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Selection Rules for Tunneling into Single-Crystal Superconductors*

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The first conclusive evidence for a tunneling selection rule for single-crystal superconductors is presented. Using tunneling data for the (001) plane of gallium obtained in two different laboratories, we show that the *zero transverse k-vector rule* of Dowman, MacVicar, and Waldram is superior to the usual group-velocity rule. The dominant tunnel direction in *real* space is the normal to the tunnel barrier and does not appear to be affected by barrier orientation or structure.

The problems involved in interpreting tunneling data obtained from single-crystal specimens were summarized recently by Dowman, MacVicar, and Waldram[1] (DMW). There are two questions involved: (1) What tunneling direction dominates across the barrier? For many reasons pointed out in Ref. 1, the barriers produced on single-crystal substrates might have a highly ordered structure, giving rise to an anisotropic tunneling probability that is not a maximum perpendicular to the barrier surface, as is usually assumed. (2) Which electrons are associated with the tunneling process? The usual rule has been to choose electrons with a group velocity perpendicular to the tunneling barrier, but application of this rule has met with little success.[2,3]

In this Letter, we will examine these problems using our data on gallium[4] and similar data of Yoshihiro and Sasaki[5] (YS).

Effect of barrier structure.—Figure 1(a) shows the reduced energy gap, $2\Delta(0)/kT_c$, as a function of crystal orientation in the (001) plane of gallium obtained by our group and by YS. (Note that the gallium phase we are dealing with, the one stable near room temperatures and atmospheric pressure, is orthorhombic.) In several directions, indicated by the dashed lines, we have identified multiple energy gaps. This identification is *not* made by YS, probably because of a difference in data analysis. A complete analysis of these data will appear in a full length article.

Aside from the difference of interpretation of multiple gaps, our experiments and those of YS were essentially the same with one exception: The tunneling barriers used in our work were untouched naturally grown oxides while YS bombarded the single-crystal surfaces with ions, to reduce barrier impedance, before the tunneling probe was applied.[6] As a result, their barriers were undoubtedly disordered while the barriers used in our work had some chance to develop an ordered structure. (However, both barriers were probably somewhat disordered.) As one can see from Fig. 1(a), there is good agreement between the two sets of measurements, with only slightly more scatter in the data obtained by YS. Some scatter in their data might be expected since the bombardment process would also produce shorts and damage in the barrier region and this might give rise to slightly imperfect tunneling characteristics.

The fact that data on two types of barriers yield the same energy-gap data is an indication that tunneling occurs in the direction perpendicular to the barrier for all orientations measured. This point can be checked further by assuming perpendicular tunneling and comparing features of the energy-gap curve with the features of the

Fermi surface.

Fermi-surface selection rules.—It has been commonly assumed that the tunneling electrons come from pieces of the Fermi surface with a group velocity perpendicular to the barrier.[2] DMW point out that a WKB calculation shows that, aside from problems associated with barrier structure examined above, the tunneling probability is maximum for electrons with k *vectors entirely normal* to the tunneling barrier (zero transverse wave vector, $k_T = 0$). These two selection rules are at times the same, but for a realistic Fermi surface the group velocity cannot always be in the normal k-vector direction. To determine which of these rules is valid it is necessary to compare *all* the features of the energy-gap curve with the Fermi surface using each rule. Only the valid selection rule can be expected to explain *all* of the features of the data.

(1) Group-velocity rule.—Since the electron group velocity is given by the gradient of the electron energy in k space, the group velocity is perpendicular to the Fermi surface in k space. Using this criterion, one must identify all groups of electrons where the normal to the Fermi surface is parallel to the tunneling direction. This is usually done by calculating the Fermi-surface contours in the reduced-zone scheme (RZS). Typical contours for gallium have been calculated by Wood,[7] using the augmented plane-wave method. There appears to be no correlation between the reduced-zone-scheme contours, given in Ref. 7, and the energy-gap features, such as multiple energy gaps, observed in our data. A similar lack of agreement with the group-velocity rule has been found in previous investigations in other materials.[2,3]

(2) $k_T = 0$ rule.—In addition to establishing somewhat firmer physical reasoning for using the $k_T = 0$ rule, DMW also argued that this rule must be applied in the extended-zone scheme (EZS) rather than in the RZS in order to preserve the true vector direction. Calculations of the EZS are tedious and have seldom been performed since Harrison developed a geometrical method for computing the RZS directly.[8] As a result, we have calculated an approximate extended-zone model for the gallium (001) plane

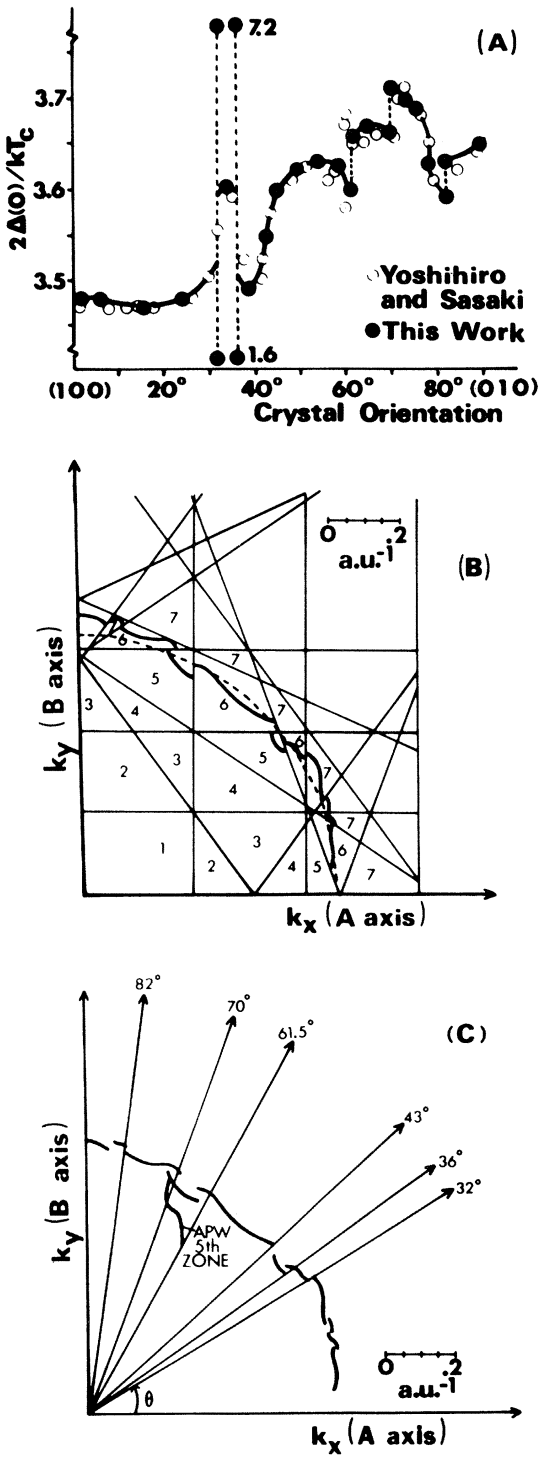

FIG. 1. (a) Reduced energy gap, $2\Delta(0)/kT_c$, as a function of crystal orientation in the gallium (001) plane. (The crystal orientation is the direction perpendicular to the tunneling surface.) Open circles are data points from Ref. 5 and solid circles are data points for this work. (b) Extended-zone-scheme plot in the gallium $k_z = 0$ plane using the nearly-free-electron approximation (Brillouin zones are numbered). (c) Same extended-zone-scheme plot as in (b) with both the nearly-free-electron and Wood's augmented plane-wave calculations included in the fifth zone near 61.5°.

by drawing the Brillouin zones for this plane, drawing in a free-electron sphere with a radius of 1.17 a.u.$^{-1}$ that is suggested by Wood's calculations, and perturbing the free-electron sphere at the zone boundaries in the usual fashion; i.e., there is an energy gap at the zone boundary and the Fermi surface should be normal to the boundary. The results of this calculation are shown in Fig. 1(b). The position and the shapes of several pieces of the Fermi surface calculated in this fashion were compared with Wood's calculation by remapping some of Wood's data back from the first zone. Since the remapping process in a plane is not totally unique, we could not obtain the complete EZS in this fashion. We did find that the Brillouin-zone crossings were reasonably well predicted by our nearly-free-electron (NFE) calculation, although the Fermi-surface shape *within* a zone is probably quite different from the artist's conception in Fig. 1(b).

If we now examine the Brillouin-zone diagram in Fig. 1(b) as a function of the angle from the k_x axis (which corresponds to the A-axis direction in real space), we find that there are several places where the k vector crosses zone boundaries and may even have an overlap with two zones at a boundary. In order of increasing angle these are at 17° (several possibilities), 32°, 36°, 43°, 64°, 70°, 82°, and 84°. We have data available at all points except near 17° and 84°. We have observed multiple energy gaps very near 32°, 36°, 64°, 70°, and 82° at which directions there is an overlap of two zones in Fig. 1(b). At 43° we observed a sharp change in the magnitude of gap and at this direction there is a change in the contribution to the Fermi surface but *no* overlap of the zones in Fig. 1(b). The multiple gap measured at 61.5° is undoubtedly associated with an overlap of the fifth and sixth zones occurring at 64° in the NFE calculation. The slight disagreement in the angle at which this multiple gap occurs is due to the approximation in the NFE model. A piece of the fifth zone, calculated by Wood, was remapped from the first zone and better agreement was found. Figure 1(c) shows the Fermi-surface diagram in the EZS with the lines marking the zone boundaries removed.

Discussion.—The $k_T = 0$ rule used with the EZS explains all of the features of the energy gap versus crystal orientation curve in the gallium (001) plane that we have observed, while the group-velocity rule is deficient. Multiple energy gaps occur at or near zone boundaries where a group of electrons from each zone may have a k vector perpendicular to the sample surface. The energy gap also changes as the dominant contribution of electrons changes from one zone to another. All of this analysis presumes that the dominant direction for tunneling in real space is that perpendicular to the sample surface. The good comparison of our data and those of YS, using different barriers, further establishes that barrier structure does not affect the tunneling direction in this case.

It would seem possible in principle to compare *quantitatively* the features of the curve of the gap versus orientation with the Fermi surface (such as the magnitudes of the gaps and the ratio of multiple-gap tunnel currents). However, such analyses are fruitless at the present time since the NFE model obviously does not yield enough information about the Fermi-surface shape within a zone.

We have looked at data for other materials to check the tunneling selection rule further but we find that data quite often have been obtained for randomly oriented single crystals and that there are insufficient data points lying in a single plane to make the comparison above. There is some possibility that the data obtained by Zavaritskii on tin[2] in the $\varphi \simeq 22°$ cone can be analyzed using the $k_T = 0$ rule, but the process will be tedious since this is a very asymmetric cone and the Brillouin zones will be hard to calculate. We have been informed that Rose and MacVicar will analyze their data on single-crystal niobium[10] in light of the above discussion.

We feel that the analysis presented above agrees well with the theory because we were fortunate enough to have chosen the highly symmetric (001) plane for the comparison. If the energy gap is related to the details of the Fermi surface, then we expect that the energy gap will have reflection symmetry about the (001) plane and hence effects due to anisotropy *off* the plane will be minimized, leading to a good comparison between theory and experiment when only two-dimensional arguments are used. It is also easier to calculate the EZS Fermi-surface model for a symmetric plane. Consequently, we would urge other workers to attempt to seed their single-crystal samples so that the energy gap is measured in one plane, preferably a plane of symmetry. If data are taken in an asymmetric plane (which, of course, will eventually be important for complete analysis of the selection rule), some care in interpretation may be necessary. Finally, we would urge theoreticians to perform

more exact calculations of the Fermi-surface properties in the EZS for those superconductors for which bulk tunneling data are available, i.e., gallium, tin, niobium, tantalum, rhenium, and lead.

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Bound Exciton Resonance in Raman Cross Sections in CdS

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We present the first direct and conclusive evidence of bound exciton resonance in phonon Raman scattering from solids. The observed enhancement in the 1LO scattering cross section at the I_1 bound exciton in CdS is a factor of ~30 for the sample with the highest impurity content. In contrast to 1LO, the 2LO scattering cross section shows no enhancement near bound excitons. An explanation of this behavior is suggested.

Various authors have invoked resonance with excitons bound to impurities (bound excitons) in a solid to explain their Raman scattering observations.[1-7] However, their arguments have been based on selection rules,[1,3,5] effects of momentum transfer,[4,6] or similar indirect evidence. By using a continuously tunable dye laser, we have obtained the first direct cross-section measurements which conclusively prove the importance of bound-exciton intermediate states in Raman scattering. We describe and discuss these results in this Letter.

Raman spectra were obtained by using a flash-lamp-pumped, pulsed dye laser.[8] Using the esculin dye dissolved in methanol, the dye laser could be continuously tuned from ~4600 to 4950 Å with a resolution of ~1 Å. With peak power ~1 kW and repetition rate ~10 pulses per sec (average power ~10 mW), a fairly good signal-to-noise ratio was obtained for the 1LO and 2LO Raman spectra. A double spectrometer and a boxcar integrator were used for analyzing and detecting the Raman spectra. High-optical-quality platelets (~50–100 μm thick) of CdS were used. CdS was chosen because its luminescence[9] and Raman spectra[10] are well known. All measurements were performed at 6°K to avoid thermal broadening. One of the problems encountered at this temperature and high laser peak power was the strong luminescence from CdS in the spectral region of interest. This was alleviated by making the laser spot at the sample relatively large (>1 mm diam) and using the geometry shown in Fig. 1(a). In spite of these, the spectra for dye-laser wavelengths shorter than 4865 Å could not be obtained because of strong luminescence.

We have studied three different samples. Sample 1, an I_1-rich sample, had a large number ($\sim 5\times10^{17}$ cm^{-3}) of impurities giving rise to strong I_1 and I_2 bound-exciton luminescence.[11] Sample 2 had strong I_2 but weak I_1 luminescence whereas sample 3 was "pure," having intermediate strength I_2 luminescence and no I_1 luminescence. Since the exact impurity densities were unknown, the strengths of I_1 and I_2 luminescence obtained with the 4765-Å line of the Ar^+ laser were used as a rough indication of relative densities.