low-frequency limit. For frequencies in the neighborhood of the Debye frequency, however, the elastic constants are nearly temperature independent. The elastic constants measured ultrasonically cannot therefore be used to calculate an effective Debye temperature as has traditionally been done. (3) For the same reason the lattice softening will not affect the superconducting transition.[13] (4) The apparent arrest of the structural transition and the anomalies in the elastic constants near the superconducting transition temperature may be explained as characteristic of the structural transition alone which suggests that the superconducting transition may have less influence on the structural transition than has been assumed. (5) The very different behavior of Nb_3Sn and V_3Si observed in the distorted structure is found to be due to different relative positions of the band edges and the Fermi level for the two materials.

[1]J. Labbe and J. Friedel, J. Phys. Radium 27, 153, 303, 708 (1966).

[2]P. W. Anderson and E. J. Blount, Phys. Rev. Lett. 14, 217 (1967).

[3]A. B. Migdal, Zh. Eksp. Teor. Fiz. 34, 1438 (1958) [Sov. Phys. JETP 1, 996 (1958)].

[4]In this expression ϵ_n denotes the electron energies, shifted as a result of the static strain and renormalized by the dynamic electron-phonon interaction.

[5]R. W. Cohen, G. D. Cody, and J. J. Halloran, Phys. Rev. Lett. 19, 840 (1967).

[6]This expression neglects the exchange enhancement due to the electron-electron interaction.

[7]B. W. Batterman and C. S. Barrett, Phys. Rev. 145, 296 (1965).

[8]R. Mailfert, B. W. Batterman, and J. J. Hanak, Phys. Lett. 24A, 315 (1967).

[9]W. Rehwald, Phys. Lett. 27A, 287 (1968).

[10]L. R. Testardi and T. B. Bateman, Phys. Rev. 154, 402 (1967).

[11]For V_3Si a weak temperature dependence of $c_{11}^0-c_{12}^0$ due to anharmonic interactions needs to be included in order that ω_q^2 remains >0 for $T=0$. In this case $c_{11}^0-c_{12}^0$ cannot be eliminated in favor of $n(0,T_m)$ as is done to obtain Eq. (19).

[12]L. J. Vieland and A. W. Wicklund, Phys. Rev. 166, 424 (1968).

[13]The shift in the band edges, on the other hand, may be expected to affect the superconducting properties.

Onset of Quantized Thermal Fluctuations in "One-Dimensional" Superconductors

J. E. Lukens, R. J. Warburton, and W. W. Webb
Department of Applied Physics and Laboratory for Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850
(Received 28 August 1970)

Measurements of the onset of the resistive transition and the current-voltage characteristics of "one-dimensional" single-crystal tin whiskers have been extended to a sensitivity of 10^{-15} V. The thermally activated quantum phase slips proposed by Langer and Ambegaokar have been observed directly and their theory for the voltage, determined by the rate of phase slippage, has been verified together with the modification of the attempt frequency proposed by McCumber and Halperin.

We have extended measurements[1-4] of the onset of the resistive transition and of the current-voltage characteristics below the critical temperature on single-crystal tin whiskers to voltages of 10^{-15} V (an improvement of six orders of magnitude over previously reported measurements) and power levels of 10^{-22} W using a superconducting femtovolt amplifier.[5] These "one-dimensional" crystals have diameters small compared with the temperature-dependent coherence length in the temperature range of the measurements. Under these conditions it is expected that the transition shape is determined by thermodynamic fluctuations.

Langer and Ambegaokar[6] (L-A) have predicted that there will be a finite resistance below the critical temperature T_c due to discrete slips of 2π in the phase difference of the superconducting wave function between the ends of the crystal. They consider this process as one of thermal activation over an energy barrier separating an initial state from a final state in which the difference in the phase is changed by 2π radians. This barrier height is calculated from the mean-field Landau-Ginzburg equations assuming constant-voltage boundary conditions. They find that the voltage V at current I in the limit of $I \ll I_c$ is

$$V = 2N\varphi_0 \sinh\left(\frac{I}{2I_1}\right) \exp\left[-\frac{1}{\pi}\left(\frac{3}{2}\right)^{1/2}\frac{I_c}{I_1}\right], \qquad (1)$$

where I_c = mean-field critical current and $I_1 = k_B T/\varphi_0$, k_B being Boltzmann's constant and φ_0 the flux quantum. If T is the critical temperature of tin, about 3.7 K, $I_1 = 2.5\times10^{-8}$ A. They have taken N, the attempt frequency, to be a constant equal to the frequency of electron scattering in the entire crystal in the normal state, about 10^{27} sec^{-1}.

McCumber and Halperin[7] (M-H) have studied the theory of the attempt frequency in much greater detail and find it to be both current and temperature dependent. It depends on both the number of statistically independent subsystems in the crystal and a characteristic relaxation rate. M-H take the number of independent subsystems to be of order $L/\xi(t)$; i.e., crystal length/temperature-dependent coherence length. This leads to a decrease by a factor of about 10^{10} from the L-A suggestion for N. The relaxation rate is found using the time-dependent Ginzburg-Landau theory. This results in a further decrease of 10^5 so that the M-H estimate of the attempt frequency is $N \cong 10^{12}$ in the range of our measurements. The current dependence of order I^2 and higher has not been calculated, and there currently are no estimates of its magnitude.[8]

Measurements of the onset of the transition employed the circuits shown in Fig. 1, where a superconducting magnetometer serves as a femtovolt amplifier arranged alternatively to measure voltage across a crystal specimen or the current circulating in a superconducting loop containing the crystal. The crystals were placed in helium exchange gas inside a copper

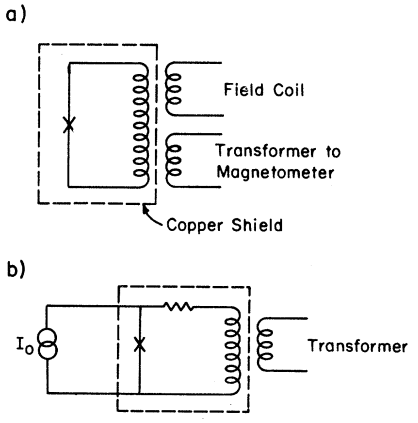

FIG. 1. Measuring circuits of superconducting femtovolt amplifier. The tin crystal is indicated by crosses. (a) Ammeter configuration using closed superconducting loop with magnetically induced current. (b) Voltmeter configuration with external current leads.

can which could be temperature regulated to ±1 μK. The ambient magnetic field level was about 10^{-5} G. The crystals were surrounded by several layers of shielding including copper and superconducting cans. The final copper can which enclosed the crystal had only high-impedence current leads entering it. These leads were well filtered. Additional filters were added at helium temperature, but no change in the results was found. The most convincing evidence that external noise had no effect on the measurements was obtained in the configuration where current was magnetically induced in the crystal. In this case no wires of any kind penetrated the shield can. Using several cans with cutoff frequencies ranging from 45 Hz to about 1 kHz, there was no change from the results obtained with circuit 1(b). Any significant magnetic noise below the cutoff frequency would have been directly observed with the magnetometer, which was part of the superconducting voltmeter.

The whisker crystals, which were prepared by conventional techniques,[9] were carefully soldered to superconducting electrodes with Wood's metal solder. A major difficulty of this experiment was production of these contacts without damage to the crystal. Such damage produced readily identifiable structure in the resistive transition. The mounted crystals were screened by examining the transition using a conventional nanovoltmeter and accepting only those which showed no obvious structure in the lower part of the transition. Only about 5% of the crystals mounted were acceptable by this criterion.[10]

The most direct evidence for the validity of the L-A model of voltage arising from unique phase slips of magnitude 2π is provided by the current dependence of the voltage V at constant temperature. For constant temperature the theory predicts, to first order, $V \propto \sinh I/2I_1$. This relationship follows directly from the model assumed and does not depend on detailed calculations of the energy barriers, on sample parameters, or on the boundary conditions.[11] Figure 2 shows a measured I-V curve compared with the sinh relation. For $I \gg 2I_1$, the theory gives $(\ln V)/I \propto 1/2I_1 = 20.4\ \mu A^{-1}$. The measured slope is $S = \Delta \ln V/\Delta I = 17.2\ \mu A^{-1} \pm 2\%$ at 0.15 μA. This value of S shows some variation, usually in the range 15-18 μA^{-1}, depending on the crystal measured and the temperature, $\Delta t = 1 - T/T_c$, of measurement. S tends to increase with Δt. Inclusion of higher-order terms in I that appear in the L-A calculation of the energy barrier gives slightly

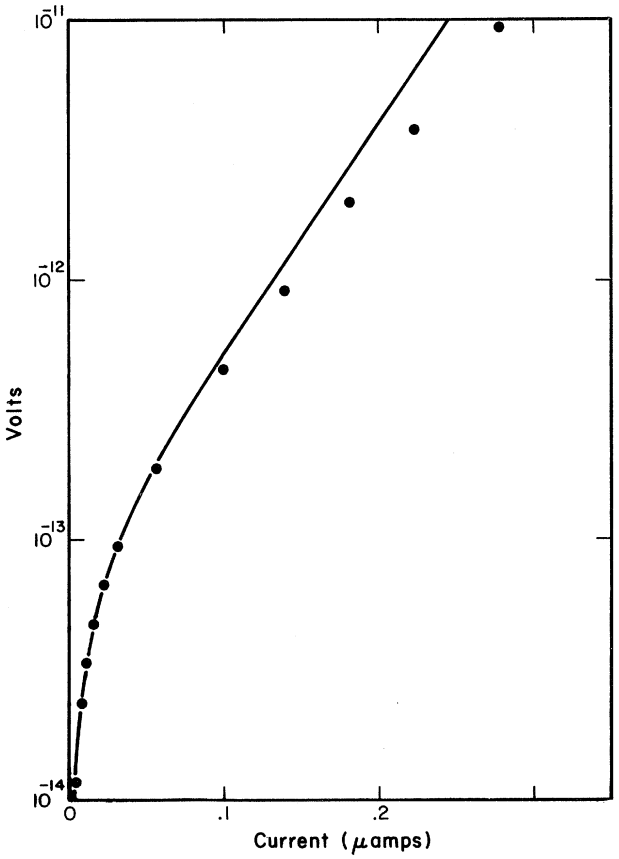

FIG. 2. Current-voltage characteristics at fixed temperature. Solid line, $V=\sinh I/2I_1$; closed circles, data points.

better agreement between theory and experiment. The still unknown higher-order current dependence of the prefactor, presumably depending both on sample parameters and on temperature, may explain the small remaining discrepancy.

The data in Fig. 2 were obtained with the crystal connected in a closed superconducting loop with an inductance of 10^{-6} H as shown in Fig. 1. Current was induced in the loop by ramping an external magnetic field and was measured with a superconducting magnetometer. The voltage was determined from the measured rate of change of flux linking the loop. The value of the inductance was then changed to 2×10^{-8} H to permit observation of flux changes through the loop of less than φ_0. As the induced current in the loop was increased toward the critical current, we observed that flux entered in discrete units of φ_0 corresponding to the 2π phase slips of the L-A model. Furthermore, at constant ambient conditions near T_c, with no induced current the loop current spontaneously fluctuated among several discrete values corresponding to the low-level quantum states. This is the same type of behavior previously observed in low-inductance loops containing thin-film weak links.[2] The value of S that was measured in the low-inductance loop remained 17.2 μA^{-1}.

The crystal was then connected in the voltmeter configuration shown in Fig. 1(b). Here the loop contains a resistance so that fluxoid quantization is not required. However, the measured value of S again remained unchanged, indicating that the voltage was still produced by discrete 2π phase slips as assumed by L-A and directly observed in the closed loop. These data also tend to confirm McCumber's calculation that the boundary conditions on the crystals are relatively unimportant.[11,12]

For $I\ll I_1$, Eq. (1) can be expressed as a current-independent, temperature-dependent resistance. Using the M-H prefactor with the temperature dependence written out explicitly, Eq. (1) becomes

$$R_s=\frac{\varphi_0}{I_1}N_0\Delta t^{9/4}\exp\left[-\frac{1}{\pi}\left(\frac{3}{2}\right)^{1/2}\frac{I_c}{I_1}\right], \tag{2}$$

where

$$N_0=\frac{L}{\xi(0)}\frac{I_1}{e}\frac{4}{\pi}\left(\frac{3}{\pi}\right)^{1/2}\left[\frac{1}{\pi}\left(\frac{3}{2}\right)^{1/2}\frac{I_{c0}}{I_1}\right]^{1/2},$$

$\xi(0)$ being the zero-temperature coherence length, is a function only of material parameters. For our crystals $N_0\simeq10^{19}$ $\sec^{-1}$. R_s is the effective resistance associated with the supercurrent. The total resistance R is assumed to be equal to the parallel combination of R_s and the normal-state resistance R_0. Figure 3 shows a typical resistive transition measured in the xero-current limit. Data on the lower part of the transition were obtained with the superconducting voltmeter using the circuit in Fig. 1(b). Data for $R>0.1$ Ω were also obtained with a Keithley nanovoltmeter. The consistency of the two measuring techniques is shown by the region of overlapping data. The solid line is the best fit by Eq. (2) taking N_0 and T_c as variable parameters but using the experimentally determined value of I_{c0} where $I_c=I_{c0}\Delta t^{3/2}$. The best-fit values of N_0 obtained in this way are less than the M-H value by factors of 10^0-10^2 for a number of samples with cross-sectional areas ranging from 10^{-9} to 10^{-8} cm^2 and electron mean free paths of 0.5×10^{-5} to 30×10^{-5} cm. This is to be contrasted to a deviation of more than 10^{14} from the attempt frequency originally suggested by L-A. Crystals with short mean free paths generally

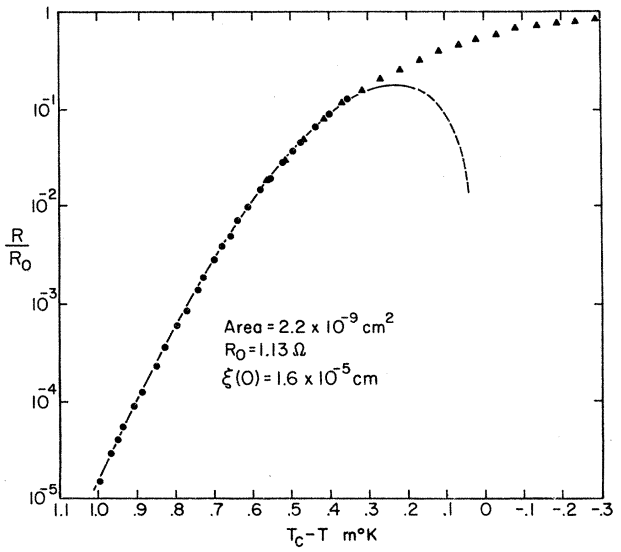

FIG. 3. Total resistance of tin crystal as a function of temperature. Closed circles, measured with superconducting femtovoltmeter; closed triangles, measured with nanovoltmeter. Line, two-parameter fit to M-H theory.

have values of N_0 closer to the theoretical value. The suggestion of Masker, Marčelja, and Parks[13] that $R \propto \Delta t^{-3}$ for small resistance is definitely excluded by the exponential decrease observed.

I_{c0} was determined in two ways: First, the temperature-dependent current necessary to produce a given resistance in the crystal (chosen to be about 1% of R_0) was measured between about 10 and 30 μA. A plot of $I_c^{2/3}$ versus temperature gave a straight line of slope $I_{c0}^{2/3}$. This slope could be determined within a few percent. Although data close to T_c were not used, it is possible, though we feel it is unlikely, that an additional error of several percent could have been introduced by the effect of fluctuations on the mean field slope. Next we checked the value of I_{c0} by comparing it with the value calculated from the measured cross-sectional area and coherence length.[14] The area was determined from the room-temperature resistance and the crystal orientation obtained from electron-diffraction patterns. The coherence length was found by determining the mean free path from the ratio of the resistance at 4.2 and 300°K and using the standard relation between mean free path and coherence length.[15,16] The uncertainty in this calculation is about 10% which is comparable with the uncertainty of ξ_0. The calculated and measured values of I_{c0} agree within this error. The best-fit value of N_0 varies by about a factor of 2 when I_{c0} is varied within its experimental uncertainty.

If all three parameters N_0, T_c, and I_{c0} are varied, the fit obtained above cannot be improved. It becomes significantly worse for values of I_{c0} deviating by more than 20% from the measured value. The three-parameter fit makes essential use of the curvature of the data on $\ln R$ vs T. This curvature is greatest for high resistance —just where one expects corrections to the theory to become important. The basic criterion for the applicability of the theory is that the ratio of the energy barrier height ΔF to the thermal energy $k_B T$ be large. In Fig. 3 the data and theory began to deviate for $\Delta T = 0.33$ mK where $\Delta F/k_B T$ is about 3. Thus, the accuracy with which the various parameters can be specified depends on where corrections to Eq. (2) become important. An independent value for T_c would define the regime where the corrections are serious, and thus permit more certain determination of the experimental parameters and allow a test of the temperature dependence of the prefactor. We are currently making measurements of the temperature-dependent penetration depth to obtain such a value.

We conclude that the voltage appearing near the onset of the transition in uniform one-dimensional crystals is determined by the rate of thermally activated quantum phase slips of magnitude 2π as proposed by L-A. The L-A calculation of the zero-current activation energy barrier also agrees with the value that we observe. The basic current dependence is also confirmed; however, significant deviations from theory are observed at higher currents where terms of order $(I/I_c)^2$ are not negligible. This discrepancy may well arise from the uncalculated current dependence of the attempt frequency, although our measurement does not distinguish this possibility from that of additional current dependence in the barrier height. The generally close agreement of the measured zero-current attempt frequency with that predicted by M-H appears to verify their statistical arguments. Relatively small impurity-dependent discrepancies remain, however, and are the subject of continuing investigation.

We are pleased to acknowledge helpful discussions with B. I. Halperin and J. W. Wilkins, and with R. Newbower, M. R. Beasley, and M. Tinkham about their work toward similar measurements. We are also pleased to acknowledge the gift of a stable magnetometer by R. A. Buhrman,

the support of the U. S. Atomic Energy Commission, and the use of facilities at Cornell provided by the Advanced Research Projects Agency.

[1]W. W. Webb and R. J. Warburton, Phys. Rev. Lett. 20, 461 (1968).
[2]J. E. Lukens and J. M. Goodkind, Phys. Rev. Lett. 20, 1363 (1968).
[3]R. J. Warburton, B. R. Patton, W. W. Webb, and J. W. Wilkins, in Proceedings of the International Conference on the Science of Superconductivity, Stanford Univ., Stanford, Calif., August 1969 (to be published).
[4]J. E. Lukens and J. M. Goodkind, in *Proceedings of the Eleventh International Conference on Low Temperature Physics, St. Andrews, Scotland, 1968,* edited by J. F. Allen, D. M. Finlayson, and D. M. McCall (St. Andrews Univ., St. Andrews, Scotland, 1969), Vol. 2, p. 803.
[5]J. E. Lukens, R. J. Warburton, and W. W. Webb, to be published.
[6]J. S. Langer and V. Ambegaokar, Phys. Rev. 164, 498 (1967).
[7]D. E. McCumber and B. I. Halperin, Phys. Rev. B 1, 1054 (1970).
[8]B. I. Halperin, private communication.
[9]W. C. Ellis, D. F. Gibbons, and R. G. Treuting, *Growth and Perfection of Crystals* (Wiley, New York, 1958), p. 102.
[10]The possibility that the observed characteristics are due to a weak link, possibly at a contact, instead of the whisker crystal itself was eliminated by two results: The critical currents in a substantial region of temperature below the fluctuation-limited regime agree with Ginzburg-Landau prediction for thin wires. No Anderson-Dayem steps, i.e., constant-voltage steps in the presence of microwave radiation, could be produced in the resistive transitions of similar properly mounted whisker crystals although such steps were readily seen in some poor contacts just as in thin-film bridges, by W. H. Henkels, in extensive experiments in our laboratories.
[11]D. E. McCumber, Phys. Rev. 172, 427 (1968).
[12]D. E. McCumber, Phys. Rev. 181, 716 (1969).
[13]W. E. Masker, S. Marčelja, and R. D. Parks, Phys. Rev. 188, 745 (1969).
[14]P. G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966), p. 184.
[15]J. W. Cook, Jr., M. J. Skove, and E. P. Stillwell, private communication.
[16]B. B. Goodman, Rep. Progr. Phys. 29, 445 (1966).

Raman Scattering from Localized Vibrational Modes in GaP†

D. T. Hon, W. L. Faust, W. G. Spitzer, and P. F. Williams
Department of Physics and Department of Electrical Engineering, University of Southern California, University Park, Los Angeles, California 90007
(Received 11 August 1970)

High-frequency localized vibrational modes of impurities in a III-V compound have been observed by Raman scattering. Three lines from the GaP samples closely correspond to some local modes previously reported in infrared studies, and depolarization measurements tend to confirm their proposed assignments. We describe several attractive features of this method for the study of semiconductor impurities.

It is well known[1] that a small concentration of impurities introduced into a perfect crystal will have little effect on the vibrational dispersion branches. But in some cases there may appear vibrational modes[1,2] lying outside of the allowed frequency range of the perfect crystal. These are called localized vibrational modes, or local modes, because the mode energy is spatially concentrated near the defect site.

Following the observation of the local mode of nitrogen[3] in GaP in luminescence, infrared absorption was observed for a number of impurities in several different III-V semiconductors.[4-11] To the best of our knowledge, this is the first report of Raman scattering from high-frequency local modes in a III-V compound. Other related system types from which Raman scattering has been reported include mixed crystals,[12-14] the U center in alkaline-earth halides,[15] and the F center in alkali halides[16]; only the second belongs to a well-defined high-frequency localized vibrational excitation. The systems we discuss here are found to give generous signal levels with impurity concentration as low as 10^{17} cm^{-3}.

The four GaP ingots used in this study were chosen from a set used in some previously reported infrared work.[10] We shall continue the labeling scheme established in Ref. 10 (ingots Nos. 1, 2, 3, 4, 5, 6), and extend it with further numerals for additional samples (see Table I). They are compensated polycrystals prepared by the vertical Bridgman technique; for the de-