Phonon Structure in Tunneling in $SrTiO_3$

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Structure has been observed at liquid-helium temperatures in tunneling-current—versus—voltage curves for contacts formed on heavily reduced strontium titanate ($SrTiO_3$). Such contacts, formed by soldering indium to a freshly polished $SrTiO_3$ crystal, behave as backward diodes. Both first- and second-derivative techniques have been used to show that the structure in the tunneling current for forward-biased (metal positive) contacts occurs at voltages corresponding to the energies of the two highest frequency $q=o$ longitudinal optical phonons of pure $SrTiO_3$, at twice these energies, and at the sum of these energies. The *semiconducting* $SrTiO_3$ used in these experiments had a *superconducting* transition temperature of about 0.25°K; however, no change in the I-V characteristics was observed when the $SrTiO_3$ became superconducting.

INTRODUCTION

STUDIES of the dependence of tunneling current on voltage in semiconductor tunnel junctions have revealed structure at energies corresponding to characteristic phonon energies and combinations of such energies in a number of materials.[1] Similar phonon structure as well as a wealth of other information has been obtained for superconductors in studies of superconductor-insulator-superconductor tunnel structures.[2] In this paper, tunneling experiments on semiconducting strontium titanate ($SrTiO_3$) are reported. The highly reduced crystals used underwent bulk superconducting transitions at very low temperatures[3] and the tunneling experiments were carried out both above and below the transition temperatures. Structure attributable to $SrTiO_3$ phonons[4] was observed in the V-I characteristic; however, the characteristics did not change on passing below the $SrTiO_3$ superconducting transition.

EXPERIMENTAL

The $SrTiO_3$ crystals[5] were degenerate n type. X-ray Laue photos showed that the [100] crystal direction was nearly normal to the surfaces used for all crystals. Thus current flow was always nearly normal to the (100) plane. Junctions were prepared by soldering with as little heat as possible small area contacts of indium, bismuth, or gallium directly onto a freshly polished and cleaned crystal surface.

The crystals were polished carefully by hand with half-micron Linde A and after rinsing in alcohol were washed in acetone just prior to forming the junctions. A given crystal was used over and over again, being polished and cleaned before each use. Typically, both top and bottom crystal surfaces were polished and cleaned and two large-area contacts were soldered onto the bottom surface. These served as Ohmic contacts. Several small contacts of about 0.5-sq-mm area were then formed on the top surface and the V-I curves were displayed on an oscilloscope or derivative curves were recorded using standard techniques. The resistance of the crystal was less than 0.1 Ω, that of the Ohmic contacts less than 1 Ω. The small area contacts varied in resistance from contact to contact from about 100 Ω to greater than 10 000 Ω.

The small-area contacts were always at least weakly rectifying. Some contacts were more strongly rectifying than others and in these the structure in the V-I curves was most pronounced. The rectification was invariably greater at low temperatures. The easy direction of current flow was with the bulk n-type $SrTiO_3$ positive and so the contacts behaved as backward diodes.

In Fig. 1 are shown several V-I curves, both at room temperature and at liquid-helium temperatures, for one of the best contacts, i.e., one of the most highly rectifying contacts and one in which the V-I structure was most pronounced. Similar structure was obtained for other contacts on the same crystal and on other crystals but generally less sharp than in Fig. 1. The crystal used here, labeled HR-24, had a room-temperature carrier concentration of about 7×10^{19} per cm^3. The structure in the forward direction in the V-I curves, Figs. 1(b) and 1(c), is shown more clearly in the recorder tracing of dV/dI versus V, Fig. 2, and in the

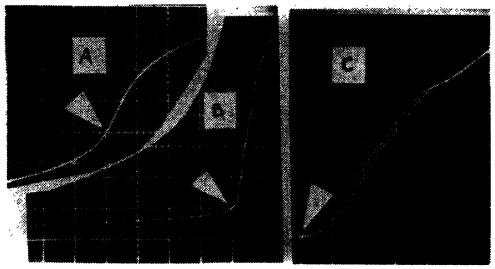


FIG. 1. $V-I$ curves for an In-$SrTiO_3$ contact: (a) room temperature, 50 mV/cm (vertical), 0.5 mA/cm (horizontal); (b) 2.3°K, 20 mV/cm (vertical), 0.02 mA/cm (horizontal); (c) 3.5°K, 20 mV/cm (vertical), 0.005 mA/cm (horizontal). In each case the origin is marked by an arrow.

[1] Cf., e.g., A. G. Chynoweth, R. A. Logan, and D. E. Thomas, Phys. Rev. **125**, 877 (1962).
[2] Cf., e.g., J. M. Rowell and L. Kopf, Phys. Rev. **137**, A907 (1965).
[3] J. F. Schooley, W. R. Hosler, and M. L. Cohen, Phys. Rev. Letters **12**, 474 (1964); J. F. Schooley, W. R. Hosler, E. Ambler, J. H. Becker, M. L. Cohen, and C. S. Koonce, *ibid.* **14**, 305 (1965).
[4] R. A. Cowley, Phys. Rev. **134**, A981 (1964).
[5] We are grateful to the National Bureau of Standards and to A. S. Barker, Jr. for the use of these crystals.

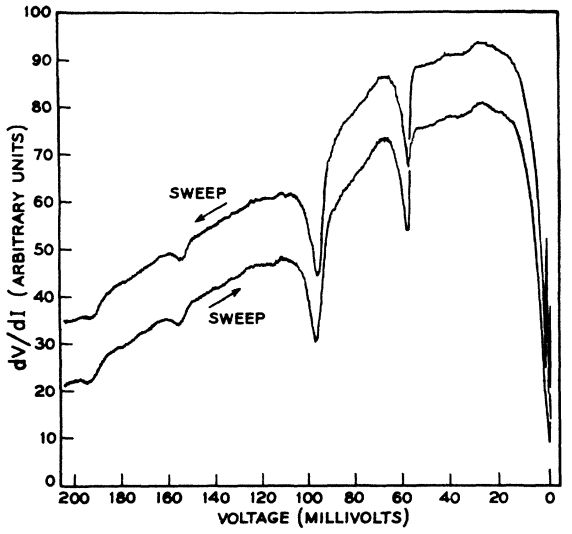


FIG. 2. Resistance (dV/dI)-versus-voltage curves in the forward direction for the In-$SrTiO_3$ contact of Fig. 1 at 1.5°K. The lower curve has been offset on the resistance axis for clarity.

d^2V/dI^2 versus V tracing, Fig. 3. In addition much more structure is revealed in the latter two figures.

RESULTS AND DISCUSSION

In order to interpret the structure in the V-I characteristics, note that the two most prominent dips (resistance minima) in Fig. 2 occur at 57 and at 97 mV, that moderately strong dips are located at 155 and 194 mV, and that a recognizable dip occurs at 115 mV. These numbers are reliable to ±1 mV. It is reasonable to identify these dips then as associated with two strong phonons at about 57 and 97 mV, their sum and their respective harmonics.

Infrared reflectivity studies on pure $SrTiO_3$ have yielded values of 58.5 and 100 mV for the two highest energy $q=0$ longitudinal optical (LO) modes,[6,7] values with which the present tunneling measurements are in excellent agreement. Note that the dispersion curves for $SrTiO_3$[4] are such that the phonon energies already deviate from their $q=0$ values by amounts on the order of millivolts at rather small q values. Further confirmation for the identification of the phonon dips as associated with $q=0$ phonons comes from the presence of the V-I structure at voltages corresponding to the sum and harmonic energies of these phonons. Similar harmonic structure involving $q=0$ phonons has been observed in several direct-gap polar semiconductors by Hall *et al.*,[8] while no such harmonic structure is expected or observed in indirect-gap semiconductors such as Ge or Si.[1]

It was anticipated that the semiconductor surface potential barrier would serve as a tunnel barrier and this was indeed the case since every contact made with a superconducting metal showed the superconducting energy gap of that metal below its transition temperature. Thus the structure near $V=0$ in Figs. 2 and 3 is due to the indium energy gap. The possibility that an insulating layer was present between the indium and the $SrTiO_3$ cannot be ruled out. However, from the ratio of forward to back resistance of typical contacts [e.g., from Fig. 1(b)] it can be established that the voltage drop across any such series insulating layer was certainly less than 2% of that across the entire contact. Thus any systematic error in phonon energy resulting from such an insulating layer is certainly less than 2%.

In a typical metal-semiconductor contact no phonon-assisted tunneling would be expected and indeed in the majority of contacts no strong structure was observed. In those contacts which did exhibit strong phonon structure a p-type inversion layer most likely formed at the $SrTiO_3$ surface thus creating in effect a p-n junction within the $SrTiO_3$, a situation in which phonons characteristic of the $SrTiO_3$ could participate in a tunneling process. The evidence for the existence of the inversion layer is the backward diode form of the V-I characteristics, the presence of the phonon structure, and, for bismuth contacts, the tendency for an Esaki-type negative-resistance region to occur as shown in Fig. 4. Thus all experimental evidence is consistent with a tunneling model despite calculations[9] implying that the space-charge layer at a metal-$SrTiO_3$ interface may be as wide as 1000 Å.

It should be noted that in a tunneling measurement of a phonon energy the phonon is emitted essentially in the p-n junction[10] and thus its energy is characteristic

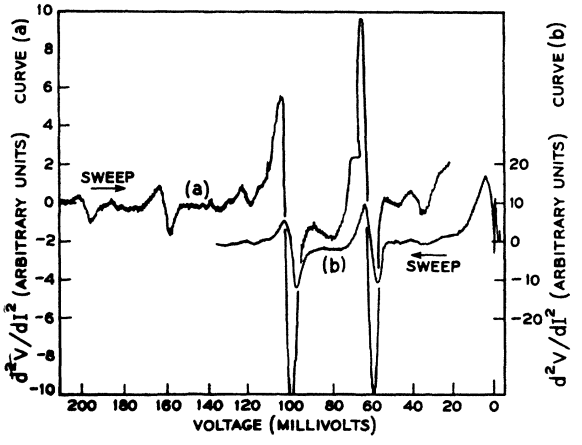


FIG. 3. Second derivative (d^2V/dI^2) versus voltage curves in the forward direction for the In-$SrTiO_3$ contact of Fig. 1 at 1.2°K. The gain for curve (a) was 5x that for curve (b).

[6] A. S. Barker, Jr. and M. Tinkham, Phys. Rev. **125**, 1527 (1962).
[7] A. S. Barker, Jr., Bull. Am. Phys. Soc. **10**, 369 (1965) and (to be published).
[8] R. N. Hall, J. H. Racette, and H. Ehrenreich, Phys. Rev. Letters **4**, 456 (1960).
[9] H. P. R. Frederikse, private communication.
[10] E. O. Kane, J. Appl. Phys. **32**, 83 (1961).

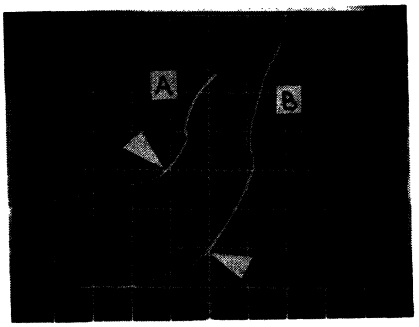


FIG. 4. $V-I$ curves for a Bi-$SrTiO_3$ contact at 4.1°K: (a) 50 mV/cm (vertical), 0.002 mA/cm (horizontal); (b) 20 mV/cm (vertical), 0.001 mA/cm (horizontal). In both cases the origin is marked by an arrow.

of pure or undoped material, provided the junction is wide enough so that uncertainty broadening is not a major factor, although an appreciable carrier concentration is present in the semiconductor bulk. Thus the present experiments yield pure $SrTiO_3$ phonon values even though infrared reflectivity measurements on semiconducting $SrTiO_3$ show a substantial change in phonon energy with carrier concentration,[7] particularly for the high-energy LO modes.

Kahn and Leyendecker[11] have made a calculation of an electron-energy-band structure for $SrTiO_3$. They find the valence-band maximum to be at the center of the Brillouin zone though the valence band is rather flat in the [110] directions. The conduction band in their calculation is a minimum at the zone center but is flat in the [100] directions. They suggest that, by virtue of spin orbit and other effects not explicitly included in their work, the conduction band should bend down by about 20 to 50 mV at the zone edge thus preserving the many-valley feature emphasized in the theory of superconducting semiconductors.[3,12]

The tunneling current, involving as it does $q=0$ phonons, is most simply interpreted as coming about via direct transitions from the conduction band to the valence band at the zone center. Thus the present tunnel measurements imply that $SrTiO_3$ may be a direct gap semiconductor[13] (and consequently a single-valley superconducting semiconductor[14]) and appear to be in conflict with the many-valley suggestion of Kahn and Leyendecker.[15]

In view, however, of the shallowness of the energy bands and the small energy difference expected between zone center and zone edge it is not unlikely that, particularly for high-concentration materials, both zone center and zone edge valleys are simultaneously occupied,[16] accounting both for bulk superconductivity and for phonon-assisted tunneling at the surface.

Finally, magnetic-susceptibility measurements showed that the $SrTiO_3$ crystals used became superconducting at sufficiently low temperatures.[17] HR-24, for example, had a gradual transition centered at about 0.25°K and about 0.1°K wide. In all junctions studied, however, no change in the V-I characteristic was observed between the normal and superconducting states. It is likely that the large inhomogeneity indicated by the broad transition smeared out and made unobservable any superconducting energy gap in the $SrTiO_3$.

ACKNOWLEDGMENTS

We wish to thank A. G. Chynoweth, at whose suggestion this study was undertaken and with whom several valuable discussion have been held. The advice of D. E. Thomas on the derivative measurement circuitry is appreciated. Our indebtness to both A. S. Barker, Jr., and to K. Andres has already been mentioned. The perseverance and patience of A. Contaldo in the often discouraging task of junction preparation as well as his excellent technical assistance are gratefully acknowledged.

[11] A. H. Kahn and A. J. Leyendecker, Phys. Rev. **135**, A1321 (1964).

[12] M. L. Cohen, Phys. Rev. **134**, A511 (1964).

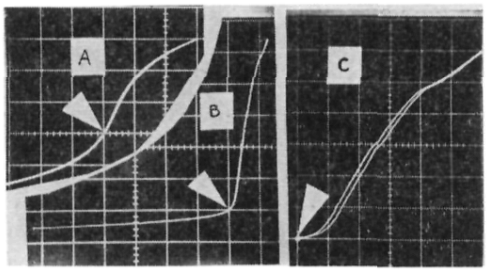
[13] Recent piezoresistive measurements on reduced $SrTiO_3$ [O. N. Tufte and E. L. Stelzer, Bull. Am. Phys. Soc. **10**, 304 (1965)] have been interpreted in terms of a single zone-center conduction-band minimum.

[14] V. L. Gurevich, A. I. Larkin, and Y. A. Firsov, Fiz. Tverd. Tela **4**, 185 (1962) [English transl.: Soviet Phys.—Solid State **4**, 131 (1962)].

[15] The occurrence of $q=0$ phonons in the tunnel current is also consistent with a direct gap in the [100] direction as pointed out by A. H. Kahn (private communication).

[16] M. L. Cohen (private communication).

[17] We are indebted to K. Andres for carrying out the superconductivity measurements in his adiabatic demagnetization apparatus.



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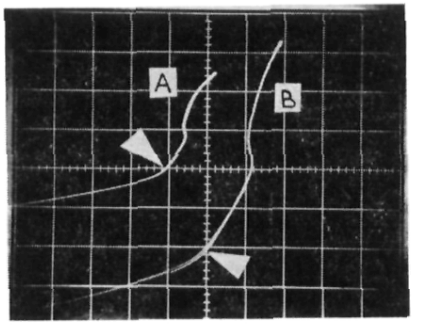

FIG. 4. $V-I$ curves for a Bi-$SrTiO_3$ contact at 4.1°K: (a) 50 mV/cm (vertical), 0.002 mA/cm (horizontal); (b) 20 mV/cm (vertical), 0.001 mA/cm (horizontal). In both cases the origin is marked by an arrow.