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## Anomalous Band Gap in Superconducting Nb<sub>3</sub>Sn

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It is well accepted by now that tunneling experiments yield direct information about the energy band structure of superconductors.<sup>1-3</sup> In the present work tunneling experiments were employed to measure the energy gap of Nb<sub>a</sub>Sn and to obtain information about the density of states function.

The samples were prepared from Nb<sub>3</sub>Sn strips, vapor-deposited on ceramics.<sup>4</sup> After mechanical and chemical polishing the strip was oxidized for several hours at room temperature. Two metallic strips (usually lead or indium) were evaporated across the Nb&Sn strip to make up two tunnel junctions. Four contacts were soldered to every junction to provide current and voltage leads. The current-voltage  $(I-V)$  characteristics and  $dI/dV$  vs V were measured with a dc method using a variable constant-current source.

Figure 1 shows two typical  $I-V$  curves for Nb<sub>a</sub>Sn-Pb junctions at 1.7°K. The one for  $H = 0$ corresponds to the lead being superconducting while the curve for  $H > H_c(Pb)$  corresponds to normal lead. The essentially zero current at the origin for the superconductor —superconductor junction eliminates the possibility of shorts across the oxide layer. (In junctions where such a short was present it always showed up as superconducting and could be quenched by magnetic field or high current densities). Figure 2 shows conductance values as a function of the applied voltage for two NbsSn tunnel junctions (one with lead and one with indium, both in the normal state) at 1.7°K. The curve in the figure was calculated assuming a constant tunneling probability $2.5.6$ and using the BCS' density of states with a value

<sup>i</sup> I. Giaver, Phys. Rev. Letters 5, 147, <sup>464</sup> (1960).

- <sup>3</sup> I. Giaver and K. Megerle, Phys. Rev. 122, 1101 (1961). <sup>4</sup> G. W. Cullen (to be published).
- <sup>5</sup> J. Bardeen, Phys. Rev. Letters 6, 57 (1961); 9, 147 (1962). <sup>6</sup> M. H. Cohen, L. M. Palicov, and J.C. Phillips, Phys. Rev.
- Letters S, 816 (1962). <sup>7</sup> J.Bardeen, L. N. Cooper, and J.R. Schrieffer, Phys. Rev. 108, 1175 (1957).

 $\epsilon = 0.95$  meV for the (half) band gap of Nb<sub>a</sub>Sn. The data for the junctions were taken with applied magnetic fields larger than  $H_c(P_b)$  and  $H_c(\text{In})$ , respectively. In Fig. 3 a similar plot is shown for  $T = 4.2$ °K. Here a magnetic field was applied to the lead junction only, as this temperature is above  $T_c(\text{In})$ . The theoretical curves in Fig. 3 correspond to  $\epsilon = 0.95$  and 0.75 meV.

As can be seen from Figs. 2 and 3, the experimental data follow a similar shape to the theoretical curves, however, there are significant departures which are discussed later. Assuming, for the moment, that the tunneling proceeds according to the simple theory, one can obtain the value of the band gap by a fit of the experimental data to a theoretical curve. As the measured<sup>8</sup> transition temperatures of the dif-



FIG. 1. Typical  $I-V$  curves for an Nb<sub>3</sub>Sn tunnel junction with superconducting  $(H = 0)$  and normal  $(H > H<sub>c</sub>)$  lead at  $1.7^{\circ}$ K.

ferent samples were around 17.5'K, the band gap of the Nb<sub>3</sub>Sn at  $0^{\circ}K$ ,  $2\epsilon_0$ , should be very close to its value at 1.7°K. Taking this last value, we obtain  $2\epsilon_0 \approx 1.3 \; kT_c$ , which should be contrasted with the theoretical relation  $2\epsilon_0 = 3.5 kT_c$ . At 4.2°K it is more

<sup>2</sup> J. Nicol, S. Shapiro, and P. H. Smith, Phys. Rev. Letters 5, 461(1960).

J. Cooper (private communication).

difficult to determine the energy gap as the curves are less sharp and the fit between the experimental data and the theory is worse. However, the most pronounced characteristics of the junction conductance is the sharp rise in the vicinity of the band edge. This rise fits the theoretical curve corresponding to  $\epsilon = 0.75$  meV rather than that corresponding to 0.95 meV and indicates a reduction of about  $20\%$  in the value of the band gap. Such an appreciable temperature dependence in the range between 1.7° and  $4.2^{\circ}$ K is much larger than predicted by the theory.<sup>7</sup>

If we examine Figs. 2 and 3 in detail, we see that at small voltages the experimental data lie much higher than the theoretical curves. The discrepancy between the experimental and theoretical conductances cannot be attributed to shorts in the oxide layer, as pointed out already, and is quite reproducible from junction to junction. It points consistently toward the possibility of the existence of states inside the conventional band gap of Nb<sub>3</sub>S<sub>n</sub>, at least in the region near the surface. This observation is further supported by the absence of a negative resistance region when the other side of the junction



FIG. 2. Conductance values relative to the normal metalnormal metal conductance for two tunnel junctions at 1.7°K together with the theoretical curve.

(lead or indium) is superconductive. In the case of lead one may try to explain the data by the value of the band gap of Nb<sub>3</sub>Sn being very close to that of lead. In the case of indium with a band gap of  $2\epsilon_0 \approx 1$  MeV<sup>3</sup>, however, one would certainly expect a negative resistance region below 3.4°K (with no magnetic field applied). All that was detected experimentally, was a small hump in the  $I-V$  curves around 0.5 mV which disappeared upon applying a magnetic field larger than  $H_c(\text{In})$ . The curves with the magnetic field on, were very similar to the one with normal lead (Fig. 1,  $H > H<sub>c</sub>$ ). By the same



FIG. 3. Relative conductance values for two tunnel junctions at 4.2°K together with the theoretical curve for  $\epsilon = 0.75$  meV. For comparison, the curve for  $\epsilon = 0.95$  meV (dashed) is also shown.

token, a negative resistance region should have been detected for the junctions with lead, in the temperature range close to  $T_c(\text{Pb})$ . Again the results were negative.

No change in the tunneling characteristics of  $Nb<sub>3</sub>Sn$  due to applied magnetic fields up to 7500 G was observed. This is not surprising as the upper critical field of the samples were above 200 kG.<sup>10</sup> The absence of an effect at these fields agrees also with thermal conductivity measurements.<sup>11</sup> It is planned to extend the measurements to higher fields. In the region of small fields  $(\leq 500 \text{ G})$  there may be perhaps some field dependence which is obscurred by the more pronounced changes due to the lead or indium.

The small value of the band gap of Nb<sub>3</sub>Sn derived by tunneling measurements is indeed surprising. However, indication for a small band gap in Nb<sub>3</sub>Sn were obtained earlier in the tunneling data of Seidel

<sup>&</sup>lt;sup>9</sup> P. Townsend and J. Sutton, Proc. Phys. Soc. (London)

<sup>78, 309 (1961).&</sup>lt;br><sup>10</sup> W. H. Cherry (private communication).<br><sup>11</sup> G. D. Cody and R. W. Cohen, Rev. Mod. Phys. **36**, 121

and Wicklund.<sup>12</sup> In view of the fact that the therma conductivity" does yield the theoretically expected value for the band gap, one is lead to the conclusion

 $12$  T. Seidel and A. W. Wicklund, Proceedings of the Eighth International Conference on Low Temperature Physics, London, 1962 (Butterworths Scientific Publications, London, to be published).

## Discussion 33

GINsBERG: Dr. Adkins mentioned that the symmetry considerations of which he is speaking would vitiate the interpretation of <sup>a</sup> certain experiment —he didn <sup>t</sup> mention which this was. I believe he was referring to the experiment which I did a couple of years ago to determine the lifetime of the quasi-particles in superconducting Pb. At that time a negative result was interpreted as indicating an upper limit for the quasi-particle lifetime but as Dr. Adkins remarked the negative effect is explained by the symmetry considerations between electrons and holes. The conclusions drawn in that paper are probably unfounded. This difhculty was first pointed out to me about a year ago by Prof. Bardeen.

RORSCHACH: Question to Kleinman, Taylor, and Burstein: In the theory of contacts between semiconductors with an insulating barrier it is important to take into account the structure of the insulating barrier to get good quantitative agreement with experiment. One must use the correct nonpropagating solutions. Is it expected that these kinds of solution should also be used to get good agreement in superconducting contacts or is it sufhcient just to consider the barrier as a pure barrier with no structure whatsoever&

L. KLEINMAN, University of Pennsylvania: All the work that has been done has assumed that the barrier has no structure. Of course we have computed *I* in units of  $I_0$  so the detailed structure of the barrier should cancel out. One thing that you might think would come in is the phonons in the barrier which could cause transitions. This is true but the barrier is 20 or 30 A thick and the region over which the phonons can cause tunneling in each superconductor is 170 A and maybe even bigger if the electron phonon matrix element of Rothwarf and Cohen is wrong as Dr. Wada has pointed out to me. He believes it is too big by a factor of

that the apparent small band gap is associated with surface properties. This will be discussed in more detail in a forthcoming paper.

## ACKNOWLEDGMENT

I wish to thank Dr. G. D. Cody for his valuable advice and encouragement in carrying out this work.

8. If it is really smaller by a factor of 8 that means  $L$  is larger by a factor of 8, i.e., phonons anywhere in either superconductor can cause transitions and we have a ratio of effective thicknesses in the superconductor to oxide of about 2500/25 so the oxide is negligible.

RowELL: In connection with the multiparticle tunneling, Taylor and Burstein commented that you could see some structure back to about  $2\Delta/4$ . If you take a characteristic and do a double differentiation on it, then you can see structure back to about  $2\Delta/12$  which frightens me off this considerably.

E. R. PIKE, Royal Radar Establishment: I wonder if I could ask a question to Dr. Kleinman regarding the use of these new basis functions for multiparticle tunneling. I wonder if he has applied them to any consideration of the same kind as those used by Prange to justify the use of the transfer term in the Hamiltonian. They are rather interesting basis functions very similar to WBK-type functions which are more or less exact solutions right through the two systems, rather than single particle states in each side.

KLEINMAN: Well these are essentially the functions that Prange used first. He then said they didn't give any tunneling and explained the reason is because they already include the tunneling. He then went on to use the Bardeen type function. If you are not interested in the normal tunneling and your only interest is the phonon assisted tunneling, this should give the correct answer. It may give errors to the order of  $T<sup>4</sup>$  because we're identifying the transfer of "left hand" electrons to the right hand side with the transfer of an electron and the "left hand electron" already has some amplitude on the right hand side. I expect this is wrong to  $T<sup>4</sup>$  but is correct to  $T<sup>2</sup>$ .