Energy Gap of V₃Si

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A new technique for measuring energy gaps, based on the proximity effect, was used to study V_4Si . A 12 000-Å V_4Si film was deposited on sapphire at 1200°C by getter-sputtering followed immediately by the deposition at 300°K of an 80-Å aluminum film. After oxidation of the aluminum, and delineation of the junction area with SiO, a lead film was deposited at 77°K. V_4Si induces by proximity effect a gap ($\simeq 2 \text{ mV}$) in the aluminum film which is in good agreement with McMillan's theory. Furthermore, one can detect the V_4Si gap itself as a dip in the relative conductance curve. In the ten samples measured, the value of the V_4Si energy gap at 1°K was very close to $\Delta = 2.80 \text{ mV}$, which correspond to $2\Delta(0^\circ K) = 3.8kT_c$. This result confirms the expectation that V_3Si is a strong-coupling superconductor. The validity of such a technique is further shown by the fact that the lead phonon peaks are displaced by an energy corresponding to Δ_{A1} + $\Delta_{Pb}\simeq 3 \text{ mV}$. Finally, the induced gap in the aluminum remains almost unchanged by a 50-kG magnetic field and disappears only at 17°K (the resistive transition temperature of the V_3Si film).

COME tunneling experiments on such β -W supercon- \mathbf{J} ductors as $Nb_3Sn^{1,2}$ and V_3Si^2 have been reported previously. The reported values of the energy gaps were as low as $1.3kT_c^{-1}$ but ranged from $1.8kT_c$ to $4.2kT_c$ in the latest study.² Furthermore, the experiments were only conducted at low temperatures, usually with both superconductors comprising the tunnel junction in the superconducting state. De Gennes and Saint-James³ raised the possibility that the difficulty in such experiments may be caused by surface damage (off-stoichiometric surface, gas contamination, etc.) which in turn will reduce or even eliminate the energy gap in a surface layer approximately 20 Å thick. As tunneling takes place over distances comparable with the coherence length ξ_0 , which is in most superconductors much larger than 20 Å, surface damage is usually not a problem. On the other hand, it may become a problem in the β -W superconductors where the coherence distance is extremely short, of the order of 20 Å.

We would like to report here a new tunneling technique based on the proximity effect which obviates the above-mentioned difficulty. This technique will be particularly useful for short-coherence-length superconductors as well as for superconductors which do not readily form a continuous thin oxide. This technique was used for V₃Si and led to the following results. For the first time a proximity effect was observed between a high-transition-temperature β -W superconductor such as V₃Si and Al. The gap induced in the Al is in good agreement with the McMillan theory ^{4,5} The energy gap of V₃Si at 1°K as measured on 10 independently prepared tunnel junctions ranged from Δ =2.60 mV to Δ =2.9 mV with most of the values falling close to Δ =2.80 mV. This latter value corresponds to 2 Δ (0°K)

¹Y. Goldstein, Rev. Mod. Phys. 36, 213 (1964).

= $3.8kT_e$. Although some of the prepared junctions had either a short or too high a resistance, the V₃Si gap, was always close to 2.80 mV whenever it could be measured; the low values of the V₃Si gap previously reported in the literature² were never observed. The V₃Si energy gap remains almost unchanged by a 50-kG magnetic held and disappears only at 16.8°K (the resistive transition temperature of V₃Si).

The basis for this new tunneling technique originates in previous tunneling experiments on superimposed films.^{4,5} In these experiments⁴⁻⁶ a gap was induced in Al, Pt, Cd, and Ag films through a proximity effect with lead films. Besides the structure in the I-V curve at the induced gap voltage, it was pointed out that the Pb density of states is reflected in the tunneling characteristics and that a bump always occurred in the I-V curve at a voltage corresponding to $\Delta_{Pb} + \Delta_{A1}$ (where Δ_{A1} is the energy gap of the measuring Al film), thus allowing the Pb gap to be measured as well. Consequently, in order to measure the gap in some superconductor, one uses this superconductor to induce a gap by proximity effect in some other material; and as long as this material is kept thin, it will be possible to measure the energy gap of the superconductor as the maximum in the dV/dI-Vcurve (as was learned from our experience with Pb). The choice for the overlay material will obviously be Al because of its ease of oxidation.

In the present experiments, a 12 000-Å V₃Si film was deposited at 1200°C on a sapphire substrate using the getter-sputtering technique. Immediately following and without breaking the vacuum, an 80-Å Al film was deposited by getter-sputtering at room temperature. The Al film was then oxidized as previously described.⁵ The junction area was then delineated by the use of a mask and the evaporation of a 1000-Å SiO film. Finally, a 0.03-cm wide strip of lead 900 Å thick was deposited by getter-sputtering at 77°K. The tunnel junction was then transferred under liquid nitrogen onto a holder with four pressure contacts and then measured. The junction area

² H. J. Levinstein and J. E. Kunzler, Phys. Letters **20**, 581 (1966); Bull. Am. Phys. Soc. **11**, 88 (1966). ³ P. G. de Gennes and D. Saint-James, Phys. Letters **4**, 151

^{*} P. G. de Gennes and D. Saint-James, Phys. Letters 4, 151 (1963).

⁴ J. M. Rowell and W. L. McMillan, Physics (to be published); Bull. Am. Phys. Soc. 11, 190 (1966).

⁶ J. J. Hauser, Physics 2, 247 (1966); Bull. Am. Phys. Soc. 11, 208 (1966).

⁶ J. M. Rowell and W. L. McMillan, Phys. Rev. Letters 16, 453 (1966).

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was approximately 1.5×10^{-3} cm² and the junction resistance a few hundred ohms at 4.2° K. The dV/dI-versus-V curves were obtained using a standard modulation technique.⁵

As the Al was deposited at room temperature, this raises the possibility of interdiffusion between Al and V₃Si. The best proof for the absence of such interdiffusion is the fact that a tunnel junction with a 30-Å Al film yielded exactly the same V₃Si energy gap values as one with 80 Å, although in the 30-Å case it is almost sure that most if not all the aluminum was oxidized. Furthermore, a tunnel junction with 30 Å of Al and with the Pb film replaced by an In film showed at 4.2°K on a derivative plot structure which can only be ascribed to the V₃Si phonon spectrum. Such phonon peaks would not come through the Al film if an appreciable amount of interdiffusion had taken place.

Figure 1 shows dV/dI-V and I-V curves for such a junction at 1.298°K. Below 1.6 mV the resistance of the junction increases very rapidly as a result of Pb energy gap. The minimum of the dV/dI-V curve at 3.4 mV represents the conductance peak of the Al displaced by the Pb energy gap. The flat maximum of the dV/dI-Vcurve at about 4.35 mV (shown enlarged by a factor of about 100 as the peak above the major derivative curve) reflects the gap in the density of states of V₃Si displaced again by the Pb energy gap. The reason why one expects to see structure at $V = \Delta_{V_3Si} + \Delta_{Pb}$ is due to the fact⁴⁻⁶ that the V₃Si density of states is reflected in the tunneling characteristics of the Al and the tunneling experiments measure the density of states at the Al-Al₂O₃ interface. Consequently, in the limit of very thin Al films the junction behaves almost as a V₃Si-insulator-Pb junction and the V₃Si gap will appear displaced by a value equal to the Pb gap. The corresponding structure in the dV/dI-V curve will be a maximum as dV/dI is inversely proportional to the density of states. If one takes $\Delta_{Pb} = 1.5 \text{ mV}$ (the average value observed in previous experiments⁵), one obtains $\Delta_{V_3Si} = 2.85 \text{ mV}$ and $\Delta_{A1} = 1.9$ mV. Taking into account the error in the determination of the maximum and the variation of this maximum from sample to sample, the value of $\Delta_{V_3S_1}$ can be taken to be 2.8 mV \pm 0.2 mV. It is also noteworthy to point out that the longitudinal Pb phonon peak as determined by the dV/dI-V curve occurs at 11.75 mV. As this peak is known to occur⁷ at $V - \Delta = 8.40 \text{ mV}$, this yields a value of Δ of 3.35 mV which agrees very well with $\Delta_{A1} + \Delta_{Pb}$. As V₃Si induces a gap in Al by proximity effect one can apply to it McMillan's theory^{4,5} which can be summarized by the following relation:

$$t = (\delta - \delta_0) [(1 + \delta)/(1 - \delta)]^{\frac{1}{2}}, \qquad (1)$$

where $\delta = \Delta_n / \Delta_{\mathbf{V}_3 Si}$, $\delta_0 = \Delta_n^{\circ} / \Delta_{\mathbf{V}_3 Si}$, and $t = \hbar \langle v_F \rangle p / 2d_n \Delta_{\mathbf{V}_3 Si}$; Δ_n is the induced gap in Al (1.9 mV), Δ_n° is the gap present in the Al in the absence of $\mathbf{V}_3 \mathrm{Si}$ (0.3 mV) and

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FIG. 1. dV/dI-V and I-V curves at 1.298°K. The voltage scale is 0.5 mV per large division; the dV/dI and I scales are arbitrary. The enlarged peak at $\Delta_{V3SI}+\Delta_{Pb}$ was obtained with a 20 times larger modulation signal (~40 μ V) and displayed with a dV/dIscale 5 times smaller.

p is the transition probability for an electron pair to cross the Al-V₃Si interface. As the Al film including the oxide is about 80 Å, $d_n \simeq 60$ Å, substituting these values in (1), one obtains $d_0 = \hbar \langle v_F \rangle p/2\Delta v_{3Si} \simeq 75$ Å which is in fair agreement with previous experiments.^{4,5} The characteristic length d_0 represents the coherence length of the Al measured at the energy of V₃Si. Its value of 75 Å is quite reasonable and can be obtained by substituting in the expression for d_0 : p=0.2, $\Delta v_{3Si}=2.8$ mV and $\langle v_F \rangle = v_F/3 = 10^8/3$ cm/sec.

The fact that the gap described above is truly the gap of V₃Si is further demonstrated in Fig. 2 which shows dV/dI-V and I-V curves taken at 4.2°K with a longitudinal field of 50 kG. This magnetic field is well above the critical field of the Pb film; and, consequently, the broad minimum of the dV/dI-V curve at about 2.75 mV must correspond to the smeared induced Al gap and the V₃Si energy gap. The value of the V₃Si energy gap is altered very little if any by the 50-kG magnetic field, which was to be expected from the very high critical field of this material.



FIG. 2. dV/dI-V and I-V curves at 4.2°K and a longitudinal magnetic field of 50 kG: The voltage scale is 0.5 mV per large division; the dV/dI and I scale are arbitrary.

 $^{^{7}\,\}rm W.$ L. McMillan and J. M. Rowell, Phys. Rev. Letters 14, 108 (1965).



FIG. 3. dV/dI-V curves as a function of temperature. The voltage scale is 0.5 mV per large division; the dV/dI scale is arbitrary. The enlarged peak at $\Delta_{V3SI} + \Delta_{Pb}$ was obtained at 4.2°K with a 20 times larger modulation signal (~40 μ V) and displayed with a dV/dI scale 5 times smaller.

Derivative curves as a function of temperature are shown in Fig. 3. A striking difference between the curve taken at 4.2°K for example and the one taken at 1.298°K in Fig. 1 is the additional minimum of the dV/dI-Vcurve at 0.65 mV. This minimum corresponds to Δ_{A1} $-\Delta_{Pb}$ and appears at 4.2°K as a result of the thermal excitations. The voltage difference between these two minima yields $\Delta_{Pb}=1.35$ mV and the sum of the voltages $\Delta_{A1}=2$ mV. Again this maximum is shown enlarged by a factor of about 100 in the upper portion of Fig. 3. Finally, the maximum of the dV/dI-V curve corresponds to $\Delta_{V_3Si} + \Delta_{Pb} = 4.25$ mV which results in Δ_{V_3Si} = 2.90 mV. The validity of the labeling of the minima and maxima of the curve is clearly demonstrated in Fig. 3 where the motion of the two minima with increasing temperature reveals the progressive closing of the Pb energy gap. The resulting dependence of Δ_{Pb} on temperature is very close to the one predicted by B.C.S. while, on the other hand, the value of Δ_{A1} remains unchanged up to 7.2°K. Although below 7.2°K the lowest minimum of dV/dI corresponds to $\Delta_{A1} + \Delta_{Pb}$, this is no longer true above 7.2°K. In the previous analysis Δ_{A1} was found to be equal to 2 mV and as can be seen in the curve of Fig. 3 taken at 7.2°K, this voltage corresponds approximately to the point where dV/dI has the same value as in the normal state (incidently, this is a conventional way to determine a gap when one of metals comprising the junction is normal). Consequently, at 7.2°K and above this temperature, the minimum in dV/dI no longer corresponds to Δ_{A1} because the tunneling characteristic now represents the density of states of the Al crossed by the large Fermi smearing of the Pb. Thus, when the Pb is normal, either by the application of a large magnetic field as above or by temperature, the exact value of the minimum is meaningless but its presence indicates the existence of superconductivity. Above 7.2°K only the V₃Si and thus the Al remain superconducting. The proof that the Al is superconducting lies in the fact mentioned above that the tunneling experiment measures the density of states at the Al-Al₂O₃ interface. As shown in Fig. 3, the gap disappears at 17°K which corresponds to the resistive transition of V₃Si. One will notice in Fig. 3 that as the temperature is raised from 7.2 to 17° K, the dV/dI-V curve is getting flatter, but the minimum remains fixed at approximately 2.75 mV. In any respect, Fig. 3 clearly demonstrates that the tunneling characteristics are truly a property of V_3Si as they only disappear at the T_c of V_3Si .

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