Selection Rule for Tunneling from Superconductors

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The selection rules imposed upon tunneling electrons by different sorts of barriers are discussed, using wave-matching arguments. It is shown that the commonly used velocity selection rule is not generally valid. This reopens the question of interpreting the energy-gap data obtained from tunneling for anisotropic superconductors.

I. INTRODUCTION

IT is well known that superconductor–insulator–normal-metal tunnel junctions show a peak in the conductance-voltage characteristic at a voltage bias corresponding to the superconducting energy gap. If a clean superconductor is used, multiple peaks are sometimes seen, and in monocrystalline specimens the peak energies may vary with the relative orientations of the crystal and the insulating barrier.[1] The reason for this is supposed to be the existence of a tunneling selection rule which restricts transmission to a set of electrons traveling in a special direction with respect to the barrier. The anisotropy of the conductance peaks is then naturally interpreted as due to anisotropy of the energy gap seen by the electrons on the corresponding region of the Fermi surface; the multiple peaks are interpreted as due to the presence of different energy gaps on different pieces of the Fermi surface, each of which can contribute to the barrier current at a given orientation.

It has been quite widely assumed that the selection rule is *group velocity in the metal normal to the barrier*,[1,2] but elementary calculations on simple models suggest that *k vector in the repeated-zone scheme of the metal normal to the barrier* is more likely. These rules are not identical even for nearly-free-electron metals or for spherical Fermi surfaces. Since it is essential that the selection rule should be properly understood before attempts are made to deduce gap anisotropy from tunnel characteristics, we have tried in this paper to find selection rules likely to operate in various junctions with realistic structures. We assume, following Cohen *et al.*,[3] that the selection rule is the same in the normal and superconducting states. We therefore discuss selection rules in the normal state in what follows, and our conclusions apply equally to superconductive and normal tunneling. Until more is known about the structure of barriers, the rule to be applied in any particular experiment must remain uncertain. One of our intentions is to provoke thought and experiment on the nature of tunnel junctions.

For any given model, the problem falls into two parts. We first ask which of the electronic states in the barrier at the Fermi energy decay least across it. For the barrier thicknesses actually used, this provides an extremely strong selection, and there is no need to consider the transmission factors at the insulator-metal interfaces in deciding which is the preferred group of electrons. Having identified the preferred group in the insulator, we then ask which electron states in the metal are coupled to it, and how strongly. We now follow this procedure for several models of the junction.

II. FREE-ELECTRON MODEL

The metal is treated as a free-electron gas, from which the electrons can escape by tunneling through a potential hill $V(z)$. In the barrier, the transverse wave number is a good quantum number, and we may take it to be real far from the edges of the film. In the WKB approximation, the wave function is

$$\psi(r)=A\lambda(z)^{-1/2}\exp\left(-j(k_1x+k_2y)-\int\lambda(z)dz\right), \quad (1)$$

where

$$(\hbar^2/2m)[k_1^2+k_2^2-\lambda^2(z)]=E-V(z).$$

At fixed energy E, ψ decays least across the film at the minimum value of $\lambda(z)$, that is, when $k_1=k_2=0$. In this model the preferred state has *zero transverse wave vector* in the barrier, and since transverse wave vector is conserved at the interface, this state will couple only to the state with *zero transverse wave vector in the metal.* This will be the state selected in tunneling.

III. IDEAL CRYSTAL LATTICES

A. Preferred States in the Insulator

In real junctions the barrier is a continuous oxide layer only a few atomic layers thick which is grown on the superconductor under study. It is quite possible that such an oxide layer will grow epitaxially and therefore

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[1] N. V. Zavaritskii, Zh. Eksperim. i Teor. Fiz. **45**, 1839 (1963); **48**, 837 (1965) [English transl.: Soviet Phys.—JETP **18**, 126 (1964); **21**, 557 (1965)].
[2] A. J. Bennett, Phys. Rev. **140**, A1902 (1965); **153**, 482 (1967). I. Dietrich, in *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962*, edited by R. O. Davies (Butterworth Scientific Publications, Ltd., London, 1963), p. 173. M. L. A. MacVicar and R. M. Rose, J. Appl. Phys. **39**, 1721 (1968).
[3] M. H. Cohen, L. M. Falicov, and J. C. Phillips, Phys. Rev. Letters **8**, 316 (1962).

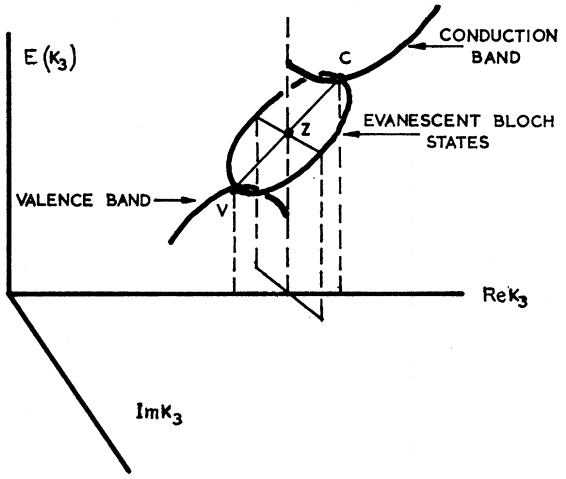

FIG. 1. $E(k_3)$ at fixed real values of k_1 and k_2 corresponding to line AA of Fig. 2.

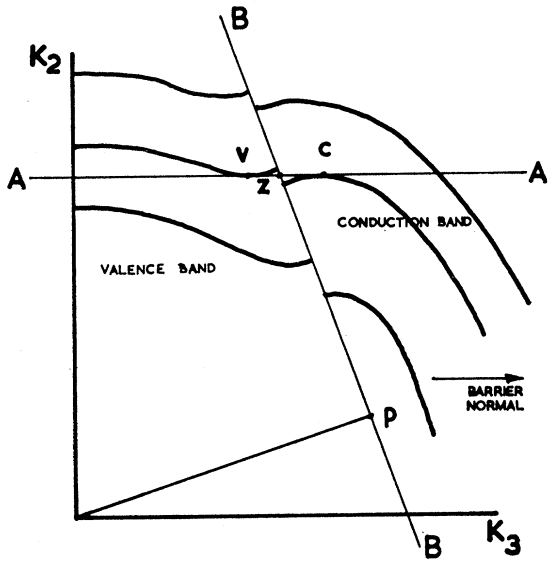

FIG. 2. Typical energy contours in real k space near a Brillouin-zone boundary BB which lies at an arbitrary angle to the barrier. The line AA corresponds to Fig. 1.

have a well-defined and uniform crystal structure.[4] Tunneling would then take place via the evanescent Bloch states lying within the insulator band gap. The transverse wave vector may still be taken as real, but k_3, the wave vector normal to the barrier, is now complex in general. Figures 1 and 2 illustrate a typical band structure for a fixed transverse wave vector, in the neighborhood of a single Brillouin-zone boundary lying at an arbitrary angle to the barrier. It is clear from the illustration that $\mathrm{Im}(k_3)$ is least (and tunneling strongest) when the Fermi level lies close to the bottom of the conduction band, or to the top of the valence band. To find the preferred state for tunneling at the Fermi level, we must now vary the transverse wave number (move line AA of Fig. 2). As we do so, C, the bottom of the conduction band, and V, the top of the valence band, may move up or down in energy in Fig. 1. We expect that the smallest value of $\mathrm{Im}(k_3)$ for electrons at the Fermi level will occur close to the point where one or other of the bands comes closest to the Fermi level, that is, close to the absolute minimum of the conduction band or the absolute maximum of the valence band. This will be the preferred state for tunneling. For instance, in Fig. 2 the absolute minimum of the conduction band lies at P and the preferred state at the Fermi level will have $\mathrm{Re}(k)$ close to P if the Fermi level lies near the top of the band gap.

This conclusion makes analysis of tunneling through a crystalline insulator a complicated matter. The position of P can only be determined if the insulator band structure is known. Moreover, P may be repeated several times in the Brillouin zone by crystal symmetry, giving several possible tunneling channels, all with different nonzero transverse wave vectors in general.

B. Wave Matching at an Ideal Interface

At a planar interface between two uniform media the transverse wave vector for incident waves is conserved. At an ideal interface between two lattices, general considerations of symmetry require that a state of wave vector $\mathbf{k}^m$ in the metal will, in general, couple to a state of wave vector $\mathbf{k}^i$ in the insulator whenever

$$\begin{aligned} k_1{}^m+g_1{}^m&=k_1{}^i+g_1{}^i,\\ k_2{}^m+g_2{}^m&=k_2{}^i+g_2{}^i, \end{aligned} \tag{2}$$

where $\mathbf{g}^m$ and $\mathbf{g}^i$ are *any* reciprocal-lattice vectors of the metal and insulator. This is equivalent to saying that any pair of states having the same transverse wave vector *in their respective repeated-zone schemes* may be coupled. This is illustrated in Fig. 3. It is clear, that if both lattices have arbitrary alignment with the barrier, the number of states in the metal which may, in principle, tunnel can be very large.

In order to decide which states are important in practice, we must note that there are two distinct

[4] There is very little evidence on the structure of oxide layers as thin as 10 Å. In slightly thicker layers the degree of order seems to differ markedly for different metals. For instance, the results of x-ray diffraction [see K. R. Lawless and A. T. Gwathmey, Acta Met. 4, 153 (1956)] and optical polarization [see F. W. Young, Jr., J. V. Cathcart, and A. T. Gwathmey, *ibid.* 4, 145 (1956)] experiments on the oxidation of monocrystalline copper at room temperature in 5 Torr of oxygen show that oxide layers of thickness 80–100 Å consist almost entirely of a highly oriented epitaxial layer of Cu_2O. The degree of orientation increases strongly with decreasing oxide thickness and decreasing pressure. For niobium, on the other hand, the thinner oxide layers are thought to contain mixtures of several different oxides [see E. A. Gulbransen and K. F. Andrew, J. Metals **188**, 586 (1950)], and electron diffraction studies [see J. Harvey and P. H. G. Draper, J. Inst. Metals **92**, 136 (1963)] of oxide layers show that layers of thickness 30 Å are always completely amorphous. There is an abrupt change to crystalline growth at a considerably greater temperature-dependent thickness, which corresponds to several thousand minutes of growth at atmospheric pressure and room temperature.

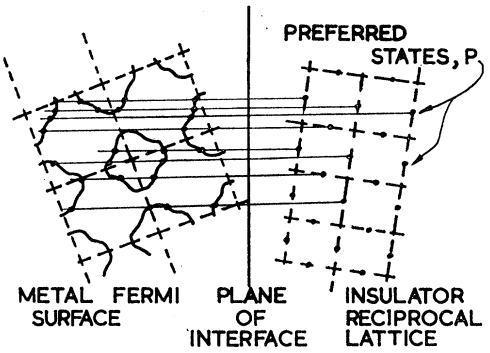

FIG. 3. To illustrate the large number of points on the metal Fermi surface which have the same transverse wave vector as the preferred tunneling states in a crystalline insulator, and may, in principle, be coupled to them.

physical reasons for the appearance of the reciprocal-lattice vectors in (2). The first is that the Bloch waves of vector $\mathbf{k}$ are mixtures of plane waves with vectors $\mathbf{k}+\mathbf{g}$. Secondly, even at its most regular, the interface between two lattices must consist of a series of microscopic facets corresponding to the intersection of crystal planes with the interface. This will have a corresponding nonuniform scattering potential which contains periodicities corresponding to the components parallel to the interface of the reciprocal-lattice vectors of both lattices; these periodicities can mix waves of different transverse wave vector at the interface. In practice, only a few plane waves are important in the Bloch functions, and the strongest periodicities of the interface potential are likely to be those created by the intersection of close-packed planes with the interface, corresponding to low-order reciprocal-lattice vectors. Both these effects tend to limit the coupling to parts of the extended-zone schemes near the origins. Moreover, if the insulator consists of an epitaxial growth, this means that its translational symmetry parallel to the interface has been distorted so as to become partly commensurate with that of the metal. This will reduce the number of pairings in the extended-zone scheme for each preferred state in the insulator, and may also reduce the number of preferred states by lowering the symmetry of the insulator lattice. But when all these effects have been taken into account, it remains true that tunneling may be possible from more than one region of the metal's Fermi surface at once, and that the regions will not be identifiable by any simple universal rule.

IV. AMORPHOUS INSULATOR

It is also possible that the very thin oxide layers used in tunnel junctions are essentially amorphous.[4] We treat an amorphous insulator as a forbidden energy region containing a high density of scattering centers arranged at random. Any plane wave incident on this region will be rapidly converted into spherical waves of the form $e^{-\lambda r}/r$, centered on the scattering centers, and memory of the original wave vector will be lost. The tunneling probability then depends on energy only. Any selection by wave vector therefore occurs before the first scatterings. Once again, the initial plane wave will be selected which decays most slowly normal to the barrier. Appreciable selection will only occur if the decay length $1/\lambda$ is shorter than the distance between scattering events, which is not out of the question.

If we treat the amorphous insulator as isotropic, the preferred state will have zero transverse wave vector in the insulator, as in the potential hill model, but this state will couple to any state in the metal having *zero transverse wave vector in its repeated-zone scheme*, at an ideal interface. This situation therefore has a comparatively straightforward selection rule.

It has been suggested[5] that for nearly-free-electron metals this rule is equivalent in practice to the commonly assumed rule of zero transverse group velocity, except close to Brillouin-zone boundaries. The idea is that it is only appropriate to consider states in the full *repeated*-zone scheme when there is appreciable mixing in the corresponding Bloch states. In a nearly-free-electron metal the only strong plane waves are those on the unremapped Fermi sphere (*extended*-zone scheme), and states with zero transverse wave vector in this scheme also have zero transverse group velocity, since the two are parallel (except close to the zone boundaries). This argument ignores the mixing of transverse wave vectors which can take place at the interface itself. The potential at a metal-insulator interface must be regarded as strong even for a nearly-free-electron metal, and one must allow for the mixing of states through the low-order reciprocal-lattice vectors which correspond to the main periodicities of the interface. In nearly-free-electron metals, then, we expect that tunneling will be strongest from states in the repeated-zone scheme which lie *near to* the unremapped Fermi sphere, but will not be restricted to states actually lying on it. The velocity selection rule will then not be generally adequate.

V. CRYSTALLINE INSULATOR CONTAINING DEFECTS

Defects may act as scattering centers. They can also create localized bound states. If these lie at or near the Fermi energy, tunneling may occur in jumps via these bound states. In both these cases, one expects selection according to the decay normal to the barrier of the initial plane wave, as in the case of the amorphous insulator, but now the medium in which the plane wave is propagating is the anisotropic lattice, and the complex selection rule discussed in Sec. III B will apply.

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[5] J. E. Dowman, Ph.D. thesis, Cambridge University, 1968 (unpublished).

VI. IMPLICATIONS OF EXPERIMENTAL REPRODUCIBILITY

A. Insulator Orientation

Tunneling data on single crystals can show reasonable reproducibility from specimen to specimen and rapid systematic variation with orientation.[1] Evidently, for some methods of manufacture at least, the selection rule is consistent and sensitive to small changes of orientation. This seems to imply one of three possibilities for the insulator: (i) The orientation of the insulator is systematically related to that of the substrate; this would be the case for epitaxial growth. (ii) The selection rule is independent of the orientation of the insulator; this would be the case if there were a single dominant preferred state at the origin of the insulator's repeated zone. (iii) The insulator is virtually amorphous.

B. Interface Irregularities

Small irregularities of the interface will simply weaken the matching by transverse wave vector and blur the selection rule. Strong blurring would lead to diffuse surface scattering which is commonly observed at oxidized surfaces in other types of experiment.[6] However, in tunneling, the fact that sharp peaks in the conductance characteristic are sometimes observed to change their voltage rapidly with orientation shows that blurring is unimportant for some junctions at least.

A further important possibility is that in growing, or subsequently oxidizing, a metal film, *macroscopic* facets may develop on the interface.[7] In this case, tunneling would proceed through several distinct crystal faces at once. However, the crystallographic nature of the facets which are sampled may not vary unless the mean orientation of the junction is changed by more than a few degrees, and within this range the *same* group of electrons should be selected from the Fermi surface of the metal. For a superconductor coupled to a barrier of this type, constant energy gaps should be observed in various small ranges of orientation, and we feel that this possible explanation should not be overlooked when considering the constant energy gaps which have been reported for tin.[1]

C. Abrupt Disappearance of Gaps

Energy-gap peaks in the superconducting conductance characteristic sometimes disappear abruptly at certain orientations.[1] This is usually assumed to derive from anisotropy in the metal. It could, however, be due to a change in the nature of facets at the interface. It could also be due to a change in the epitaxial film structure.

VII. CONCLUSIONS

All the selection rules which we have deduced have been restrictions on transverse wave vector and not on the group velocity. Two possibilities (randomly oriented crystalline oxide, and strong blurring) are excluded by the fact that, in some systems at least, systematic and reproducible results are obtained. Of the remaining cases considered, two (selection independent of insulator orientation, and amorphous insulator) lead to the simple rule *transverse wave vector zero in the repeated-zone scheme.* But in two other cases (epitaxial insulator, macroscopic faceting) the preferred transverse wave vector need not be zero, and will vary with orientation. These conclusions apply equally to superconducting- and normal-metal tunneling.

We feel that deduction of superconducting gap anisotropy from tunneling data on single crystals should only be accepted if the observations have been repeated with a variety of barrier structures and methods of preparation. If the results are consistent, a selection rule of zero transverse wave vector in the repeated-zone scheme becomes a plausible assumption, since it is rather unlikely that a number of such differently prepared junctions would consistently give any other rule.

ACKNOWLEDGMENTS

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[6] Observations of the anomalous skin effect and the size effect in the electrical resistance of small samples show that the surface scattering is diffuse, except for semimetals such as bismuth which have an unusually long electron wavelength. [See R. G. Chambers, Proc. Roy. Soc. (London) **A202**, 378 (1950); **A215**, 481 (1952).] Observations of magnetic surface levels in the same metals prepared in similar ways, however, have been explained by a mechanism which requires almost perfect specular reflection: See M. S. Khaikin, Zh. Eksperim. i Teor. Fiz. **39**, 212 (1960) [English transl.: Soviet Phys.—JETP **12**, 152 (1961)]; J. F. Koch and C. C. Kuo, Phys. Rev. **143**, 470 (1966); R. E. Prange and T. W. Nee, *ibid.* **168**, 779 (1968). Even in the absence of blurring, the periodicities of the ideal surface potential discussed in Sec. III B would be expected to introduce nonspecular reflections, unless the surface happened to be a low-order crystal plane. In many of the observations of magnetic surface levels, the surface was a low-order plane. In other cases it might conceivably have been so by accident through the development of macroscopic facets in preparing the surface. A careful study of the anisotropy of the linewidth of magnetic surface levels coupled with anomalous-skin-effect measurements on the same samples could be of considerable interest.

[7] A. J. W. Moore, *Seminar on Metal Surfaces: Structure, Energetics, Kinetics, American Society for Metals* (American Society for Metals, Cleveland, Ohio, 1962), p. 155.