SUPERCONDUCTING TUNNELING IN THE LOW-TEMPERATURE PHASES OF GALLIUM*

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The two low-temperature metastable phases of gallium have superconducting energy gap to transition temperature ratios, $2\Delta_0/kT_c$, of 4.5 for "amorphous" gallium and 3.9 for the crystalline phase, β-Ga. Beta-gallium shows considerable structure in the tunneling current indicating the presence of several well-defined peaks in the phonon density of states. Structure observed in the "amorphous" gallium tunneling current appears to be a smeared-out version of that observed in β-Ga.

Tunneling measurements on Al-I-Ga junctions reflect in several ways the difference in the superconducting properties of the two low-temperature phases of Ga. A determination of the superconducting energy gap at $T=0°K$, Δ_0, and of transition temperature T_c, and an investigation of the phonon-induced structure in the tunneling current have been made.

In its room-temperature stable phase, gallium (α-Ga, orthorhombic crystal structure with four atoms per primitive lattice cell) is a superconductor with a T_c of 1.08°K.[1] Tunneling measurements[2] indicate that the ratio of the superconducting energy gap to the transition temperature is $2\Delta_0/kT_c=3.63$, which is reasonably close to the BCS weak-coupling limit of 3.52.[3] When condensed onto substrates held at approximately 4°K, Ga films have a T_c of 8.4°K.[4,5] Electron-diffraction patterns of these films closely resemble those of liquid Ga.[6,7] Thus the term "amorphous" has been used to characterize this high-T_c phase of Ga. Annealing the amorphous phase at ≃15°K produces a sharp phase transition to a crystalline state (β-Ga, crystal structure unknown) as evidenced by a rapid drop in resistance and a change in the electron-diffraction pattern from diffuse halos to well-defined rings.[6,7] Beta-gallium is superconducting with resistively determined T_c's varying from 6.0 to 6.5°K.[4,5,8,9] Further annealing results in the room-temperature stable phase, α-Ga, being formed at approximately 60°K.

Al-I-Ga diodes were fabricated by oxidizing Al strips, which had been condensed onto crystalline quartz substrates, in room air for approximately 10 min. The cryostat was then cooled to ≃1.1°K and cross strips of Ga condensed. It was possible to hold the Ga below its transition temperature ($T_c=8.4°K$) at all times during the condensation process. The junction area was 0.2 mm² and impedances ranged from 10 to 400 Ω. Curves of I, dI/dV, dV/dI, and d^2V/dI^2 vs V, where V and I are the diode bias and tunneling current, respectively, were taken in both the normal and superconducting states of Al and Ga. The electronic circuitry used was essentially the same as that described by Adler and Jackson.[10]

Superconducting energy gaps were determined from the $(dI/dV)_S$-vs-V characteristics of five junctions at ≃1.1°K with both Al and Ga in the superconducting state. It was assumed that the zero in dI/dV occurring after the first peak is at $V=\Delta_{Ga}-\Delta_{Al}$ and that $(dI/dV)_S=(dI/dV)_N$ at $V=\Delta_{Ga}+\Delta_{Al}$. Energy gaps for gallium determined in this way agree well with those determined using the following procedure described by McMillan and Rowell.[11] A sharp kink appears in $(dI/dV)_S$ at the superconducting transition temperature of Al. By carefully controlling the temperature this point can be located quite accurately. The voltage at which this kink appears is equal to the energy gap of Ga at the T_c of Al.

For the amorphous phase we find a transition temperature $T_c=8.4\pm0.1°K$ and a superconducting energy gap extrapolated to $T=0°K$ of $\Delta_0=1.65\pm0.03$ meV. Thus $2\Delta_0/kT_c=4.5$. Annealing this phase of gallium at temperatures between 15 and 60°K decreases the energy gap to $\Delta_0=1.04\pm0.02$ meV for the crystalline β-Ga. While the resistively determined superconducting transition of amorphous Ga is very sharp and always occurs at the same temperature, β-Ga exhibits a broad transition with nonreproducible features. This is possibly the result of a mixture of phases in the film edges due to incomplete transformation to the β phase. Despite this we observe only one energy gap in the annealed phase indicating that most of the current must be tunneling into the β phase. Using the temperature at which the ratio of $(dV/dI)_S$ to $(dV/dI)_N$ at $V=0$ is equal to 1,[12] we obtain a T_c of $6.2\pm0.1°K$ for β-Ga. Therefore $2\Delta_0/kT_c=3.9$ for β-Ga.

Minnigerode and Rothenberg[2] have kindly communicated to us the results of their recent tunneling measurements on Ga films prepared in the same way as in this experiment. From I-vs-

V curves at $T = 0.6°K$ they deduce energy gaps of 1.65 meV for amorphous Ga and 1.06 meV for β-Ga. These values are in excellent agreement with our results. Cohen, Abeles, and Weisbarth[13] have observed three superconducting energy gaps in Ga films prepared at room temperature while maintaining an oxygen pressure of 10^{-4} mm Hg in the evaporation system throughout the condensation process. They postulate that their films are made up of small Ga particles separated by oxide barriers. One of their observed gaps, $\Delta_0 = 1.03$ meV, agrees with our result for β-Ga, $\Delta_0 = 1.04$ meV. However, their gap of 1.53 meV, which they tentatively attribute to amorphous gallium, differs by $\simeq 7\%$ from the results of this work on amorphous gallium, $\Delta_0 = 1.65 \pm 0.05$ meV. We have observed no gap corresponding to Cohen, Abeles, and Weisbarth's Δ_0 of 1.38 meV which they ascribe to another metastable phase of gallium, γ-Ga.

Since the ratio $2\Delta_0/kT_c$ for both the amorphous and β phase of gallium is considerably larger than the BCS weak-coupling limit of 3.52,[3] we would expect to see reasonably well-developed phonon-induced structure in the tunneling currents of both phases.

Schrieffer, Scalapino, and Wilkins[14] have shown that, for a normal metal-insulator-superconductor (M-I-S) tunnel junction at $T = 0°K$,

$$\frac{(dI/dV)_S}{(dI/dV)_N} = \frac{N_T(E)}{N(0)} = \mathrm{Re}\left(\frac{E}{[V^2-\Delta^2(E)]^{1/2}}\right),$$

where the first term is the normalized conductance, the second term is the normalized effective tunneling density of electron states in the superconductor, and $\Delta(E)$ is the complex energy-dependent gap parameter. The gross features of the departure of this normalized conductance from that predicted by the BCS constant-gap model can be accounted for in terms of general features of the density of phonon states in the superconductor. In particular, sharp decreases in the normalized conductance are to be expected at energies (measured from the gap edge) where peaks are located in the phonon density of states.[15] In addition to this normalized electron density-of-states variation, which is due to the general shape of the phonon spectrum, Scalapino and Anderson[16] have shown that there should be superimposed fine structure related to critical points (Van Hove–type singularities) in the phonon density of states. For example, the d^2I/dV^2-vs-V curves for a M-I-S tunneling junction should exhibit a logarithmic singularity and jump discontinuity at energies where infinite discontinuities occur in the phonon density of states. Fine structure such as this is not readily identifiable in M-I-S junctions, probably because of thermal smearing; so we will confine our discussion in this Letter to structure observed in the normalized effective tunneling density of states which can be related to general features of the phonon spectrum.

In Fig. 1 the normalized conductance for both amorphous Ga (curve C) and β-Ga (curve B) is plotted as a function of $V-\Delta_0$. Also shown is $(d^2V/dI^2)_S$ vs $V-\Delta_0$ for β-Ga (curve A). These data were taken at 2°K with Al normal and with a modulation level of 50 μV rms. Thus the smearing of the data due to kT smearing of the Fermi surface in Al and to the modulation voltage are of the same order of magnitude (kT for $T = 1°K$ is approximately 86 μeV). These contributions to smearing are not expected to remove structure in the junction conductance since the energy scale over which the structure appears is large relative to 100 μeV. Data taken with the Al superconducting show no more structure than is seen in Fig. 1.

The deviation of the normalized conductance from the BCS constant-gap prediction is proportional to $(T_c/\Theta_D)^2$. Normalizing to the 5% deviation observed for M-I-Pb junctions[15] we obtain $\simeq 0.6$ and $\simeq 0.3\%$ for the expected deviations in the normalized density of electron states for

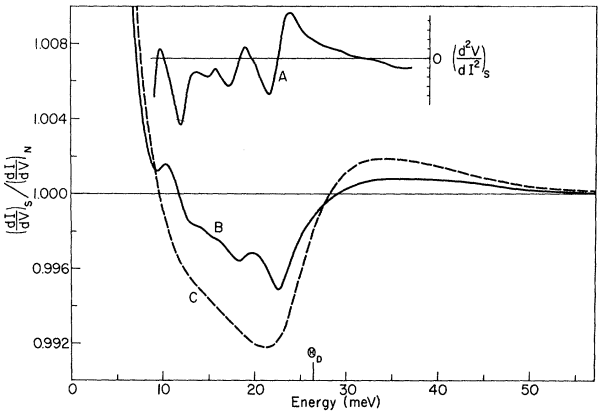

FIG. 1. Derivatives of the I-vs-V curves of an Al-I-Ga tunnel junction at 2°K. Curve C is the normalized conductance of amorphous Ga versus $V-\Delta_0$, taken immediately after condensation of the Ga onto a substrate held at 4°K. Curve B is the normalized conductance versus $V-\Delta_0$ of the same tunnel junction after annealing at temperatures between 15 and 60°K to produce a crystalline phase, β-Ga. Curve A is a derivative of Curve B. The negative peaks in Curve A can be correlated with the location of peaks in the phonon density of states for Ga.

amorphous Ga and β-Ga, respectively. This is in reasonable agreement with the deviations displayed by curves C and B in Fig. 1.

The rather smooth departure of the normalized conductance from the BCS constant-gap prediction seen for amorphous Ga (curve C) is in striking contrast to the structure observed in the normalized conductance of β-Ga (curve B). The departure from BCS for amorphous Ga, which appears to be a smoothed-out version of that seen in β-Ga, probably results from a phonon density of states with smeared-out peaks and no structure due to Van Hove–type singularities. Although the lattice structure of this so-called amorphous Ga is probably liquidlike, one cannot rule out, on the basis of this experiment and the electron-diffraction result,[6,7] the possibility of a structure composed of very small crystallites of the order of perhaps 10 Å in size. Zavaritskii[17] and Chen et al.[18] have studied Al-I-Bi tunnel junctions with the Bi condensed at helium temperatures. Both investigators report structure in the normalized conductance of amorphous Bi which is similar to our observations for amorphous Ga.[19]

The rapid decreases in the normalized conductance of β-Ga, which are related to peaks in the phonon spectra of this crystalline phase, can be more accurately located by the negative peaks in $(d^2V/dI^2)_S$ vs $V-\Delta_0$. See curve A in Fig. 1. Note that there are four well-resolved negative peaks in $(d^2V/dI^2)_S$ ranging in energy from 11.9 to 21.6 meV, indicating a somewhat complex phonon density of states. The crystal lattice structure of β-Ga is not known, but perhaps it is not too different from that of the room-temperature-stable phase, α-Ga. As stated previously, α-Ga has four atoms per primitive lattice cell. Thus there are three acoustical and possibly nine optical branches contributing to the phonon spectra of α-Ga. It is not difficult to imagine that a slight modification of this structure will retain a sufficiently complex phonon spectra to account for the phonon induced structure observed in curves A and B of Fig. 1

To summarize, by condensing Ga onto substrates held near 4°K, it is possible to produce two metastable phases which are strong-coupling superconductors. Both phases have well-defined superconducting energy gaps and definite superconducting transition temperatures. The initial phase is amorphous or liquidlike and exhibits phonon-induced structure in the tunneling current which appears to be a smoothed-out version of that observed in the crystalline β phase. This β phase, formed by annealing the amorphous films at 15°K, has a complex phonon-induced structure which indicates the presence of at least three peaks in the phonon spectrum.

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IMPURITY-STATE–OPTICAL-PHONON COUPLING IN A MAGNETIC FIELD IN InSb

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A number of peaks in photoconductivity have been observed in n-type InSb when the impurity-shifted cyclotron resonance frequency is near the longitudinal optical phonon frequency. Certain of these peaks are interpreted as due to photon absorption resulting in the creation of an LO phonon and simultaneous excitation of the electronic impurity state. We present a theory based on the Fröhlich-type electron-phonon interaction.

Interactions between optical phonons and free or bound charge carriers are responsible for a number of optical effects in semiconductors. One such effect is the phonon-assisted excitation of charge carriers bound to impurity atoms. In this process, photon absorption leads to the creation of one or more optical phonons, with the simultaneous excitation of the charge carrier to a discrete impurity state. Transitions of this type have been reported previously for the II-VI polar semiconductor ZnTe,[1,2] and for diamond.[3] In both of these cases the impurity binding energy was considerably larger than the optical phonon energy, and the transitions were observed in the absence of a magnetic field.

We wish to report the observation of phonon-assisted donor impurity excitations in InSb, a III-V semiconductor in which the impurity binding energy is nearly an order of magnitude smaller than the optical phonon energies. The excitations could be observed only in the presence of a magnetic field of suitable magnitude. The observed magnetic field dependence of the transition energies provides information pertinent to the problem of polaron coupling in InSb.[4-6]

The spectral dependence of the photoconductivity of relatively pure n-type InSb near 4.2°K has been measured at photon energies between 4 and 45 meV, in magnetic fields up to 55 kG. Previous work[7] has shown that in these circumstances the spectral response of the photoconductivity is identical to that of the absorption constant, within experimental error. Most of the experiments were done on two samples, of thickness 30 and 100 μ, with net donor concentration of approximately 7×10^{13} cm^{-3}. Spectra were obtained using an interferometric spectrometer in conjunction with a superconducting solenoid and light-pipe optics; the apparatus and techniques have been described elsewhere.[7] Apart from overall signal amplitude, no dependence of the photoconductivity on the magnitude of the biasing electric field was observed, for the electric fields used. No magnetic-field-dependent structure in the magnetoresistance of the samples was observed when the latter were shielded from infrared radiation by cold filters.

For magnetic fields smaller than about 25 kG, the photoconductivity spectra contained two sharp peaks, due to cyclotron resonance absorption by free electrons and electrons bound to impurity atoms. As the field was increased to bring the cyclotron resonance and optical phonon energies into proximity, the photoconductivity spectra became increasingly more complex, as shown in Fig. 1. At sufficiently high fields, the spectra again contained only the two cyclotron resonance peaks. By cooling the samples to about 1.5°K and obtaining spectra at small field intervals, it was possible to exclude signal peaks due to free carriers and to plot the energies of the transitions of the bound electrons versus magnetic field. A composite plot for the two samples, each measured using light propagating either parallel or perpendicular to the magnetic field, is shown in Fig. 2. Lines have been drawn through the data points, showing the field dependence of the positions of individual photoconductivity peaks. Peak