periment 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).

An important parameter of the film deposition process is substrate surface temperature during deposition. The temperature of the substrate surface was checked by means of a resistance thermometer consisting of a 30 000-Å-thick indium film. This film was deposited at the position of the iron film using a conventional bell jar vacuum system. Indium films are well suited as thermometers because their superconducting transition temperature is that of bulk indium (3.4°K) regardless of vacuum during deposition.[6] The substrate with the indium film on it was then sealed into the evaporation bulb. By pumping on the helium bath it was possible to cycle up and down through the transition temperature of the indium film. By noting the helium-bath temperature at which the resistance disappeared, it was possible to establish the substrate temperature rise due to opening the shutter and also due to operating the iron filament at various current inputs. In this way it was found that during an iron evaporation a substrate surface temperature of 3.3°K could be maintained by pumping the liquid helium to a temperature of 2°K.

Measurements of temperature above 4.2°K were made with a gold +2.1 at.% cobalt versus copper thermocouple fastened to the upper surface of the substrate.[5] Resistance measurements on the films were made by the four-probe method with maximum currents in the 10^{-9}–10^{-8} A range.

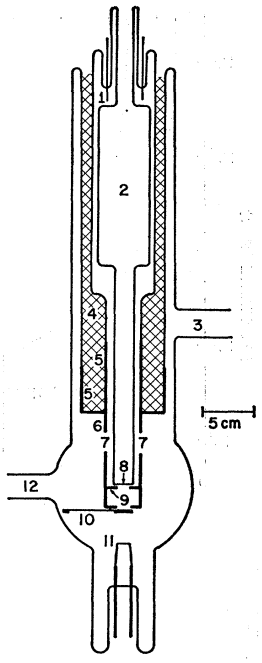

FIG. 1. Evaporation chamber: 1—feed-throughs for film current and potential probes; 2—liquid-helium Dewar; 3—to pumps; 4—liquid-nitrogen jacket; 5—Kovar cylinders; 6—copper; 7—holes in copper in order to pump by condensation onto 4.2°K surfaces; 8—substrate; 9—mask; 10—magnetically operated shutter; 11—filaments; 12—to cold-cathode magnetron gauge.

RESULTS

Our principal result is that at no time did the iron films show evidence of superconductivity even when evaporated at as low a temperature as 3.3°K and subsequently cooled down to 2.5°K.

We checked the evaporation and measuring technique by evaporating vanadium, a 3*d* metal known to be superconducting in bulk form (T_c=4.9°K[7]), and also known to be very sensitive to gaseous impurities.[8] Several vanadium films were evaporated and were found to be superconducting with transition temperatures greater than 4.6°K.[5] The vanadium wire used for the filaments was relatively impure (99.5%).

An abrupt, irreversible decrease in film resistance of about a factor of 4 for iron and 20 for vanadium was observed during the evaporations (Fig. 2). This decrease occurred at a film thickness very roughly estimated to be 50 Å for the iron and 200 Å for the vanadium. The evaporation of one vanadium film was stopped just after this resistance decrease had occurred. On initially warming this film to room temperature a positive temperature coefficient of resistance was observed over the entire temperature range, and the resistance versus temperature curve was essentially identical to that of a well-annealed film. *Prior* to the abrupt resistance decrease this film was not superconducting down to 3.5°K.

In order to investigate the effect on the electrical properties of gaseous impurities in the film, an iron film was evaporated at an oxygen pressure of 10^{-8} Torr. This oxygen pressure was produced by bleeding oxygen into the evaporation chamber through a silver leak.[9] The film deposition rate was about 2 Å/min which corresponds to about one oxygen atom hitting the substrate for each iron atom hitting the substrate. The resulting film was metallic looking and its resistance was of the same order of magnitude as expected for a metal.

This film did not show a resistance drop during evaporation even though it was slightly thicker than the iron film of Fig. 2. However, heating the film produced a sudden, irreversible drop in resistance at 75°K. This drop is shown as curve A of Fig. 3. On the following day the film was cooled down to 4.2°K and the film resistance followed the lower, reversible branch of curve A. (Curves B and C of Fig. 3 show data by Lazarev *et al.*[4] which will be discussed later.)

DISCUSSION

In Table I we have set down for comparison the principal experimental parameters of this type of experiment. In the first two investigations, ultra-high vacuum technique was not used and no measurements were made of vacuum during evaporation. In lieu of an actual measurement, it was impossible to estimate the vacuum during evaporation with any accuracy. This is

[6] H. L. Caswell, J. Appl. Phys. **32**, 2641 (1961).
[7] From the *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill Book Company, Inc., New York, 1962).
[8] J. D. Blades, J. F. Gerber, and C. T. Thomson, Solid-State Electron. **1**, 319 (1960).
[9] N. R. Whetten and J. R. Young, Rev. Sci. Instr. **30**, 472 (1959).

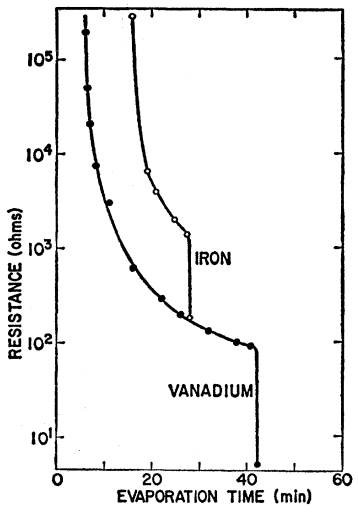

FIG. 2. Film resistance during evaporation. The substrate temperature is 3–4°K.

largely because liquid-helium-cooled surfaces are extremely high-speed pumps, but under certain conditions they may pump gas directly onto the substrate. Lazarev *et al.*[4] did, however, measure a pressure of 10^{-7} Torr prior to sealing off their evaporation chamber and immersing it in liquid helium.

How good a vacuum is necessary? For our films, assuming a sticking coefficient of unity, a rate of 5 Å/min at 5×10^{-10} Torr results in about 1% of impurity in the film due to residual gas. Data by Seraphim on oxygen, nitrogen, and hydrogen in bulk tantalum[10] indicate that 1% of any of these gases will lower the superconducting transition temperature by about $\frac{1}{2}$°K. On the assumption that a similar sensitivity applies for gaseous impurities in iron, we see that ultra-high vacuum is just barely good enough for obtaining reasonably pure iron films. As shown in Fig. 3, curve A, evaporation at 10^{-8} Torr greatly changes the film properties at these slow deposition rates.

The other parameters listed in Table I require little discussion. Important parameters not included in Table I were the same for all three investigations, e.g., type of substrate, range of film thickness and type of evaporation source.

Abrupt resistance decreases similar to those of Figs. 2 and 3 have been observed by others. Buckel and Hilsch[11] have made simultaneous resistance and electron diffraction measurements on a considerable number of materials. These measurements were made immediately after evaporation onto liquid-helium-cooled substrates and during subsequent warming of the film to room temperature. Many elements such as aluminum, zinc, and lead were found to condense on the cold substrate in their usual crystalline structure. These elements characteristically showed resistance versus temperature curves similar to curve C of Fig. 3. The resistance immediately after evaporation was abnormally high and this resistance gradually decreased upon initially warming the film to room temperature.

Two elements, bismuth and gallium, were found by Buckel and Hilsch to be amorphous immediately after deposition. These amorphous films were superconducting (T_c=6–8°K) even though bulk bismuth is not superconducting (except under high pressure[12]), and bulk gallium has a very low transition temperature (1°K). Heating these films after evaporation causes a sharp transition from the amorphous or highly quenched structure to a crystalline structure. This structure change is accompanied by a large, abrupt, irreversible change in film resistance.

We suggest that the sharp resistance decreases shown in Figs. 2 and 3 also indicate an amorphous to crystalline transition. In relatively pure films this transition occurs at 3°K during evaporation (Fig. 2), and in films heavily doped with oxygen this transition occurs at about 75°K (Fig. 3). Our interpretation of these resistance changes is suggested by these facts: (1) the resistance changes are abrupt, large, and irreversible as in the cases of bismuth and gallium; (2) the superconducting transition temperature of the vanadium was influenced by the change occurring at the resistance drop; (3) the vanadium showed a positive temperature coefficient of resistance when initially warmed to room temperature; and (4) the resistance decrease is strongly influenced by film thickness and impurity content as discussed below.

Antimony films deposited at low temperature have been found to be amorphous.[13] Also, antimony films deposited at room temperature have been found to be amorphous or crystalline depending upon the film thickness and impurity content. Ultra-high vacuum (10^{-9} Torr) antimony films are crystalline,[14] whereas

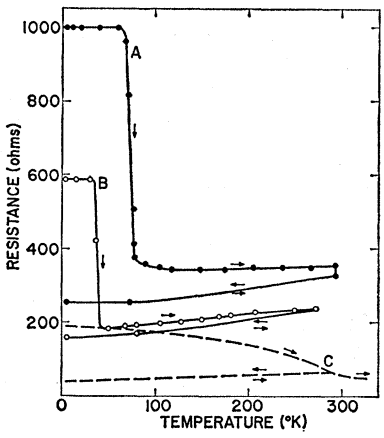

FIG. 3. A. Resistance of an iron film heavily doped with oxygen; B. Resistance of an iron film by Lazarev *et al.* (Ref. 4); and C. Resistance of a copper film by Lazarev *et al.* For curve C the numbers on the ordinate axis should be divided by 10.

[10] D. P. Seraphim, D. T. Novick, and J. I. Budnick, Acta Met. **9**, 446 (1961).
[11] W. Buckel and R. Hilsch, Physik. Verhandl. **2**, 102 (1951), and Z. Physik **138**, 109 (1954).
[12] P. F. Chester and G. O. Jones, Phil. Mag. **44**, 1284 (1953).
[13] W. Buckel, *Structure and Properties of Thin Films* (John Wiley & Sons, Inc., New York, 1959), p. 56.
[14] G. A. Condas and F. O. Wooten, J. Appl. Phys. **32**, 323 (1961).

TABLE I. Important parameters in low-temperature iron deposition studies.

Investigator	Vacuum during evaporation	Rate of evaporation (Å/min)	Substrate temperature during evaporation (°K)	Lowest measuring temperature (°K)	Method of measurement
Mikhailov *et al.*[a]	not measured est. 10^{-6} Torr[c]	2–3	~5[d]	4.2	inductance
Lazarev *et al.*[b]	not measured est. 10^{-7} Torr	1	not measured	1.2	resistance
This work	5×10^{-10} Torr	1–10	3.3	2.5	resistance

[a] See Ref. 3.
[b] See Ref. 4.
[c] B. T. Matthias (private communication).
[d] R. Chentsor, Usp. Fiz. Nauk **72**, 817 (1960) [translation: Soviet Phys.—Usp. **3**, 949 (1960)].

high vacuum films (10^{-6} Torr) are amorphous for slow evaporation rates.[15] The amorphous antimony films spontaneously transform to crystalline films when the film thickness becomes greater than a critical thickness in the range 100–300 Å.

Vanadium films deposited at room temperature have been observed by electron diffraction to have a thickness-dependent structure change.[16] Films with a thickness of 60–70 Å showed a face-centered cubic structure which is unknown in bulk vanadium. Vanadium films greater than 100 Å in thickness had the usual body-centered cubic structure. In addition to vanadium, unusual crystal structures were also observed in very thin films of beryllium, chromium, nickel, and cobalt. These results were explained[18] by assuming an additional term in the free energy, $2\sigma+\sum w_{ik}\sigma_{ik}$, where σ is the metal to vacuum surface energy, σ_{ik} is the metal-to-metal surface energy, and w_{ik} is the intergranular contact area. This term in free energy becomes important for very thin films and may give a normally unstable phase the lower free energy.

Returning again to iron films, we note that Mikhailov *et al.*[3] have observed that iron films thicker than 1000 Å are no longer superconducting. Also, they have observed that films heated above 20°K are irreversibly no longer superconducting. This strongly suggests that we may identify the superconductivity observed by Mikhailov as a property of a low-temperature structure modification, the presence and properties of which are strongly dependent upon impurities of some kind. Since our oxygen-doped films did not show superconductivity, we must conclude that either we did not have the right amount of oxygen in the film or, more likely, that gaseous (or metallic) impurities other than oxygen were important in the films of Mikhailov *et al.*[3]

Although Lazarev *et al.*[4] did not find superconductivity in their iron films, they did observe an abrupt resistance decrease at about 40°K. A curve from their paper is reproduced as curve B of Fig. 3. A rather remarkable resemblance to curve A may be noted. This suggests to us that the iron films of Lazarev *et al.* may have contained appreciable amounts of gaseous impurities. For comparison, data on copper by Lazarev *et al.*[4] is shown as curve C in Fig. 3.

CONCLUSION

We conclude that neither pure nor highly oxygen-doped films of iron are superconducting. Our results with very thin iron and vanadium films suggest that the results of Mikhailov *et al.* may be partly explained in terms of a low-temperature structure modification. Our results with oxygen-doped films suggest that the presence and properties of these modifications are strongly dependent upon film purity.

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[15] G. A. Condas, Rev. Sci. Instr. **33**, 987 (1962).
[16] A. I. Bublik and B. Ya. Pines, Dokl. Akad. Nauk SSSR **87**, 215 (1952).