Nonlinear Microwave Effects and the Switching Speed of Superconducting Tin

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The nonlinear response of various superconducting tin surfaces has been observed when both a high-amplitude rf magnetic field at 9200 Mc/sec and a dc bias field were applied to such surfaces. Harmonics at 18 400 Mc/sec were generated because of the change of the superconducting surface resistance with field during the rf cycle. Data are presented on the variation of this harmonic output with temperature, with dc bias magnetic field, and with the rf power level. Results are given for the surfaces of pure bulk specimens, of alloy bulk specimens, and of thin films of various thicknesses. The amount of harmonic power observed is never more than a few percent of that which is calculated under the assumption that the surface resistance changes instantaneously and completely from its superconducting value to its normal value when the total applied field changes from less than to more than the critical value. The conclusion is drawn that the switching between states is only partial or incomplete at such high frequencies. A discussion is given which appears to qualitatively account for most of the salient experimental facts. For the alloy and thin film specimens and for the pure specimens near T_c, this discussion is based on consideration of the Ginzburg-Landau order parameter. For the pure specimens at lower temperatures, a new approach is proposed which is based on spatial effects: The switching field is confined to such a small skin depth that the presence of the large amount of adjacent unswitched material inhibits the transition from taking place. In neither case is it found necessary to include any purely temporal limitation on the switching speed in order to explain the experimental observations.

I. INTRODUCTION

CERTAIN nonequilibrium properties of superconductors, such as the speed of the magnetic field induced transition between the normal and superconducting phases, are of considerable interest since such effects are, at present, not directly derivable from the microscopic theory of superconductivity. Those transition speed experiments are well understood which involve the quasiequilibrium growth of a pre-existing superconducting nucleus by the motion of the superconducting-normal boundary.[1–4] However, at very high frequencies such superconducting-normal boundaries will not have time to move an appreciable distance and the switching mechanism will instead depend primarily on the process of nucleating the new phase rather uniformly over the surface of the sample. The purpose of this paper is to describe some experiments bearing on such processes and to give a theoretical basis for the qualitative discussion of the observed effects.

Other somewhat similar experiments have previously been performed, but not at as high a frequency. Several investigations of the switching speed have been made by pulse techniques. In these experiments the rate of growth of resistance was studied as a function of time after a step function of magnetic field was applied to the superconductor. Switching speeds as short as 1.5×10^{-10} sec have been reported in such experiments.[5] In this case it is possible that the switching should be ascribed to a thermal mechanism, namely, that the temperature of the superconducting element is raised above the transition temperature by the eddy currents induced by the pulse. An analysis of such thermal effects has been given and velocities of such thermal switching waves of 10^6 cm/sec have been observed.[6] Somewhat similar effects, but at much lower speeds, have also been observed elsewhere.[7] A pulse measurement in which such thermal switching effects should have been absent[8] has shown that the nonthermal switching speed is at least as fast as 1.5×10^{-8} sec. These pulse techniques are difficult to extend to times much shorter than $\sim10^{-9}$ sec.

It is much easier to obtain information at higher frequencies if the impressed magnetic field is made an rf sine wave, $H_{\mathrm{rf}}\sin\omega t$, and if some nonlinear effect is measured. Since the resistance in the normal state, R_N, is considerably greater than that in the superconducting state, R_S, various types of nonlinear effects should be observable if switching takes place during a cycle. An early experiment[9] in which a rectified voltage was measured when a direct current and an alternating current were simultaneously applied to a superconducting wire was performed in 1941. The highest frequency used was 10^7 cps and the authors concluded from this work that the switching speed was faster than 2×10^{-8} sec. A more recent paper[10] gives other references and describes an experimental method of investigating the switching by measurement of the instantaneous flux penetrating a bulk cylindrical specimen of tin. The frequencies used were on the order of $100\rightarrow10\,000$ cps

[1] A. B. Pippard, Phil. Mag. **41**, 243 (1950).
[2] T. E. Faber, Proc. Roy. Soc. (London) **A219**, 75 (1953).
[3] W. B. Ittner, Phys. Rev. **111**, 1483 (1958).
[4] A. J. W. Duijvestijn, IBM J. Res. Develop. **3**, 132 (1959).
[5] D. Abraham, Solid State Electron. **1**, 340 (1960).
[6] R. F. Broom and E. H. Rhoderick, Solid State Electron. **1**, 314 (1960).
[7] J. W. Bremer and V. L. Newhouse, Phys. Rev. Letters **1**, 282 (1958).
[8] A. E. Brennemann (private communication).
[9] B. G. Lazarev, A. A. Galkin, and W. I. Khotkevick, Zh. Eksperim. i Teor. Fiz. **11**, 573 (1941).
[10] A. A. Galkin and P. A. Bezuglyi, Zh. Eksperim. i Teor. Fiz. **28**, 463 (1955) [translation: Soviet Phys.—JETP **1**, 197 (1955)].

and most of the effects were attributable to the motion of the superconducting-normal boundary inward from the surface. Even so, the authors conclude that at $T=3.62°$ the "time for the formation of a superconducting nucleus" is $\sim 10^{-4}$ sec, while that for the "formation of a normal nucleus" is shorter than 10^{-6} sec. These times may be those relevant to the process of covering rather uniformly the surface with the new phase by the nucleation and subsequent lateral growth of small nuclei, rather than to the process of *initiating* this new phase uniformly over the surface with no lateral growth involved.

A somewhat related experiment[11] has also been performed by observation of the difference frequency produced when two magnetic fields alternating at different frequencies were simultaneously applied to a thin superconducting film. Input frequencies ranging from 240 to 840 Mc/sec were used with a constant difference frequency of 40 Mc/sec. One input frequency, ν_1, was applied to only one side of the thin film. The other input frequency, ν_2, was applied to both sides of the film and served to switch the film from normal to superconducting and vice versa. Since the frequency ν_1 can reach the output loop only when the film is normal, the difference frequency $\nu_2-\nu_1$ should be present at the output loop. It was found that this difference frequency power (and, hence, the conversion loss) was relatively independent of frequency for values of ν_1 between $240 \rightarrow 840$ Mc/sec. The conclusion drawn from this fact was that the switching speed is faster than 0.6×10^{-9} sec. However, the absolute value of the conversion loss was found to be quite large. This conversion loss should have been small if, as was expected, the degree of shielding by the film in the superconducting state were always large for $H<H_c$. A separate measurement showed that this shielding was in fact not large and that it varied only slowly with field rather than abruptly at $H=H_c$. This behavior was ascribed by the authors to impurities or strains in the thin films. Their results on switching speeds may therefore have been specific only for such strained or impure films.

The present paper describes a somewhat different method of assessing the nonlinearities. Also, the experiments were performed at the much higher frequency of 9200 Mc/sec. In this method harmonics at 18 400 Mc/sec were observed; these harmonics were produced when a steady dc bias field plus the large amplitude rf field at 9200 Mc/sec were applied to the superconducting surface. Some preliminary results have previously been given.[12] The major advantages of this method are the following: Calculation of the amount of harmonics expected is much more straightforward than calculation of the conversion loss for the mixer; both thin films and the more reproducible and better understood surfaces of bulk samples can be investigated; the distribution of the fields in the interior of the bulk samples is well known; heating effects are much less for the bulk surfaces; and, finally, relatively simple structures can be used.

From the amplitude of the observed harmonics it can be said that none of the samples studied give evidence that the switching is more than very partial or incomplete at a frequency of 9200 Mc/sec. Thus, the switching speed appears to be considerably slower than $\tau=1/2\pi\nu\approx2\times10^{-11}$ sec. The samples studied include pure bulk specimens, alloy bulk specimens, and thin films of various thicknesses. Data are given on the dependence of the harmonics on the temperature, on the bias field, and on the switching field.

Finally, a model for the switching speed is developed which appears to account for most of the experimental observations. A preliminary account of this approach for $T\ll T_c$ has previously been given.[13] In addition, a new discussion will be given for the thin film and alloy samples and for the pure bulk samples near T_c on the basis of the Ginzburg-Landau theory.

II. DESCRIPTION OF THE EXPERIMENT

The magnitude of the microwave surface resistance of a superconductor, R_s, is a function of both the temperature and the magnetic field. If a dc field is applied to a superconductor and if the temperature is below T_c, the specimen will remain superconducting if this field is everywhere less than the critical value, H_c. If an additional field from a microwave source is applied parallel to the dc bias field and if the total field exceeds the critical field during some part of the cycle, the surface resistance will tend to assume the normal state value, R_N, during this part of the cycle. Since the change in resistance may take place quite steeply over a small range of values of H near H_c, the change from R_S to R_N would be very rapid if the surface resistance follows the field instantaneously. This abrupt change of resistance would lead to an unequal absorption of the incident wave for the two parts of the cycle. Thus, a distorted wave should be reflected from the surface and harmonics should be present in the output.

The experimental arrangement is shown schematically in Fig. 1. Microwave power at 9.2×10^9 cps is coupled through the iris into the rectangular cavity. One end of the cavity is closed by the superconducting sample. The microwave power, augmented by the Q of the cavity, is incident on this sample approximately as a plane wave. The smaller waveguide is beyond cutoff at the fundamental frequency. It thus closes the other end of the cavity. However, harmonics generated by the superconducting sample can enter this smaller waveguide through the tapered section and can, thus, leave without being reflected or suffering a mode change.

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[11] D. L. Feucht and J. B. Woodford, Jr., J. Appl. Phys. **32**, 1882 (1961).

[12] A. H. Nethercot, Jr., in *Proceedings of the Seventh International Conference on Low Temperature Physics, 1960* (University of Toronto Press, Toronto, 1960), p. 231.

[13] A. H. Nethercot, Jr., Phys. Rev. Letters **7**, 226 (1961).

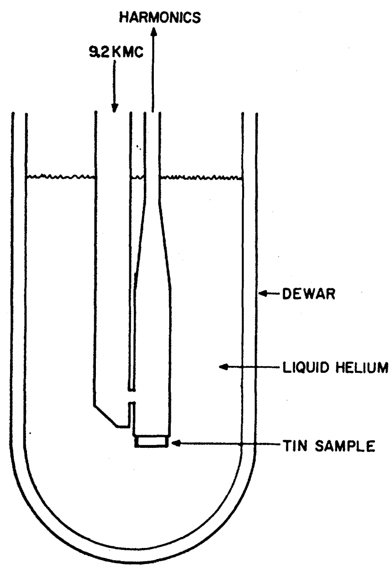

FIG. 1. Schematic representation of the sample and cavity.

These harmonics are subsequently detected with a crystal detector.

A Fourier analysis shows that the second harmonic produced will have its largest amplitude when the bias field, H_0, is such that $H_0 \approx H_c$. With the tin sample considered as a variable resistance, R_L, at the end of the waveguide (reactive effects are for the moment ignored), the following transmission line equation holds:

$$\Gamma = V_2/V_1 \approx 1 - 2R_L/Z_0 = 1 - \epsilon, \quad (1)$$

where Γ is the voltage reflection coefficient and it is assumed that $R_L \ll Z_0$. Z_0 is the characteristic impedance of the waveguide and V_1 and V_2 are the incident and reflected "equivalent" voltages, respectively. If switching is instantaneous and $H_0 \approx H_c$, $R_L = R_S$ during one half of the cycle and $R_L = R_N$ during the other half. For the moment, it will be assumed that the temperature is sufficiently low that $R_S \ll R_N$. The reflected voltage varies with time as $V_2 = (1-\epsilon)V_1$ for $0 \leq t \leq \pi/\omega$ and as $V_2 \approx V_1$ for $\pi/\omega \leq t \leq 2\pi/\omega$. If $V_1 = V_0 \sin\omega t$, the result of a Fourier expansion is

$$V_2 = V_0\left(\sin\omega t - \frac{\epsilon}{2}\sin\omega t + \frac{2\epsilon}{3\pi}\cos 2\omega t + \cdots\right). \quad (2)$$

The reflected power is

$$P \approx \frac{V_0^2}{Z_0}\left(\langle \sin^2\omega t\rangle_{\text{av}} - \epsilon\langle \sin^2\omega t\rangle_{\text{av}} + \left\langle \frac{4\epsilon^2}{9\pi^2}\cos^2 2\omega t\right\rangle_{\text{av}} \cdots\right). \quad (3)$$

The sum of the first two terms gives the reflected power at the frequency ω, and the third the reflected power at the frequency 2ω. Consideration of the nonlinear reactance would increase this harmonic power by less than a factor of 2. Equation (3) can conveniently be written in the form of the ratio of second harmonic power to absorbed power, or

$$P(2\omega)/P^a(\omega) = 4\epsilon/9\pi^2. \quad (4)$$

The value of the surface resistance of bulk tin at 10^{10} cps has been measured[14] to be 0.007 Ω/square in the normal state. Since in a waveguide the terminating total surface resistance and the guide characteristic impedance are proportional to each other (their ratio is independent of waveguide dimensions), the value of $\epsilon/2$ at 9200 Mc/sec is given by 0.0065/377. The harmonic power relative to the absorbed power is thus $P(2\omega)/P^a(\omega) = 1.6\times10^{-6}$. Relative to the effective power incident on the surface, the efficiency of harmonic production for perfect switching is only $\sim 6\times10^{-11}$. Clearly, a rather large incident power must be used and a fairly sensitive detector employed.

In the present experiment, a cavity of $Q_0 \approx 3000$ and of length $3\lambda_g/2$ was used. An input power from the magnetron of 680 W should produce a field, H_{rf}, of 33 G at the tin surface (70 000 W would be necessary if no cavity were used). The harmonic power produced under these conditions would be 4×10^{-6} W for perfect switching. This power would give an observed signal to noise of about 1500 with a good 1 Mc/sec bandwidth video amplifier. Under these conditions, the power absorbed by the tin would be about 2.5 W. To reduce the absorbed energy, the 2J51 magnetron was operated in pulses of about 1-μsec duration repeated at a 60 cps rate. The size of the rf field predicted above was experimentally checked since harmonics were observed only when $(H_0 - H_{\text{rf}}) < H_c$ if $H_0 > H_c$. It should be mentioned that all surfaces of the cavity except the tin sample were made of brass. Since much more power was absorbed by the brass than by the tin the Q of the cavity and, hence, the size of H_{rf} did not change significantly during a cycle.

Several advantages can be encountered for the particular cavity design used. The small output waveguide completely blocks the large amplitude fundamental power from reaching the detector. The nonresonance of the cavity at 2ω simplifies the design. It also simplifies the analysis of the results since the harmonic power does not return to the superconducting sample where it might cause higher order effects. A very important feature is that the cavity acts as a filter to prevent the very strong magnetron harmonics from reaching the detector: The size of the coupling iris is adjusted for critical coupling of the waveguide to the high-Q resonance of the cavity at the frequency ω; at 2ω, since the cavity is nonresonant at this frequency, the coupling is very small.

The magnetron was operated at a low-duty cycle and

[14] C. J. Grebenkamper and J. P. Hagen, Phys. Rev. 75, 673 (1952).

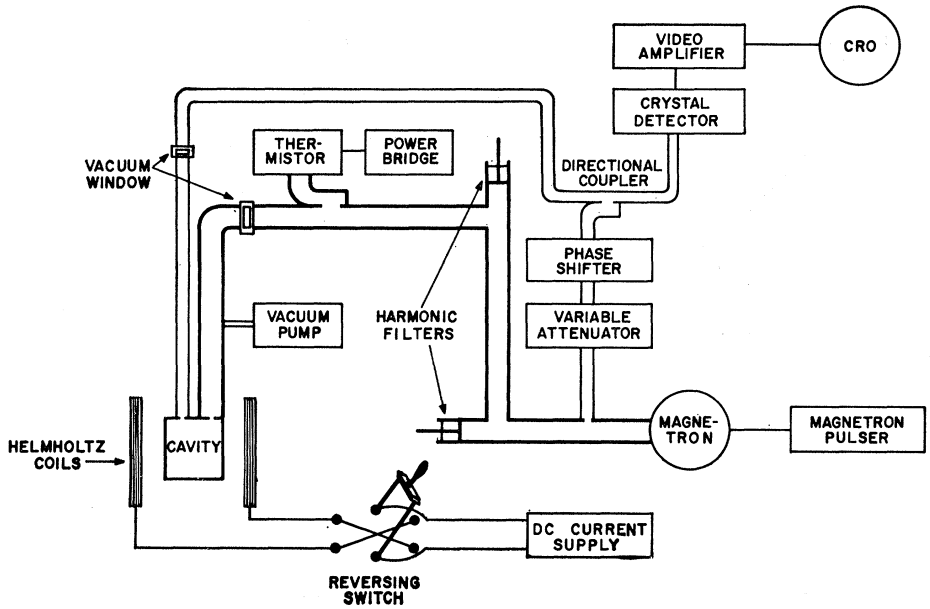

FIG. 2. Over-all block diagram of the experiment. The large waveguide carries the 9.2 kMc/sec (X band) power and the small carries the 18.4 kMc/sec (K band) harmonics.

the average power absorbed by the sample was less than 10^{-4} W/cm^2. A calculation shows that this would cause a temperature rise of the sample of less than 10^{-2}°K if the thermal contact between bath and sample limited the average heat loss. The peak power during the magnetron pulse will cause a somewhat greater heating in general. If the thermal diffusion equation is used, it is found that the surface of a semi-infinite bulk sample heats up during a pulse by about 10^{-2}°K for pure bulk tin. For the alloyed tin-indium samples the corresponding temperature rise would be about 0.2°K. The thin film samples were deposited on single-crystal quartz substrates to minimize this temperature rise. Even so, this rise is expected to be 10^{-1}°K or more. Obviously, the thin film and alloy samples could not be operated at values of $H_{\rm rf}$ as great as for the pure bulk tin. It can also be shown that the temperature changes due to the latent heat of the transition are always small compared to the above effects.

In addition to the filtering action of the cavity on the magnetron harmonics, two additional filters were used which consisted of tee sections with adjustable plungers to short out these harmonics. Despite these added precautions, these leakage harmonics were still large enough to be bothersome. Therefore, it was decided to use magnetron harmonics as local oscillator power in a mixing arrangement; this increases the detection sensitivity and also gives phase information about the signal. An additional amount of harmonic power was introduced to the 1N26 detector crystal through a directional coupler, the amplitude and phase of this power being adjustable. The total local oscillator power was the sum of the leakage harmonics plus this additional power. The low-frequency video signal from this superheterodyne (or homodyne) detector was amplified in a shielded video amplifier (voltage gain $=100$) and presented on an oscilloscope.

An over-all schematic view of the apparatus is shown in Fig. 2. The dc bias field of up to 350 G was produced by water cooled Helmholtz coils. The cavity and tin sample were cooled by liquid helium contained in a standard set of Dewars. A manostat was provided for control of the operating temperature. The cavity was evacuated to a pressure $<5\times10^{-6}$ mm Hg to prevent any sparking that might be caused by the very strong rf electric field.

The early data were taken with the tin sample cemented by epoxy resin to the end of the cavity. The back of the sample was thus in direct thermal contact with the liquid helium. It was difficult to make tight seals consistently by this method of mounting and it was later abandoned in favor of another method that could also be used for thin film samples. In this method the sample was held inside a demountable vacuum chamber. A spring-loaded cold finger pressed against the back of the sample. This provided good thermal contact to the bath. Although this arrangement did somewhat increase the size of heating effects, it provided much more flexibility in the handling of various types of samples.

III. EXPERIMENTAL RESULTS

A. Pure Bulk Tin

The initial experiments were done with pure bulk tin. This tin was specified as 99.999% pure and was obtained from the Vulcan Detinning Company. Samples of several geometric shapes were used since it was originally thought that the intermediate state pattern, which would depend on the shape, might influence the

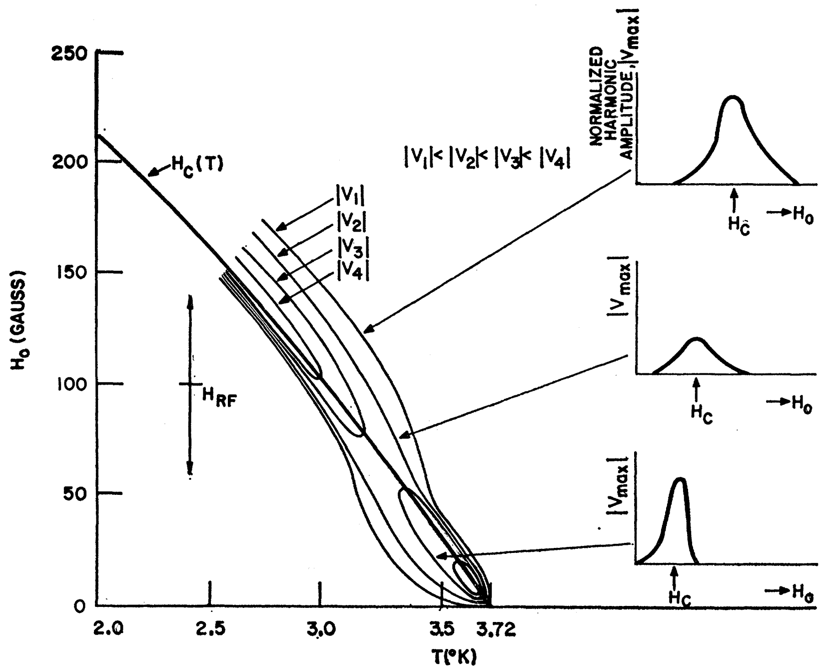

FIG. 3. Schematic representation of the harmonic amplitude, $|V|$, for pure bulk samples versus bias field, (H_0) and temperature (T). Contours of constant $|V|$ are shown. The insets give the harmonic amplitude versus H_0 at constant T.

switching behavior. These shapes were a cylinder 4 in. long and 1 in. in diameter, a rectangular plate 1 in.$\times\frac{1}{2}$ in.$\times\frac{1}{16}$ in., and several disks 1 in. in diameter by 2 or 3 mm thick. The disks were run frequently during the course of the experiment and served as checks on the consistency of the data. All these samples were formed by casting the metal in air or in a vacuum. They were polycrystalline with crystallite dimensions on the order of a millimeter. The surface exposed to the microwaves was polished on successively finer grades of emery cloth up to No. 4/0. Finally, a dull mirror finish was achieved by polishing with soft cardboard. The samples were usually left at room temperature for several days before being used; no additional annealing was done since the polishing method should not have introduced serious deep strains. Values of R_N for somewhat similarly prepared surfaces[14] were used.

Data were taken as follows: A standard amount of second-harmonic magnetron power, A_{LO}^2, was introduced into the crystal detector. Then harmonics from the tin, A_S^2, were introduced in addition to this local oscillator (LO) power. This altered the height of the pulses appearing on the oscilloscope. The total amplitude at the detector is given by $A_T \approx A_{\mathrm{LO}} + A_S \sin\delta$, where δ is the relative phase of the two signals. The signal on the oscilloscope, W, is proportional to A_T^2. Let V_M be the difference between the values of W for $\delta = 0°$ and $\delta = 180°$. Thus, $V_M \propto A_{\mathrm{LO}} A_S$. It is particularly convenient to observe values of V_M since a reversal of the direction of the bias field changes the phase δ by 180° (the effect is that of a half-wave rectifier rectifying on either the positive or negative half of the cycle). The value of V_M is found by continuously reversing the bias field while the phase δ is being adjusted. The maximum value of V found is just V_M. This procedure ensures that only harmonics caused by the switching of the tin are measured since spurious or leakage signals will not change on reversal of the bias field.

In order to obtain the absolute value of the harmonic power, the detection system was calibrated with the strong second-harmonic output of the magnetron: This power was sent unattenuated to a thermistor and power bridge and was also sent through a series of calibrated attenuators to the crystal detector; comparison of these two signals furnished the calibration of the detector.

In general, the temperature and input power were set at some predetermined value. The bias field, H_0, was then changed and values of V_M versus H_0 recorded. This procedure was then repeated for a different temperature or input power level. The data were always taken starting from $H_0 = 0$ since any possible flux trap-

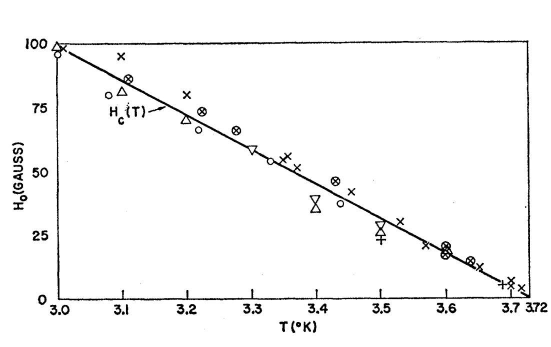

FIG. 4. Observed values of the bias field for maximum harmonic output versus temperature. Data are shown from a large number of samples. The solid curve is the critical field versus temperature.

ping effects would thus be minimized. All samples and geometries under all operating conditions showed less than 1 or 2% as much harmonic power as would be predicted for perfect switching. Thus, none of these samples showed any evidence for more than very partial switching in times on the order of $1/\omega \approx 2\times 10^{-11}$ sec. Since the observed switching effects were so small, it is likely that the switching time is actually much longer than this value.

Figure 3 shows schematically the kind of results obtained for pure bulk samples. The main figure is a contour map of harmonic amplitude versus bias field and temperature. Cross sections of this profile at constant temperature are shown in the insets. The insets, thus, correspond to the way in which data were taken. Since the harmonic amplitude should be proportional to the degree of switching, it is seen that switching is essentially completely absent both at low temperatures if $H_0 < H_c$ and also at $T \approx T_c$ if $H_0 > H_c$.

Figure 3 shows the *absolute* value of the harmonic amplitude, but the phase of this signal is not included. It was found that the phase changes rapidly by about 120° when the bias field changes from $H_0 < H_c$ to $H_0 > H_c$. The reasons for the occurrence of this phase change are not very clear; but due to the basic lack of symmetry, there is no particular reason to expect the phase to be the same when the rf field switches the specimen from fully superconducting to slightly less superconducting ($H_0 < H_c$) as when it switches the specimen from normal to only slightly superconducting ($H_0 > H_c$). In fact, under certain circumstances, it is possible for the surface resistance in the superconducting state to be greater than that in the normal state.[15] If it is speculated that this can occur when the switching is from normal to only slightly superconducting, this would lead to a phase change of 180° between the two cases. Also, nonlinear reactive effects are present and would lead to similar changes in phase, but probably not as large as 120°.

Within the fairly large scatter of the data, the results for all pure bulk specimens were the same, independent

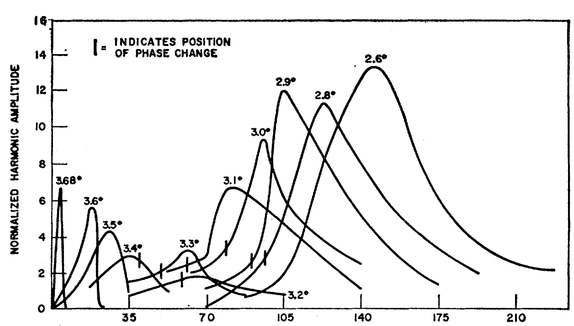

FIG. 5. The observed harmonic output versus bias field for a number of temperatures. These are smoothed curves for the cylindrical bulk sample.

[15] P. B. Miller (private communication).

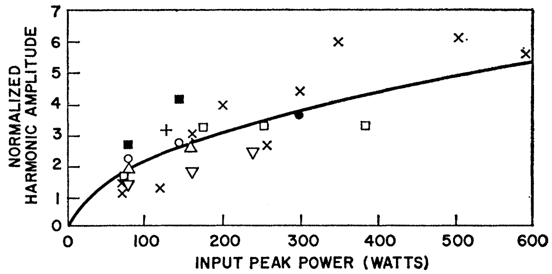

FIG. 6. The observed maximum harmonic output at 3.1°K versus input rf power. The solid curve is drawn for the harmonic power proportional to P_{rf}.

of the shape of the specimen or of its method of preparation. It might have been conjectured that the sample shape would be of considerable importance since the effect of the intermediate state on the switching behavior would be large if switching took place by movement of the boundary regions separating the normal and superconducting phases.[16] If these boundaries could move a substantial distance during a microwave period, the total surface area transformed from superconducting to normal would be proportional to the number of such boundaries. In the case of the long cylinder with axis perpendicular to H_0 (face parallel to H_0 and to H_{rf}), the intermediate state pattern would be fairly widely spaced and, for perfect symmetry, would also be perpendicular to the axis.[17] Therefore, very few of these boundaries would be found on the surface even if the experimental alignment were not perfect. If motion of the boundaries is necessary for harmonics, this geometry should then show practically no harmonics. The flat disk would have a much more finely spaced pattern and this pattern should intersect the surface exposed to the microwaves.[17,18] Thus, a much larger amplitude of harmonics would be expected. The two geometries showed the same harmonic amplitude, thereby ruling out boundary motion as the switching mechanism at these high frequencies. Further evidence on this point is given by the fact that no increase of harmonics was observed when an additional bias field was applied perpendicular to the disk since this should also increase the number of boundary regions. In addition, later experiments on thin films, where the intermediate state pattern should be very finely divided, also showed roughly the same magnitude of harmonics.

Figure 4 shows values of the bias field for which maximum harmonics were observed plotted against temperature. The points are for several specimens of pure bulk tin of various shapes. The solid curve is a plot of H_c versus T. It is seen that the points lie closely on this curve as would be expected from the simple

[16] B. Serin (private communication).
[17] A. L. Schawlow, Phys. Rev. **101**, 573 (1956).
[18] Even for quite accurate alignment of the surface of the disk parallel to the bias field, such a pattern should be observed. See also M. D. Reeber, IBM J. Res. Develop. **3**, 140 (1959).

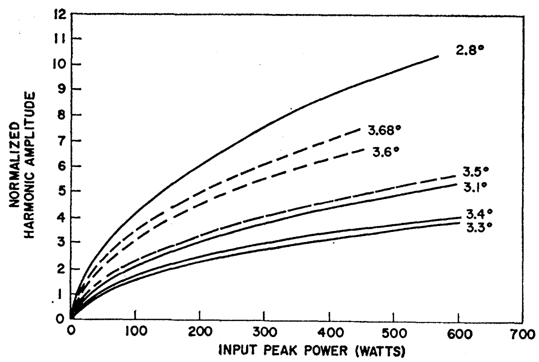

FIG. 7. Smoothed curves for the observed harmonic output versus input power at a number of temperatures.

analogy to a biased half-wave rectifier. It should be remarked that this was true only for the lower input power levels. Otherwise, heating gave rise to a shift of the points away from the $H_c(T)$ curve. This fact enabled a simple test for such heating effects to be made.

Figure 5 shows smoothed values of the harmonic amplitude observed versus bias field at constant input power for a number of temperatures. The curves shown are for the cylindrical sample of tin but are also typical of those for all sample geometries. The shapes of these curves can be roughly explained as will be shown later. The envelope of this series of curves gives the maximum harmonic amplitude produced versus temperature.

Figure 6 shows this observed maximum harmonic amplitude at a temperature of 3.1° versus peak input power delivered to the cavity. All the data taken over a period of eighteen months on a variety of specimens of different shapes are shown. All the points lie within $\pm 50\%$ of the solid curve. However, it should be remarked that the points shown as open circles, squares, or triangles have been adjusted somewhat relative to the others: the value of the input power was increased arbitrarily by 30% and the output power decreased by 30%. These data were taken after a move of the apparatus from one location to another and after several changes to this apparatus and the measuring equipment. In view of the difficulties involved in measuring absolute microwave power under such circumstances, it is felt that this adjustment, although arbitrary, is certainly conservative. The solid curve is drawn for the assumption that the output amplitude is proportional to the square root of the input power. Such a variation is expected if the nonlinear surface resistance changes abruptly with magnetic field. If the resistance change were gradual, the output amplitude should be proportional to the input power.

Similar curves have been obtained for other temperatures. For all such other temperatures except 2.8° and 3.0°, 90% of all points lie at worst within $\pm 50\%$ of a solid curve similar to that of Fig. 6 (the scatter at 2.8° and 3.0° is worse and it is also possible that these curves are fitted better by a linear rather than a parabolic curve; the data at these two temperatures should be considered with some caution because of bad statistics). Figure 7 shows a series of such curves. They are averages at each temperature of some 20 to 30 individual points taken over a wide period of time on many different samples.

Figure 8 shows the maximum output amplitude at a given input power versus temperature. The data from Fig. 7 were used to construct Fig. 8 and it is thus an average of a great many points. The initial increase in harmonics as the temperature falls below 3.73° is expected since R_S is rapidly decreasing. As the temperature decreases farther and $R_S/R_N \rightarrow 0$, the harmonic amplitude should become independent of temperature *if* the switching speed is independent of temperature. The amount of harmonic power observed is always less than a few percent of that which would be predicted for instantaneous complete switching. The minimum in harmonic power at intermediate temperatures may be connected with a change between the behavior predicted by the Ginzburg-Landau theory near T_c and that predicted at lower temperatures as will be explained later.

B. Tin-Indium Alloys

Inasmuch as the electronic mean free path is greatly reduced in an alloy, there might be several reasons for expecting switching to be faster than for a pure metal. The shortened mean free path might be effective either directly through the relaxation time for the normal and superconducting distribution functions or it could enter more indirectly through its effect on the coherence distance or on the skin depth. Of course, even if the switching time were independent of the electronic mean free path, the harmonic amplitude observed should be larger for an alloy because R_N and, hence, ϵ in Eq. (3) should be larger. Several tin-indium samples were investigated. The first was in the form of a 0.001-in. foil and was obtained from Alpha Metals, Inc. The indium content was 3.5% by weight. A foil was used in order

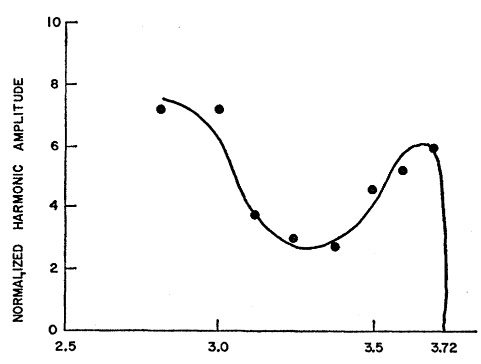

FIG. 8. The observed maximum harmonic output versus temperature. This curve is an average over all the data taken for all the pure bulk samples.

to decrease the over-all thermal resistance by a decrease of the thickness of the high-resistivity alloy material. This foil was mounted on a block of pure tin. It was either cemented on or pressed on by a hydraulic press. The latter method gave a better thermal contact between the foil and the block. It was found experimentally that this construction led to less heating than was found for a thin block completely composed of 3.5% indium alloy. In addition, a 1% sample was made in the form of a thin disk by melting and mixing together the correct amounts of the metals in a vacuum: the sample was then rapidly cooled. Both these samples were checked for the correct percentage of indium by x-ray fluorescence measurements. Also measurements of the lattice parameter by x-ray diffraction techniques indicated that the 3.5% sample was probably single phase and homogeneous.

Heating effects were difficult to avoid with these samples, both because of their greater power absorption and because of their lower thermal conductivity. This made it difficult to obtain detailed information on the harmonic output versus bias field. No harmonics were observed from the 3.5% sample with $H_0>H_c$. Heating may have been in part responsible for this fact, but, as will be explained later, one would not expect to observe harmonics for $H_0>H_c$ if the Ginzburg-Landau theory applies (as it should for short electronic mean free paths). At fields slightly less than H_c, data could be obtained only in a transient manner since the heating appeared to build up enough over a number of microwave pulses to make the sample normal. If the temperature of the sample is estimated by equating the field for maximum harmonic production to the critical field, $H_c(T)$, it is found that the data indicates that temperature shifts relative to the bath of up to $\frac{1}{2}°$ occurred for an rf field of 10 G. The actual peak temperature rise might have been greater than this since the temperature was changing during a pulse.

Values of the surface resistance, R_N, were estimated

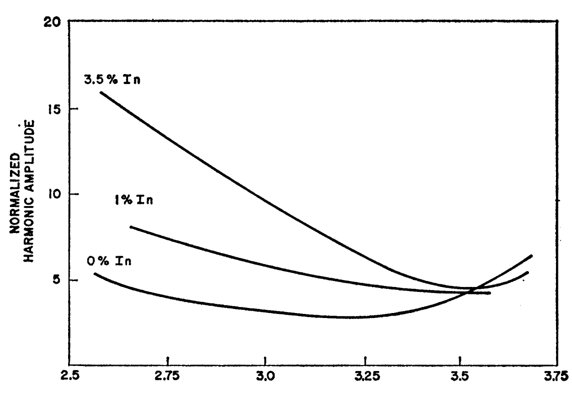

FIG. 9. The observed maximum harmonic output versus temperature for bulk alloy samples.

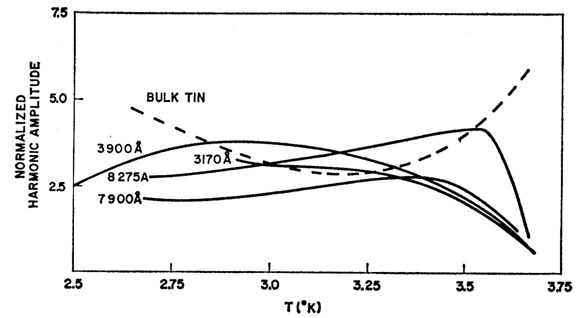

FIG. 10. The observed maximum harmonic output for thin film samples of various thicknesses.

from the data of Sturge.[19] His values of $r \equiv R_S/R_N$ at 4800 Mc/sec for samples of 0, $\frac{1}{2}$, 1, and 2% indium concentration were extrapolated to 3.5% with the aid of the classical skin-effect theory (corrections for the anomalous skin effect are small except for the 0% sample). The values for the 1 and 3.5% samples were than scaled upwards in frequency by the semiempirical relationship $r(\nu)/r(\nu')=\nu/\nu'$, which should be valid for the range $\nu=5\rightarrow 10$ kMc/sec. The values of R_N for the 1 and 3.5% samples are then found to be 1.6×10^{-2} and 3.1×10^{-2} Ω/square. R_N for pure bulk tin is 0.7×10^{-2} and therefore it would be expected simply from the increased surface resistance that the alloy samples should give an harmonic amplitude 2.3 and 4.4 times larger.

Some of the data on harmonic amplitude versus temperature for alloy samples are shown in Fig. 9. It is seen that at low temperatures the harmonics are increased by factors of 1.7 and 3.0 over that for the pure samples (the 1% curve is less reliable because of the much smaller number of points). This increase is slightly less than was predicted above from the increased surface resistance alone. Thus, no evidence is found for a faster switching speed in these alloys. Near T_c, the results are probably unreliable because the heating is too great. There is also some evidence that the increase in harmonic amplitude with input power is less than for the pure bulk samples. This is again probably evidence of heating and the correct harmonic amplitude may be underestimated somewhat for this reason. Some effects of heating are even evident in Fig. 9 for the pure bulk sample in this sample holder. In summary, the data on alloys do give at lower temperatures a fairly reliable indication of the amount of harmonic output, but the results cannot be trusted as to the finer details.

C. Thin Films

Data were also taken on a number of thin tin films. The original expectation was that, as for the tin-indium samples, the reduced electronic mean free path and

[19] M. D. Sturge, Proc. Roy. Soc. (London) **246**, 570 (1958), and private communication.

other effects might increase the switching speed. However, no evidence was found for an increased switching speed for any film and, further, it was found that films thinner than about 2000 Å showed almost no evidence of harmonic output.

All the films investigated were evaporated on z-cut single crystal quartz substrates which were carefully precleaned (quartz was used for its good low-temperature thermal properties). The tin charge was outgassed before evaporation and the substrates were cooled to liquid-nitrogen temperatures. Some of these films were supplied by R. H. Blumberg and were deposited under highest vacuum conditions. The others were evaporated when the vacuum was at least 5×10^{-7} mm Hg before the evaporation was begun. The film thicknesses were measured by standard interferometry methods. All the films had no obvious imperfections and had good mirror surfaces, but they were not individually examined in detail.

The dc bias field was applied to both sides of the film. The rf field was applied to only one side. Under these conditions, the rf field should decrease to a very small value on the other side.[20] This should be true in the normal state as well as in the superconducting state: The normal skin depth, δ_N, is simply substituted for the penetration depth, λ, in the results of Ref. 20. The presence of a copper surface on the other side of the thin quartz substrate should further ensure that this field is small.

The heating was rather large and was comparable in magnitude to that for the tin-indium alloy. Other uncertainties might arise from the effects of strains, defects, occluded gas, grain structure, and crystal orientation. Except for such effects, the data for the thicker films should approach that for bulk tin samples.

In Fig. 10 curves are shown for the harmonic amplitude observed for a number of these films of different thicknesses, d. The temperatures shown are not the bath temperatures, but (as for the alloys) are the values of temperature derived by equating the bias field for maximum harmonic output to the critical field. The shape of these curves is quite different from that for bulk specimens and indeed the shape even varies somewhat from specimen to specimen. This latter is probably an effect of heating. In addition to the results shown in Fig. 10, similar power outputs were observed for several other films of the following thicknesses: 2000, 3500, and 3600 Å. It can be seen that the maximum harmonic output is comparable to that observed for the pure bulk samples. Therefore, there is no evidence for an increased switching speed for these films.

Also, a number of thinner films of the following thicknesses were investigated: 800, 1280, 1420, and 1780 Å. Practically no harmonics were observed from any of these films and it might therefore be concluded that the switching of films thinner than approximately 2000 Å at these high frequencies is even more difficult than for the other types of samples. However, it will be seen later that the explanation for this lack of harmonics probably lies elsewhere.

[20] E. Erlbach, R. L. Garwin, and M. P. Sarachik, IBM J. Res. Develop. 4, 107 (1960).

IV. THEORY AND DISCUSSION

It is obvious that the usually discussed limitation on the switching speed, namely, the growth of domains as limited by eddy currents, has no relevance when the switching fields are confined to a distance small compared to the coherence distance and when the frequency is so high that any lateral motion of any pre-existing domains must be small. For the pure bulk specimens at the lower temperatures, the switching can be discussed on the basis of a nucleation mechanism which has been proposed in a previous paper.[13] In brief, this mechanism is that the switching speed is limited by a spatial rather than by a purely temporal effect: At fast switching speeds and, hence, at high frequencies, the skin depth becomes so small that this thin layer is prevented from changing its state by the presence of the large amount of unswitched adjacent material. This mechanism leads to the prediction of a rather long switching time ($\sim10^{-10}$ sec). Hence, any purely temporal restrictions on the switching speed would probably not be observable in the presently described experiments.

The Ginzburg-Landau phenomenological theory of the behavior of superconductors in applied magnetic fields[21] should correctly describe the effects observed for the pure bulk samples at temperatures near T_c and for the alloy samples to rather lower temperatures. It will be seen that consideration of the variation of the order parameter with field, particularly in the metastable supercooling and superheating regions, does provide a good qualitative understanding of the observations.

A. Pure Bulk Specimens

(1) At the lower temperatures, a straightforward treatment of the high-frequency, high-field behavior from the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity is presently not possible. Therefore, the subterfuge will be adopted here of considering as a normal metal all parts of the superconducting metal in which a current or field greater than the critical value is present. If this hypothesis is made, the results of theories directed at the analysis of layers or sandwiches of superconducting and normal metals[22,23] can be used.

The approaches of Parmenter and Cooper lead to substantially the same results in this application. Since the latter can be more intuitively explained, our considerations will be limited to it here. The BCS

[21] V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950).
[22] R. H. Parmenter, Phys. Rev. **118**, 1173 (1960).
[23] L. N. Cooper, Phys. Rev. Letters **6**, 689 (1961).

theory shows that the energy gap for a pure superconductor is determined by

$$\epsilon_0 = 2(\hbar\omega)_{av} \exp[-1/N(0)V], \tag{5}$$

where $N(0)V$ is the density of electrons at the Fermi surface multiplied by the negative of the interaction energy per electron pair. $N(0)V$ should clearly vary from metal to metal. It is positive for superconducting electron pairs in a superconducting metal. Since it is energetically unfavorable to find such superconducting pairs in a normal metal, $N(0)V$ should be negative (or at the least zero) in this case. Cooper has assumed that $N(0)V$ is zero in this case. Thus, the effect of a layer of normal metal on a superconducting metal is to just dilute $N(0)V$ according to the relationship

$$[N(0)V]_{N+S} = [N(0)V]_S [t_S/(t_S+t_N)]. \tag{6}$$

Thus

$$\epsilon = 2(\hbar\omega)_{av} \exp\left[-\frac{1}{N(0)V_S}\frac{(t_N+t_S)}{t_S}\right]. \tag{7}$$

(The factor involving electron reflection at the interface is absent in our case since only one metal is involved.)

The factor $(t_N+t_S)/t_S$ will be different in the two cases where the normal metal is being switched to superconducting or the superconducting metal is being switched to normal, that is whether the bias field is such that $H_0 > H_c$ or $H_0 < H_c$. In the first case, $t_S = \delta_N$, where δ_N is the skin depth in the normal material. The value of (t_N+t_S) is determined by letting $(t_N+t_S) = \xi_0$. (It is assumed that the switching frequency is high enough that the switching is only partial and therefore that the spatial configuration of the magnetic field does not vary during the switching cycle.) It is necessary to establish a criterion for whether or not switching has taken place. It will be assumed that switching does take place if the surface resistance changes at least from R_N to $(R_S+R_N)/2$, that is by one-half as much as it would for perfect switching [if $H_0 < H_c$, the change must be at least from R_S to $(R_S+R_N)/2$]. It can be shown from inspection of experimental data on R_S versus T that R_S at 10 000 Mc/sec becomes equal to $(R_S+R_N)/2$ for an energy gap $\epsilon \approx kT$. This is approximately equivalent to $\epsilon \approx \epsilon_0/5$ for the temperature range of interest. This size of gap is predicted when t_N/t_S is such that

$$\exp\left[-\frac{1}{N(0)V_S}\frac{t_N}{t_S}\right] \approx \frac{1}{5}. \tag{8}$$

This equation is satisfied, for $N(0)V_S = 0.30$ and $\xi_0 = 2500$ Å, by $t_S = \delta_N = 1700$ Å. The normal skin depth has this value at approximately 5000 Mc/sec, which corresponds to a switching speed of $1/2\pi\nu = 0.3 \times 10^{-10}$ sec. Thus, at 10 000 Mc/sec and at low temperatures the switching would be only incomplete or partial, as is observed experimentally.

The amount of switching for the second case, $H_0 < H_c$, would be very much smaller than this. Since $t_N \approx \lambda = 500$ Å, the field changes $[N(0)V]_{N+S}$ only from $N(0)V_S$ to $\frac{4}{5}N(0)V_S$ in a switching cycle; this increases R_S only slightly from its already small value. Thus, practically no harmonics should be observed for $H_0 < H_c$ at low temperatures, in agreement with experiment. It might be objected that this approach leads at low temperatures to a frequency independent limitation on switching. However, at sufficiently low frequencies new effects can occur such as motion of *S-N* boundaries and nucleation and growth of new sites. These effects will then allow switching to take place.

The above treatment could in principle be improved in one respect: the assumption that $N(0)V$ is zero for $H = H_0 + H_{rf} > H_c$ is obviously incorrect. In the presently used sense, $N(0)V$ is probably zero for $H = H_c$, but it may become increasingly negative as H becomes greater than H_c.[24] However, the way in which $N(0)V$ might vary with H is unknown. Even if some arbitrary variation were assumed, this would bring at least one new parameter into the theory which could not be evaluated from presently available experimental information. Thus, improvements over the present simple assumption that $N(0)V = 0$ for $H > H_c$ probably cannot be made until the microscopic theory is extended to include both high field and spatial variation effects.

(2) Although at the lower temperatures, harmonics are observed primarily only when $H_0 > H_c$ (as is expected from the above considerations), at $T \sim T_c$ the situation is reversed and harmonics are observed mainly for $H_0 < H_c$. This can be understood by reference to the Ginzburg-Landau (G-L) theory. One condition for the validity of the G-L theory is that $\lambda(T) > \xi_0$. For pure bulk tin, this is strictly true only if $3.68 < T < 3.72°$. However, use of the G-L theory gives fairly reasonable results in other contexts to rather lower temperatures and it does not appear unreasonable to discuss the switching behavior down to 3.4° at least qualitatively from the G-L theory.

A discussion of the dependence of the G-L order parameter, ϕ, on magnetic field for thin films has recently been given.[25] A similar discussion has been given[26,27] for the case of the semi-infinite bulk superconductor. The type of variation obtained for such semi-infinite specimens is shown in Fig. 11, where ϕ_e and H_e are the values at the surface of the specimen

[24] Similar considerations have recently been discussed [D. H. Douglass, Jr., Phys. Rev. Letters **9**, 155 (1962)] in a treatment of layers of dissimilar metals. In this treatment, the negative free energy of the superconducting metal was averaged spatially with the positive free energy of the normal metal in the superconducting state, the magnitude of the latter being different for different normal metals. For very thin normal metal layers, the spatial averaging of the free energy is identical with the averaging of $N(0)V$ as suggested by Cooper. For thicker layers these procedures are not identical and, because of the cooperative nature of the superconducting state, the latter is perhaps to be preferred.

[25] P. M. Marcus, in *Proceedings of the Eighth International Conference on Low Temperature Physics* (to be published).

[26] P. M. Marcus (private communication).

[27] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **34**, 113 (1958) [translation: Soviet Phys.—JETP **7**, 78 (1958)].

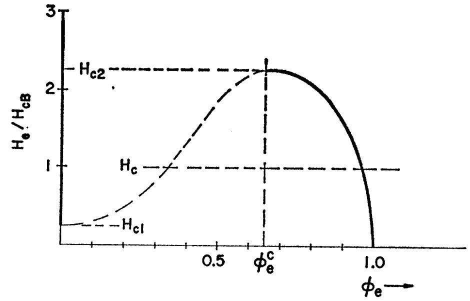

FIG. 11. The approximate dependence of the G-L order parameter, ϕ, at the surface of a pure bulk specimen versus the value of the bias field at the surface. H_{c1} is the value of the field for maximum supercooling and H_{c2} that for maximum superheating. A value of $\kappa=0.165$ is assumed.

(H_{cB} is the critical field for bulk material). For static or slowly varying fields, the order parameter follows the heavy curves as the field is changed *as long as* H is not between $H_{c1}<H<H_{c2}$ (in this range the superconductor will, in general, enter the intermediate state). However, for rapidly varying fields there will be insufficient time available for the superconductor to enter the intermediate state and the order parameter will *always* follow one of the heavy lines depending on whether $H_0>H_c$ or whether $H_0<H_c$ (in the latter case we consider only the superconducting fraction of the surface area). The lack of harmonics for $H_0>H_c$ is now readily understood. In this range of bias fields the order parameter and hence the energy gap *remains strictly zero* as long as $H=H_0\pm H_{\mathrm{rf}}>H_{c1}$. Since both theoretically[27] and experimentally[28] $H_{c1}\approx H_c/4$, large rf fields are necessary before the gap could begin to develop at all. Even then the surface resistance would be decreased only at the peak of the rf cycle, thus producing only a small harmonic output. In fact, it is not clear that such a first-order phase transition for $H<H_{c1}$ can take place at all in the very short time available. Thus, the pronounced supercooling effectively prevents switching from taking place for $H_0>H_c$.

The conditions for a change of the gap are not so stringent if $H_0<H_c$. In this regime, $\partial\phi_e/\partial H\neq 0$ and there is always some change in surface resistance with field. This change is not large because even the maximum possible change in ϕ_e is only $1-\phi_e{}^c=0.35$ (the surface resistance changes from R_S to R_N only if ϕ_e changes from 1 to 0). It should be noted that the full range of superheating can be traversed by the rf field in contrast to the case for a dc field. Again, it is not clear that a first-order phase transition can occur in these very short times even if $H>H_{c2}$.

It should be recognized that the type of switching discussed above should not be thought of as a permanent change of state. The surface of the metal is still superconducting, but the energy gap at the surface has been substantially reduced and this increases the microwave surface resistance for a part of the rf cycle.

The above discussion gives a good qualitative understanding of how the harmonic power output for pure bulk samples depends on temperature and on bias field. The only apparent difficulty is in the dependence of the harmonic amplitude, A_2, on the power level of the switching field, P_{rf}. The solid curves in Figs. 6 and 7 are drawn for $A_2\propto P_{\mathrm{rf}}{}^{1/2}$ and these curves appear to fit the experimental data reasonably well. This is the dependence that would be expected if the switching were complete. It corresponds to an *abrupt* change of the surface resistance between a constant value characteristic of the superconducting state and a constant value characteristic of the normal state. The experimental data are most reliable for $T\ll T_c$. Theoretically, in this range whether the surface resistance changes abruptly or not with H depends on whether $[N(0)V]_{N+S}$ changes abruptly or not. The experimental data thus indicates that $[N(0)V]_{N+S}$ does change rather rapidly with field in the neighborhood of H_c. However, very near $T\sim T_c$ there appears to be no reason for the order parameter to change in this abrupt manner and therefore A_2 should in principle be proportional to P_{rf}. Heating effects and the scatter of the data near T_c may make such detailed comparisons based on the experimental data unwarranted.

B. Alloy Bulk Specimens

The results for the 1 and 3.5% indium samples differ from those for the pure tin samples in two respects. The harmonic power produced is greater and it is generated primarily at $H_0<H_c$ at all the temperatures investigated (the data for the 1% sample may not be quite complete on these points). Since the electronic mean free paths of the 1 and 3.5% samples should be about 2×10^{-5} cm and 0.5×10^{-5} cm, respectively,[19] the coherence distance, ξ_0, will be considerably reduced from its bulk value of 2.5×10^{-5} cm in both cases. Thus, the condition, $\lambda(T)>\xi_0$, for the validity of the G-L theory is satisfied down to much lower temperatures and, therefore, harmonics are expected over a wide range of temperatures only if $H_0<H_c$, as is observed.

The amount of harmonics expected for the alloy samples should be greater just on the basis of their higher surface resistance. In fact, the observed power is near that predicted from the results for pure samples by use of existing experimental data on the surface resistance of tin-indium alloys. However, the G-L theory predicts that relatively more harmonic power than this should be expected for these alloys. The shape of the curve of Fig. 11 depends on a parameter, κ, where $\kappa\approx\lambda_0/\xi_0$. $\kappa\approx0.2$ for tin and it increases with increasing alloying since λ_0 is increased and ξ_0 decreased. $H_{c2}/H_c\propto1/\sqrt{\kappa}$ and also $\partial\phi_e/\partial H\propto\kappa$ for small H.[27] Thus, an increase in κ should increase the change in gap (and hence in surface resistance) for a given H_{rf}. This increase

[28] T. E. Faber, Proc. Roy. Soc. (London) **241**, 531 (1957).

should be quite substantial for the 3.5% alloy, but experimentally this increase is not observed.

The fact that less power is observed from the alloy samples than is predicted could be caused by experimental difficulties, especially heating, as described previously. It is also slightly possible that presence of the mixed state is responsible since the interphase surface energy becomes negative in the region of $3 \rightarrow 3.5\%$ indium. However, it is not clear that the mixed state would behave very differently from the intermediate state except at $H_0 > H_c$.

C. Thin Film Specimens

The thin film specimens show a behavior rather similar to that of the alloy samples if the film thickness is such that 2000 Å $<d<$ 10 000 Å. However, films thinner than 2000 Å show practically no harmonic output. The first of these facts is rather difficult to explain, while the second (although it seems the more unexpected) does have an explanation from the G-L theory.

It would be expected that the thicker samples would behave rather similarly to the pure bulk samples since for these samples $\xi_0 < d < 4\xi_0$. These films were carefully evaporated and presumably should not be sufficiently contaminated to make the G-L theory apply. Thus, except near T_c, harmonics should be expected only for $H_0 > H_c$, while experimentally harmonics apparently are present as well for $H_0 < H_c$. It is conceivable that heating effects for these thin films are sufficiently great to make the experimental result unreliable (especially since, for the reasons previously described, H_c is essentially defined as the bias field for which maximum harmonic output is observed) or that sufficient gas is present in the film that the G-L theory applies.

If the G-L theory applies for the thinner films (there is some uncertainty as to whether boundary scattering effects can be treated identically to impurity scattering effects in determining ξ_0), the lack of harmonics for $d<2000$ Å can be understood by reference to Fig. 12, which is reproduced from Ref. 25. This figure gives the locus of points for which ϕ becomes zero for various values of the field applied to the two sides of a thin film. In the present experiments, the bias field was applied equally to both sides of the film, so that $H_1 = H_2 = H_0$. Maximum harmonic output was observed when $H_0 \approx H_c$ and these bias points are shown by the two crosses for the two film thicknesses. The rf field was applied to only one side of the film and, thus, varied only the value H_1. Thus, $H_1 = H_0 \pm H_{rf}$. For the thicker films an increase of H_1 tends to make the film normal and a decrease makes it more superconducting. For the thinner films, both an increase and a decrease tend to make the film more normal. Even if $H_0 < H_c$, it can be seen that the change in order parameter and hence in surface resistance is fairly symmetric about H_0 and, thus, the second harmonic output should be greatly decreased (the third harmonic should still be present, but probably is at too low a level to be detected).

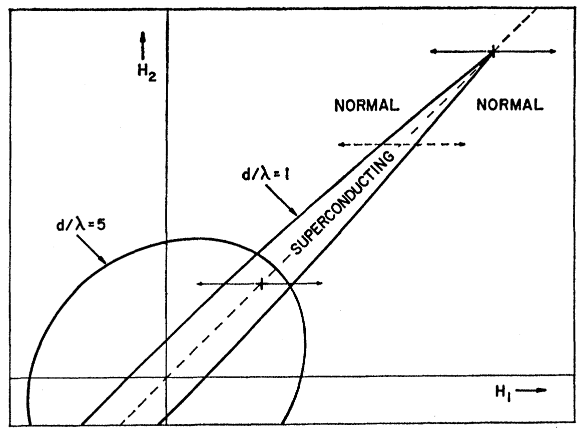

FIG. 12. The stability limits of the superconducting state for thin films of different thicknesses as functions of the magnetic fields at the two surfaces of the film. (Ref. 25) The crosses show preferred values of the bias field, $H_0 \approx H_c$, for the two films, and the arrows show the range of fields then covered by the rf magnetic field.

Thus the lack of harmonic output does not necessarily mean that the film is not switching. If the switching signal were unidirectional, switching would take place and the amount of switching might be comparable to that observed for the bulk specimens and for the thicker films. It would also be expected that for the very thin films harmonics would be observed if the rf field were applied in phase to *both* sides of the film since in that case H_1 is always equal to H_2 and the arrows denoting H_{rf} should be drawn at 45° to the axes. Such experiments have not been performed.

In recapitulation, the above discussion does give a good qualitative description of almost all the salient experimental facts. The few exceptions seem to be for cases in which heating effects may make the experimental findings not completely trustworthy. The discussion does not include any purely temporal limitations on the switching speed. This should not be construed to mean that such limitations do not exist, but only that they are not necessary to explain the results of the presently described experiments.

Note added in proof. Production of the third harmonic of 9400 Mc/sec waves by thin tin films has recently been reported by K. Rose and M. D. Sherrill [Bull. Am. Phys. Soc. 8, 233 (1963)]. The size of the film and the microwave tuning structure were adjusted for optimum impedance matching. This greatly increased the sensitivity since the microwave power absorbed by the film and hence the harmonic power radiated were both maximized. It is not yet clear whether the amount of third harmonic power observed corresponded to complete or partial switching. However, it appears that this experiment would not be limited by the same physical phenomena that are discussed above. Thus, their experiment may indicate whether or not there is a purely temporal limitation on the switching speed. This is seen by reference to Fig. 12 above. The rf field would carry the film during one rf cycle from the origin first approximately in the direction $-45°$ and later at $+135°$ to the H_1 axis. The G-L order parameter therefore should change from its maximum value to zero twice during the cycle. There thus would appear to be no spatial or symmetry limitations on the *third* harmonic production, and this experiment may therefore be able to reveal any purely temporal limitations on the switching speed of fairly thin films. However, for thicker films and for bulk material where the critical fields are large and the transition may be a first-order one, the ultimate speed is probably always limited by nontemporal effects similar to those discussed above.

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Question of Superconducting Iron

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Iron films have been evaporated in ultra-high vacuum onto substrates cooled to liquid-helium temperature. Contrary to the results of Mikhailov *et al.*, no evidence of superconductivity was found in these films. Vanadium films evaporated under similar conditions had superconducting transition temperatures of approximately bulk value. A low-temperature structure modification was indicated for very thin films of iron as well as vanadium. Measurements on oxygen-doped films showed that the low-temperature structure was greatly stabilized by gaseous impurities.

THE detection of superconductivity in a ferromagnetic superconductor is complicated by the masking effect of the spontaneous magnetization. Ginzburg[1] and others[2] have shown that this masking effect might be considerably reduced for samples in the shape of thin films. Thus, it was of interest to look for superconductivity in thin ferromagnetic films; and in fact, Mikhailov *et al.*[3] have reported the existence of superconductivity in thin films of iron evaporated onto liquid helium-cooled substrates. In a more recent investigation Lazarev *et al.*[4] did not confirm this result. In view of this disagreement and the general interest in the relation between superconductivity and ferromagnetism, we felt it would be desirable to repeat the experiment under carefully controlled conditions.

EXPERIMENTAL

Figure 1 shows our evaporation chamber. The innermost Dewar is Pyrex and was filled with liquid helium. The lower end of this Dewar is flattened and polished. It serves directly as the substrate. Thus, liquid helium is in direct contact with the upper surface of the substrate. This design ensures that radiation from the hot-evaporation source will not cause appreciable heating of the lower substrate surface. Platinum electrodes were painted and fired onto the substrate to serve as contacts for resistance measurements.

The evaporation source was a series of three parallel, independent 0.4-mm-diam iron wires. Evaporation took place by sublimation of the wires by resistance heating. The iron wire as purchased was 99.999% pure with respect to all elements except carbon, oxygen, and nitrogen. The wire was fired by us in hydrogen to remove most of these remaining impurities before being placed in the vacuum system.

To reduce film contamination caused by the residual gas in the vacuum system, ultra-high vacuum techniques were used. Pressures in the 10^{-14} Torr range have been measured prior to film evaporation. *During* evaporation of iron a pressure of 5×10^{-10} Torr could be maintained at an evaporation rate of approximately 10 Å/min. Details of the vacuum technique have been published elsewhere.[5]

[1] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **31**, 202 (1956) [translation: Soviet Phys.—JETP **4**, 153 (1957)].
[2] G. F. Zharkov, Zh. Eksperim. i Teor. Fiz. **34**, 412 (1958) [translation: Soviet Phys.—JETP **7**, 286 (1958)].
[3] Yu. G. Mikhailov, E. I. Nikulin, N. M. Reinov, and A. P. Smirnov, Zh. Tekhn. Fiz. **29**, 931 (1958) [translation: Soviet Phys.—Tech. Phys. **4**, 844 (1959)].
[4] B. G. Lazarev, E. E. Semenenko, and A. I. Sudovtsov, Zh. Eksperim. i Teor. Fiz. **40**, 105 (1961) [translation: Soviet Phys.—JETP **13**, 75 (1961).
[5] J. C. Suits, in Transactions of the Ninth National Vacuum Symposium, 1962 (unpublished).