltage characteristic of junction No. 1 at several temperatures. Curves I, II, III, IV, and V correspond to $\epsilon = 1.48\times10^{-3}$, 1.97×10^{-3}, 2.45×10^{-3}, 2.94×10^{-3}, and 3.91×10^{-3}, respectively. In obtaining these curves the quasiparticle current was subtracted from the full tunneling current assuming a fixed resistance of 70.5 Ω. The corresponding resistance for junction No. 2 (not shown) was 11.4 Ω. (b) Excess current-voltage characteristic of junction No. 1 ($\epsilon = 2.45\times10^{-3}$). The dashed curve is calculated from Eq. (1) with parameters obtained by fitting to the peak current I_P and peak voltage V_P.

The peak of the excess current in zero magnetic field occurs when $\omega/\Gamma_0 = 1$. Consequently the peak voltage V_P is proportional to the pair relaxation rate and a plot of it as a function of ϵ is a direct measure of the temperature dependence of the relaxation rate. This is shown in Fig. 2(a). The pair relaxation rate appears to be a linear function of ϵ, but increases more rapidly with ϵ than theory predicts. In Fig. 2(b) we show a plot exhibiting the temperature dependence of the peak current. Figure 2(c) exhibits the tempera-

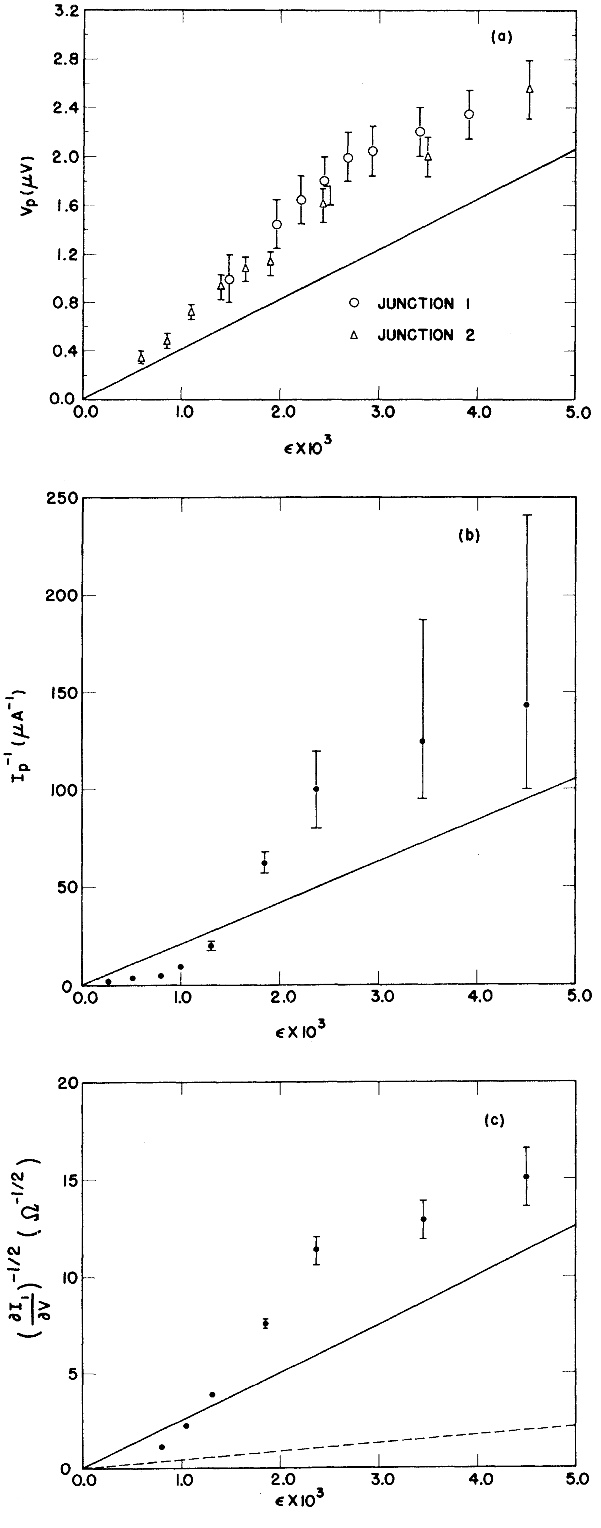

FIG. 2. (a) V_P vs ϵ for the two junctions. The solid line is computed using Eq. (2) and the transition temperature of junction No. 1 which was 3.720°K. The transition temperature of junction No. 2 was 3.886°K. The pair relaxation frequency determined from the data is approximately 1.5 times the theoretical value. (b) I_P^{-1} vs ϵ for junction No. 2. The solid line is computed from Eq. (1). The junction area A, film thickness d, normal resistance R_N, maximum Josephson current at $T=0$, and transition temperature were 1.035×10^{-4} cm^2, 1.5×10^{-5} cm, 2.1 Ω, 3.4×10^{-4} A, and 3.886°K. The corresponding quantities for junction No. 1 (not shown) are 3.1×10^{-4} cm^2, 1.5×10^{-7} cm, 5 Ω, 1.7×10^{-4} A, and 3.72°K. Standard values for lead and tin were used for other parameters. (c) $(dI_1/dV)^{-1/}$ vs ϵ evaluated at zero bias. The solid curve is computed from Eq. (1). The dashed curve is estimated using Eq. (1) of Ref. 10 and is based on the work of Ref. 2.

ture dependence of the fluctuation conductivity in the zero-voltage limit. The agreement between experiment and theory is seen to be semiquantitative. Discrepancies may be expected at low ϵ where mean-field theory may be inadequate.

The voltage V_P corresponding to the maximum of Eq. (1) in a nonzero magnetic field is a measure of the finite-q pair relaxation frequency:

$$V_P=(\hbar/2e)\Gamma_0[1+(2e/\hbar)^2(\lambda'+\tfrac{1}{2}d)^2\xi^2(T)H^2]. \qquad (5)$$

A plot of peak voltage against H^2 which can be used to test Eq. (5) is shown in Fig. 3. Additional results which are not shown indicate that the initial slope of the curve in Fig. 3 is dependent on temperature. The apparent saturation of the variation of V_P with H^2 is not understood.

In conclusion, we believe that we have measured the pair susceptibility of a superconductor as there is overall agreement between experiment and theory. I-V characteristics exhibit an

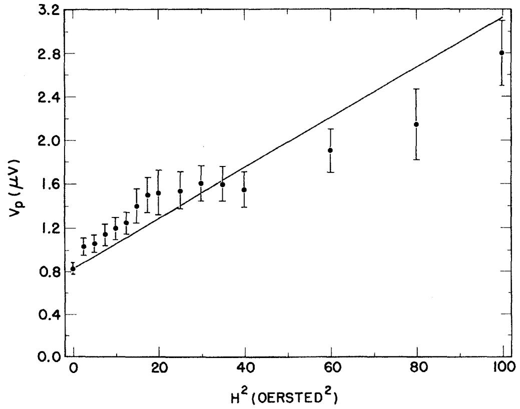

FIG. 3. V_P vs H^2 for junction No. 2. The solid line is a slope calculated from Eq. (3) with the coherence length computed in the clean limit; $\xi_0=2300$ Å, $\lambda'=390$ Å, and $d=1500$ Å, $\epsilon=1.055\times10^{-3}$. We have also used the experimental value of the pair relaxation frequency as determined from the slope in Fig. 2(a). More detailed experiments (not shown) indicate that the initial slope is temperature dependent.

excess current which has the resonant behavior of the pair-fluctuation current. As precautions have been taken to minimize the possibility of structural defects, the quantitative discrepancies between experiment and theory are an indication that corrections to the mean-field susceptibility are needed.

The authors would like to thank Professor D. J. Scalapino for his continued interest and helpful suggestions. They would also like to thank J. C. Solinsky for technical assistance.

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*Work supported in part by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-1569.

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PARAMAGNETIC SUSCEPTIBILITY OF A 2p UNPAIRED ELECTRON IN A CRYSTALLINE FIELD

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(Received 22 June 1970)

Paramagnetic susceptibility of the cubic crystal $O_2^+(As^VF_6)^-$ between 4.2 and 300°K reveals a complete quenching of the orbital moment of the $2p_{\mathrm{I}}^4 2p_{\mathrm{II}}^3$ configuration of the O_2^+ molecular cation. No ordering of the O_2^+ molecular cations has been detected in the range of measured temperature because of the large interatomic distance O_2^+-O_2^+ of 4.00 Å.

The molecular cation O_2^+ is obtained by ionizing the molecule O_2 subtracting one unpaired outer electron from its 2p shell and leaving O_2^+ with only one unpaired antibonding π level. The O_2^+ is thus isoelectronic with the molecule NO which also has only one unpaired electron compared with the two unpaired electrons of O_2 free gas. Hence, O_2^+ and NO are both in the π state. The χ of the NO free-gas molecule has been calculated by Van Vleck[1] and found to be

$$\chi = \frac{N\beta^2}{3kT} \frac{4\exp(-x) + (4/x)[1-\exp(1-x)]}{1+\exp(-x)}, \qquad (1)$$

where $x = \Delta/kT$. Taking the interval between $^2\pi_{3/2}$ and $^2\pi_{1/2}$ to be $\Delta = 124\ \mathrm{cm}^{-1}$, a good agreement can be found between the theoretical and experimental χ. Relation (1) predicts that $\chi \to 0$ when $T \to 0$ and n_{eff} is asymptotic at $2\mu_{\mathrm{B}}$. The cubic crystal $O_2^+(As^VF_6)^-$ can be considered as a case where the free-gas molecule of NO is inserted in a crystalline field, and will allow a comparison of the strength of the crystalline field Dq with that of the spin-orbit coupling λ. The only magnetic measurements performed on O_2^+ ion crystals are those[2,3] on its isomorphous $O_2^+(Pt^VF_6)^-$ and $NO^+(Pt^VF_6)^-$ between 80 and 300°K. The molecular cation NO^+ is diamagnetic because it has lost its unpaired electron. By subtracting χ of $NO^+(Pt^VF_6)^-$ from that of $O_2^+(Pt^VF_6)$ it was[3] possible to separate χ of O_2^+ from that of Pt^V and this was found[3] to confirm the χ of the free-gas NO as given by relation (1). The slightly lower χ of O_2^+ was interpreted[3] as stemming from a larger splitting of the two $^2\pi$ molecular orbital states as compared with that of the free NO gas. The Pt^V in the $NO^+(Pt^VF_6)^-$ crystal is in a low spin state with $S = \frac{1}{2}$, rather than the high spin value of $S = \frac{5}{2}$.