Tunneling study of technetium

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In an effort to find the energy gap and to estimate the strength of the coupling in technetium, a study has been made of Tc/Ta-I-Pb tunnel junctions with technetium interlayers of various thicknesses. The effect of a technetium layer on the parameters of the Tc is eliminated by extrapolating Δ_0, the energy gap at $T = 0$, and the ratio $2\Delta_0/kT_{cr}$ to a zero thickness of the normal Ta layer. The first experimental result for technetium has been obtained: $\Delta_0 = 1.49 \pm 0.03$ MeV. The ratio $2\Delta_0/kT_{cr} = 4.1 \pm 0.1$ is typical of strong-coupling superconductors. The value found for $2\Delta_0/kT_{cr}$ is compared with an estimate from the Geilikman-Kresin formula. That formula gives a good description of the parameters of strong-coupling superconductors, but it works poorly in the case of technetium, presumably because it contains a strong and selective electron-phonon interaction.

The tunneling of electrons is recognized as a source of information on both the energy gap and the electron-phonon interaction function. In the present study we have used this method to learn about technetium, which is a transition metal with an hcp structure and which has attracted attention because of a high critical temperature ($T_{cr} = 7.8$ K for bulk technetium). We have also studied some features of the phonon dispersion curves.

The only information which has been available on the energy gap Δ has consisted of estimates based on magnetic measurements.[1] From these measurements it has been concluded that a weak electron-phonon coupling occurs in this material. However, the presence of pronounced anomalies on the phonon dispersion curves,[2] which have been attributed to a selective electron-phonon interaction,[3,4] cast doubt on the magnetic estimates, as does the high value of the critical temperature. The ratio $\beta = 2\Delta_0/kT_{cr}$, where Δ_0 is the size of the energy gap at $T = 0$, and k is the Boltzmann constant, is known to be a measure of the strength of the electron-phonon coupling. This ratio ranges from 3.5 (the weak-coupling limit) to $\beta \lesssim 4.5$ for substances with an extremely strong electron-phonon interaction. Tunneling measurements of the energy gap may accordingly cast light on this situation.

The possibility of tunneling experiments rests on the quality of the tunnel barrier, which is usually formed by oxidizing the test sample. In those cases in which the material of interest does not form a well-insulating layer (and technetium does not form insulating oxides at all[5]), a thin film of some other metal, whose oxide will serve as a tunnel barrier, is deposited on it *in situ*. An incompletely oxidized film of a normal metal forms an S/N-I-M structure, whose study is the subject of proximity-electron-tunneling spectroscopy.[6] This method has recently been used primarily to study transition metals and alloys.[7,8] An appropriate material for the barrier layer is chosen for each specific case. The reason is that systems exhibiting a proximity effect always present a problem of interdiffusion, with the result that the boundary becomes blurred; if the diffusion rate is high, the entire tunnel junction is degraded. We have observed this situation in Tc/Al sandwiches, where the interdiffusion of the layers was significantly greater than in V/Al sandwiches (for example). As the coating for the Tc we studied Zr and Ta in addition to Al. The best results were achieved with the tantalum coating.

In a study of S/N-I-M structures, it is necessary to consider how the N layer will affect the parameters of the superconductor. To resolve this question requires knowledge of several parameters of the S and N metals, e.g., their Fermi velocities $v_{FS,FN}$, the electron state densities at the Fermi level, $N(0)_{S,N}$ and the layer thicknesses $d_{S,N}$ (Ref. 6). For layers with a thickness of 10–20 Å we can at best find a rough estimate of v_F and $N(0)$. It is thus more promising to use the following procedure experimentally: We study several tunnel junctions, with normal interlayers of various thicknesses and we find the parameters of the superconductor by extrapolating to a zero thickness of the normal layer.

In the present experiments we studied Tc/Ta-I-Pb junctions with deposited tantalum layers ranging in thickness d_{Ta} from 15 to 50 Å (specifically, 15, 20, 30, and 50 Å). The thickness of the technetium film was $d_{Tc} = 500$ Å. The Tc/Ta sandwiches were fabricated in an ultrahigh-vacuum ion-sputtering apparatus (the purity of the initial technetium was 99%, and that of the Ta 99.96%). The Ta was oxidized in air for 30–40 min; the resistances of the junctions ranged from a few ohms to hundreds of ohms.

Figure 1 shows current voltage characteristics and the first derivative of a typical Tc/Ta-I-Pb tunnel junction at $T = 1.6$ K. The quality of the junctions is seen to be quite high; in the better junctions, the conductivity at a zero bias voltage is 10^{-3} of the conductivity in the normal state. At high voltages we can clearly see the phonon structure of lead (the peaks in the second derivatives d^2I/dV^2 at energies of 4.5 and 8.5 meV, measured from the edge of the gap, and structural features produced by multiphonon processes). The entire structure disappears when a magnetic field $H = 1$

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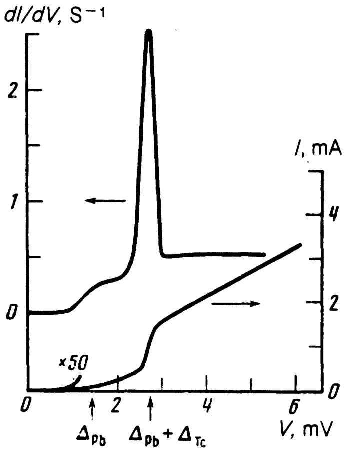

FIG. 1. Current voltage characteristic and first derivative (dI/dV) of a Tc/Ta-I-Pb tunnel junction at $T = 1.6$ K and $d_{Ta} = 20$ Å. The resistance of the junction in the normal state is $R_N = 2\ \Omega$.

kOe is imposed. We observe no structural features due to Tc or Ta phonons; we will discuss the reasons for this result below.

Figure 2 shows Δ_0, $2\Delta_0/kT_{cr}$, and T_{cr} of Tc/Ta sandwiches versus the thickness of the tantalum layer. Most of the measurements were carried out at a temperature $T = 4.2$ cr ($T/T_{cr} \lesssim 0.5$), and the values of the corresponding quantities at a zero temperature were calculated from Mühlschlegel's table.[9] The critical temperature was taken to be the temperature corresponding to the middle of the resistive transition. The value of T_{cr} determined from the appearance

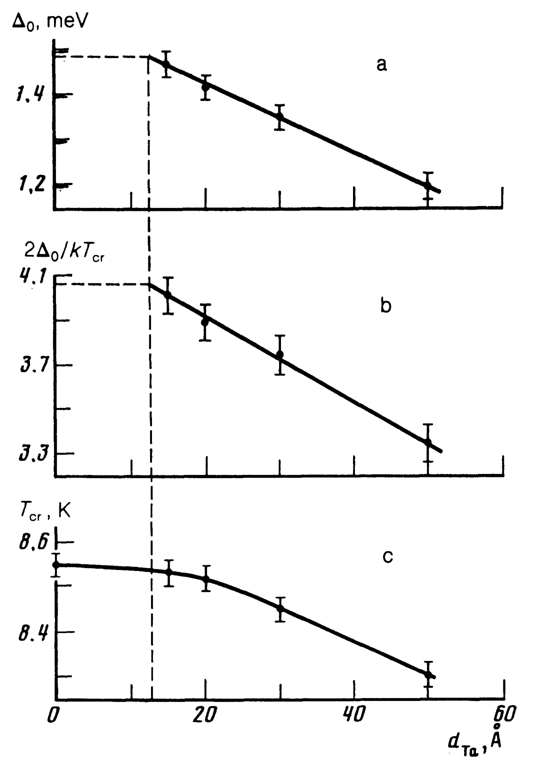

FIG. 2. a—The energy gap Δ_0 at $T = 0$; b—the ratio $\beta = 2\Delta_0/kT_{cr}$; c—the critical temperature T_{cr}—all for Tc/Ta sandwiches, plotted against the thickness of the tantalum film. The vertical dashed line is an estimate of the thickness of the oxidized layer of tantalum.

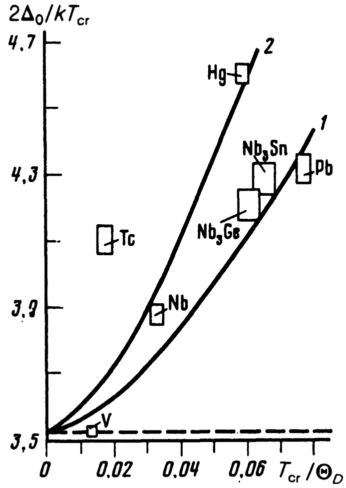

FIG. 3. $\beta = 2\Delta_0/kT_{cr}$ versus the ratio of T_{cr} to the Debye temperature Θ_D for various superconductors. The results on Tc are from the present study; the other results are taken from Ref. 15. Dashed line—weak-coupling BCS limit; 1,2—curves calculated from expression (1) for $\omega_0 = \omega_D/2$ and $\omega_0 = \omega_D/3$, respectively.

of superconducting tunneling structural features on the dI/dV curves agrees with the "resistive" value, but the error in the determination by this method is significantly larger (0.3 K in contrast with 0.08 K).

It can be seen from the plot of Tc versus d_{Ta} (Fig. 2c) that at thicknesses $\sim$10–15 Å the Ta layer has a negligible effect (in the Tc film, $T_{cr} = 8.55$ K). We can thus estimate the thickness of the oxide layer on the Ta to be 10–15 Å. An extrapolation of Δ_0 and β to this value yields $\Delta_0 = 1.49 \pm 0.03$ meV and $2\Delta_0/kT_{cr} = 4.10 \pm 0.1$ for pure technetium. We wish to stress that these are "lower-bound" estimates of these parameters, since there is probably a thin damaged layer of technetium with the properties of a normal level at the Tc/Ta interface. This damaged layer would have formed as a result of ion sputtering of Ta. Further evidence for this conclusion comes from the behavior of the first derivative, dI/dV, which differs from the BCS curve for an S_1-I-S_2 tunnel contact at $V \gtrsim \Delta_{Tc} + \Delta_{Pb}$ (Fig. 1). The appearance of leakage currents at $V \sim \Delta_{Pb}$ suggests that there are regions of the Tc film in which superconductivity is suppressed. Tunnel junctions for all the tantalum thicknesses, including $d_{Ta} = 15$ Å (in which case essentially all of the deposited film is oxidized), exhibit a first derivative with similar behavior. It is this damaged layer with the properties of a normal metal which explains the absence of phonon structural features of Tc in the tunnel junctions studied.

Values $\beta \gtrsim 4$ have been observed for only a few superconductors. Among them are certain compounds with the $A\,15$ structure[8,10] and certain chevrel phases,[11] while among the elements only Hg (Ref. 12) and Pb (Ref. 13) fall in this category.

According to the Geilikman-Kresin theory,[14] β is related to the ratio T_{cr}/ω_0 by

$$\beta = \frac{2\Delta_0}{kT_{cr}} = 3.53\left[1 + 5.3\left(\frac{T_{cr}}{\omega_0}\right)^2 \ln\frac{\omega_0}{T_{cr}}\right], \qquad (1)$$

where ω_0 is some characteristic phonon frequency. The value found experimentally for β for all strong-coupling superconductors agrees well with expression (1), if ω_0 is taken to be the frequency of the low-energy peak in the electron-phonon interaction; this situation corresponds to $\omega_D/3 < \omega_0 < \omega_D/2$, where ω_D is the Debye frequency (Fig. 3). In order to find the experimental value $\beta = 4.1$ for Tc we would need to set $\omega_0 = 6$ meV in (1). Experimental studies of the dispersion curves,[2] of the phonon state density, and of the microcontact function of the electron-phonon interaction[3] in technetium do not reveal such low-energy structural features.

The reason for this pronounced discrepancy between our results and expression (1) may be a selective electron-phonon interaction in technetium; such a selectivity has been called upon to explain experimental results.[3] The Éliashberg equations, from which expression (1) was derived, are the result of taking an average over momenta in the Gor'kov equations. The Éliashberg equations give a good description of isotropic and slightly anisotropic superconductors, but in the case of technetium they lead to significant errors.

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