Heat Effects in the Magnetization of Silicon Iron

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A brief description is given of the method used by Bates and his co-workers which permits the measurement of the thermal changes which accompany the step-by-step magnetization of ferromagnetic metals. The method has now been used to examine the behavior of 0.5 and 4 percent silicon iron in the untreated and annealed states when magnetized along the virgin curve and in cycles with fields up to 380 oersteds. In this work, some twenty copper-constantan thermocouples generate currents when a magnetic field acting on the ferromagnetic specimen is changed, and these are transmitted ballistically via a toroidal Mu Metal transformer to a highly sensitive moving coil galvanometer of long period. As the thermal changes in the present work were very small, a new technique had to be developed to deal with them. The measured thermal changes are plotted as functions both of the intensity of magnetization and of the effective magnetic field. The several errors and experimental difficulties, including asymmetry in thermal readings, stray induction effects, heating due to eddy currents, and thermal and electromagnetic disturbances experienced during the measurements are briefly discussed, and the methods used to overcome them are briefly outlined.

The results are examined in the light of current domain theory and a theoretical procedure developed by Stoner and Rhodes, in which the thermal contribution resulting from change in intrinsic magnetization, often described as the magnetocaloric effect, is subtracted from the recorded thermal change, and the residue is considered in detail. Another procedure recently applied to results for nickel was also examined, but it was found inapplicable to the silicon iron data. An unusual depression or dip is found in the curves of thermal change plotted as a function of the applied field when the region of low field values is reached upon reducing the field from the maximum used in describing a hysteresis cycle. This observation provides evidence in support of Kittel's theory of flux closure which Bozorth has used to explain the low remanence of such alloys which exhibit little magnetostriction and magnetic anisotropy and small internal strain. It is suggested that the strange depression may be correlated with some peculiar domain boundaries recorded by the Bitter powder technique on the (100) surface of a single crystal of silicon iron when it is demagnetized either thermally or in the above manner. These boundaries "wriggle" in an extraordinary manner which suggests that they separate regions either of flux closure in opposite directions or domains whose magnetization vectors meet head-on.

I. INTRODUCTION

IN a series of papers,[1–7] experiments on the thermal changes which accompany the magnetization of some ferromagnetic metals on making step-by-step changes in an applied magnetic field have been reported. The study has so far been confined to low and moderate fields, and the purpose of the investigations is to gain insight into the complicated hysteresis phenomena which exist in these regions. The behavior of iron, nickel, and cobalt and of many of their alloys have been described, and a resumé of the more important results was given at the Grenoble Colloquium (1950).[7] In the present communication are reported experiments made with specimens of silicon iron containing approximately 0.5 and 4 percent silicon, both in the untreated and in the annealed states.

Ewing was the first to emphasize the smallness of the temperature changes which result on taking a specimen of iron of reasonable purity through a single hysteresis cycle, and it is now well known that if temperature changes are to be measured as a cycle is described with step-by-step changes in magnetic field, the recording system must be capable of detecting changes of the order of 10^{-6} °C. The method used in the present work follows that described by Bates and Weston in 1941 and will be only briefly outlined here.

The specimen under investigation is usually in the form of a rod or stout wire, some 40 cm long and about 0.5 cm or less in diameter. It is mounted symmetrically inside a vertical water-cooled solenoid which supplies the magnetizing field, while the vertical component of the earth's magnetic field is separately compensated. The magnetizing current can be varied in steps by connecting or cutting out resistances in parallel with the magnetizing solenoid, a choke of high inductance and low resistance being permanently in series with the supply from the mains, to avoid too rapid field changes with consequent serious eddy-current heating of the specimen.

Attached to the specimen are the "hot" junctions of some 20 copper-constantan thermocouples, the "cold" junctions being close to, but not in contact with, the specimen. Each thermocouple has its own primary winding on a Mu Metal spiral core or transformer, the secondary winding of which is connected to a sensitive galvanometer of long period. The galvanometer scale distance is of the order of 8 meters, and the ballistic deflections are observed with a large telescope. When the field is changed, the temperature of the specimen changes by about 10^{-5} °C, and a current flows in each thermocouple circuit; the flux through the secondary winding of the transformer changes and then remains constant for a short time so that the galvanometer gives a ballistic deflection, after which the galvanometer spot returns to its zero position.

[1] L. F. Bates, J. phys. et radium 10, 353 (1949).
[2] L. F. Bates, J. phys. et radium 12, 459 (1951).
[3] L. F. Bates and J. C. Weston, Proc. Phys. Soc. (London) 53, 5 (1941).
[4] L. F. Bates and A. S. Edmondson, Proc. Phys. Soc. (London) 59, 329 (1947).
[5] L. F. Bates and E. G. Harrison, Proc. Phys. Soc. (London) 60, 213 (1948).
[6] L. F. Bates and D. R. Healey, Proc. Phys. Soc. (London) 55, 188 (1943).
[7] L. F. Bates and J. H. Davis, Proc. Phys. Soc. (London) 63A, 1265 (1950).

These deflections are calibrated by producing a calculated adiabatic cooling of the specimen by suddenly hanging a weight from its lower end, in accordance with the Joule expression

$$\Delta T = -\alpha TF/J\rho SA \quad \text{or} \quad \Delta Q = -\alpha TF/A,$$

where ΔT is the change in temperature which occurs when a tension F dynes is applied to a rod of coefficient of expansion α; specific heat is S, density ρ, and area of the cross section A, at the absolute temperature T. It is usually more convenient to calculate the corresponding quantity of heat ΔQ expressed in ergs per cc.

The magnetizing solenoid, 70 cm long, consisted of some 10 000 turns of No. 21 S.W.G. glass-covered wire wound in 15 layers on the outside of two concentric brass cylinders through which cooling water circulates at a maximum rate of over a liter per minute. The solenoid is energized from the 220-volt dc mains.

II. PREPARATION AND MOUNTING OF SPECIMENS

The silicon iron specimens were supplied as long bars, one inch in diameter, which were cut into four quadrants. From these quadrants specimens were ground to shape by hand because of the brittle nature of the material. The final surface was not as satisfactory as those of specimens normally used in such work, and, since the specimens were not of strictly uniform diameter, the average diameter for use in the calculation of intensities of magnetization was therefore found by measuring the length of fine wire in a search coil of known number of turns wound tightly upon a specimen.

The prepared specimen was attached by sockets and grub screws to a brass extension piece supported from the top of the solenoid housing; a second brass extension piece carrying a link to support the calibration load was similarly attached to the lower end of the specimen. The constantan portions of the thermocouples were made as short as possible, and the thermojunctions were filed thin to give minimum thermal capacity. The thermocouples were made of strips of copper and constantan, 3 mm wide, rolled from No. 20 S.W.G. wire, and were shaped in a jig to fit the specimens. The thermocouple leads were made as thick as possible and as long as necessary to give a good distance between the solenoid and Mu Metal core.

The thermojunctions were bound to the middle third of the specimen with waxed thread, for it is important that the specimen shall be able to expand and contract as freely as possible. When the junction was covered with a small quantity of paraffin wax, the disturbing effects of galvanometer drift resulting from convection currents within the solenoid were very greatly reduced, although of course the thermal capacity of the thermocouple system was thereby increased and the sensitivity of the arrangement reduced.

When a change is made in the solenoid current, it is found that a sudden, "inductive" motion is in general superimposed upon the true, leisurely, "thermal" deflection of the galvanometer. This inductive effect is produced by magnetic pick-up in the thermocouple leads. It is eliminated by placing in the stray field of the solenoid a small coil which is connected to its own primary winding on the Mu Metal core, the total resistance of the coil circuit being the same as that of a thermocouple circuit. If the coil is suitably placed with respect to the specimen, a pick-up effect equal and opposite to that induced in the thermocouple leads is supplied, and only the "thermal" deflection of the galvanometer remains. Incidentally, the galvanometer was a commercial Tinsley Type 4789 with its control magnet shunted.

III. DETAILS OF SPECIMENS

Five specimens were investigated and details of their composition and relevant physical constants are given below.

Specimen I: 4 Percent Si-Fe Unannealed (Stalloy)

Length, 37.20 cm at 18°C. Volume, 8.32 cc. Mean area of cross section, 0.224 sq cm. Coefficient of expansion between 18 and 100°C, *12.8×10⁻⁶ per °C*. Demagnetizing factor, 0.0085.

Specimen IA: 4 Percent Si-Fe Annealed

This was specimen I after annealing. The actual treatment as carried out by G.K.N. Research Laboratories staff was the normal works anneal, i.e., approximately 15 hours heating up to 830°C, 20 hours at 830°C "in own atmosphere," followed by approximately 48 hours in the town's gas supply.

Specimen II: 4 Percent Si-Fe Annealed

This was a specimen cut from the same bar as specimen I and annealed by G.K.N. as follows: 16–20 hours at 830°C, the total time occupied including heating-up, time at high temperature, and cooling-down extending over 34 hours. Some oxidation of the surface took place. Length, 37.69 cm. Volume, 7.16 cc. Mean area of cross section, 0.230 sq cm. Coefficient of expansion between 18 and 100°C, 13.3×10^{-6} *per °C*. Demagnetizing factor, 0.0085.

Specimen III: 0.5 Percent Si-Fe Untreated (Lohys)

Length, 37.95 cm. Volume, 7.16 cc. Mean area of cross section, 0.189 sq cm. Coefficient of expansion between 18° and 100°C, 12.7×10^{-6} *per °C*. Demagnetizing factor, 0.0071.

Specimen IIIA: 0.5 Percent Si-Fe Annealed

This was specimen III after annealing. The treatment received was the same as specimen IA. Both these specimens oxidized slightly, with some scaling of the surface, and had to be cleaned with emery cloth.

IV. EXPERIMENTAL MEASUREMENTS

The magnetic hysteresis curves of the specimens were found by the usual ballistic method, correction being made for demagnetization effects, using the following expression for the demagnetization factor:[8]

$$(N/4\pi)_{\mu=\infty}=(4.02\log_{10}m-0.92)/2m^2 \quad \text{for} \quad m\gg 10,$$

where m is the ratio of the length to the diameter of the rod specimen.

The thermal readings were difficult to obtain, because of their smallness, and the number of steps for a given hysteresis cycle of chosen maximum field was naturally somewhat less than the number used in describing the magnetic cycles. Reference has already been made to the elimination of the "inductive" effect by means of a compensating coil. In most of the previous work the position of this coil did not have to be determined with great accuracy, but in the present work the coil settings for certain field changes were relatively widely spaced and frequently very critical, a displacement of 0.5 mm often giving appreciable "inductive" deflections. The position of the coil had also to be predetermined before the final thermal measurements could be made. The position was considered correct when the galvanometer deflection was the same whether one made a field change from, say, $+H_1$ to $+H_2$ in one sense or the other, i.e., with the north-seeking end of the specimen upwards or with the south-seeking end upwards. (The technique of using the compensating coil for virgin curve measurements was slightly different and need not be described here.)

But a new technique had to be developed for making accurate thermal measurements when the galvanometer deflections were about 1 mm; incidentally, the deflection could easily be read to at least 0.1 mm. The inductive effect, which had hitherto been regarded as a spurious and unnecessary evil, was now used to estimate the true thermal deflection. For a number of positions of the compensating coil in the vicinity of the true compensation setting, the successive deflections accompanying a given field change made in each of the two senses were recorded and plotted against the corresponding position of the coil as read from a graduated bar. In this way two lines were obtained, one on each side of the true compensation position, each corresponding to a true thermal effect upon which was superimposed an increasing inductive effect in the same direction. Consequently, if the inductive effect is a continuous function of the distance of the coil from the solenoid, the intersection of the lines gives the true thermal deflection and also, incidentally, the true compensating position. This method proved to be very effective with small deflections. The sensitivity of the galvanometer was frequently checked by reversing a standard current in a control circuit.

[8] H. Neumann and K. Warmuth, Wiss. Veröffentl. Siemens-Konzern **11**, 25 (1930).

In spite of precautions such as the use of a shunted solenoid circuit and the use of a large choke in the supply from the mains, thermal effects produced by eddy currents remained surprisingly large, particularly in view of the high resistivity of silicon iron, and the over-all heating for a complete cycle depended on the number of steps in its description. Correction for eddy current heating was made by assuming that the difference between the sum of the thermal deflections recorded in describing one-half of a cycle and the corresponding $\int HdI$ was the result of eddy current heating. Then this difference D was assumed to be proportional to ΣdB_n^2, where dB_n is the change of magnetic induction associated with the nth step, and therefore the eddy current heating in any particular step dB_1 could be calculated from the ratio $D\cdot dB_1^2/\Sigma dB_n^2$. It is realized that this procedure is not entirely satisfactory, as it presupposes that the time constant of the circuit remains constant throughout the cycle and that Warburg's law holds.

Asymmetry in readings, i.e., in the values for the deflections obtained on describing a half-cycle in the two possible directions, which had been noted by previous workers, was at first extremely pronounced in the present work. It was finally traced to an interaction between the transformer core and the combined stray field of the solenoid and specimen, which gave rise to slow galvanometer deflections very like those caused by true thermal changes. But it was interesting to note that even when the asymmetry was great, the mean of the two deflections in the two directions was undoubtedly correct, and therefore it is not necessary to balance out the asymmetry exactly. It was greatly reduced by raising the transformer and rotating it in a horizontal plane, and it is certain that with an ideally wound transformer it could be avoided altogether, a remark which also applied to spurious deflections produced by stray fields arising from sources outside the laboratory.

For the Joule calibration a load of 1500 g was generally employed. This produced a temperature change of about 5.3×10^{-4} °C, with a corresponding galvanometer deflection of about 250 tenths of 1 mm. Consequently, 0.1 mm corresponded to about 2.1×10^{-6} °C. Several workers have enjoyed a greater sensitivity, but in the present case some sensitivity was sacrificed to obtain improved stability. For the first time on record, the Joule calibration was found in the present work to depend on the state of magnetization of the specimen. Actually, this was traced to a slight movement of thermocouple leads when the calibrating load was applied; this gave rise to a disturbing inductive effect which caused a galvanometer deflection. The effect was, of course, avoided by always attaching the calibration load to a demagnetized specimen.

It was convenient to express the galvanometer deflections in units of 0.1 mm, and the greatest deflections were seldom more than 100 units. For example, in the 40-oersted cycle with the specimen of 0.5 percent silicon iron in the untreated state, the sum of all the deflections in the half-cycle was only 45 units. Naturally, when the number of very small deflections in a cycle is large, the over-all accuracy of the measurements suffers, apart from the much increased experimental difficulties, and readings were recorded only when there was no doubt that they were taken when the galvanometer was free of drift, etc.

Since the hysteresis loops were so narrow, the value of $\oint HdI$ was found as follows. A graph of H was plotted against ΔI, where ΔI is the difference in the values of I for the same value of H, and the area under this graph was measured.

V. EXPERIMENTAL RESULTS

It will readily be appreciated that the results described below are characteristic of the particular specimens investigated, and that other specimens, nominally of the same composition and heat treatment, might give different results; in particular, structure-sensitive properties such as coercivity, remanence, and hysteresis loss might be greatly different.

We turn first to the magnetic I, H data for 4 percent silicon iron, specimens I and II. We were surprised to find that the values of I for maximum fields of 40, 200, and 400 oersteds, respectively, were consistently less for the annealed specimen. The measurements on both specimens were repeated with substantially the same results. These observations were rather disturbing, as one would expect annealing to relieve strain and increase permeability. Measurements by Smith and Shermann[9] on the effects of compression and tension on the permeability of silicon steel indicate that at low inductions compression reduces permeability, while at high inductions the reverse is found. But it seems difficult to explain our observations on these lines.

The untreated specimen was then annealed according to the given specification. On repeating the I, H measurements, we now found values of I, as expected, to be everywhere greater over the whole field range than with the same specimen before heat treatment. The values of I at 400 oersteds were practically the same, and the slopes of the curves showed that the difference between them was less as the field was increased, finally becoming zero at saturation. The forms of the curves for the two annealed specimens were not the same, the initial slope of the virgin curve of specimen II being slightly greater with the knee of the curve occurring at a lower value of the induction. The curve for specimen I after annealing, referred to as IA, was more rounded, and at fields greater than 2.3 oersteds it was above that for specimen II.

The following explanation of these observations is suggested. Sixtus,[10] by using torque measurements, x-ray analysis, and a method involving reflection from crystal surfaces, showed that preferred orientation exists in cold- and hot-rolled silicon iron both before and after annealing. He concluded that in hot-rolled silicon iron the highest permeability was to be found in directions at 45° to the rolling direction, with smaller values in directions at 0° and 90°, in that order. The reason therefore was the preferred orientation of the crystals set with their [100] axes at 45° to the rolling direction.

Now, although specimens I and IA were cut from the same bar, it is possible either that they were not cut exactly along the same direction or that the crystal orientation was different in different parts of the bar. Some evidence of this is found in the values of the coefficient of expansion, that of specimen I being less than that of specimen II. If the orientation was assumed to be more favorable in specimen I, this would explain the higher values of the induction found for this specimen in high fields. In low fields, below the knee of the I, H curve, where boundary movements predominate, the effect of annealing would be to facilitate such movements and to outweigh the effects of less favorable crystal orientations. Above the knee, where boundary movements are much less frequent, the effects of crystal orientation would predominate and therefore the induction should be greater in specimen I. At very high field values, both specimens should have the same induction, and this was indicated in the I, H curves. We therefore conclude that very close comparison of the I, H or thermal curves for specimens I and II is unwarranted, and that if we wish to make detailed comparison of such curves they must always be obtained with one single specimen, first in the untreated state and secondly after it has been annealed. The same specimen of the 0.5 percent silicon iron was so used in the untreated and annealed states. We may record that annealing in the case of specimen I increased I_R from 265 to 385 gauss and reduced H_c from 0.65 to 0.33 oersted for the 40-oersted cycle, the corresponding values for the annealed specimen II being 170 gauss and 0.176 oersted. In the case of the 0.5 percent silicon iron specimen, annealing increased I_R from 605 to 980 gauss and reduced H_c from 1.92 to 0.278 oersted. When the I, H curves were plotted on a very large scale to obtain $\oint HdI$, a peduliar 'waist' was found for the 40- and 400- oersted cycles. This phenomenon seems also to have been observed by MacLaren[11] in hysteresis loops for low content silicon steels.

We shall now review a few of the thermal curves obtained in the course of the work. The virgin curves will not be reproduced here as most of their main features are to be seen in the curves for the closed cycles of magnetization, which are usually much more informative and more satisfactory for making comparison between experiment and theory. Following the general procedure of earlier work, we save space by plotting only one-half of the $\int dQ, I$ or $\int dQ, H$ curves, since the

[9] C. M. Smith and G. W. Shermann, Phys. Rev. 4, 267 (1914).
[10] K. J. Sixtus, Physics 6, 105 (1935).
[11] M. MacLaren, Trans. Am. Inst. Elec. Engrs. 31, 2025 (1912).

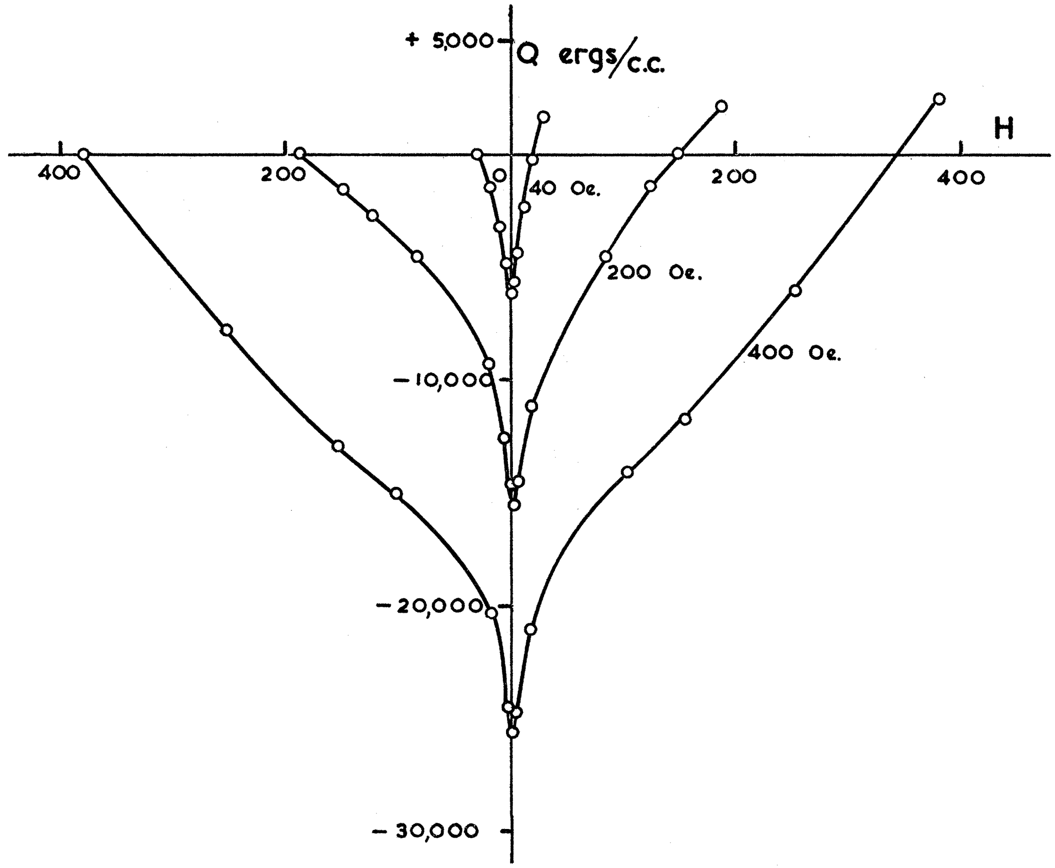

FIG. 1. Four percent silicon iron, untreated (specimen I). Q, H curve for $H_{\max}=40$, 200, and 400 oersteds, approximately.

remaining portion may be obtained from the plotted portion by suitable displacement and rotation. For convenience, we always start demagnetization from the left-hand side of the figure.

In Fig. 1 are reproduced a series of Q, H curves for the untreated 4 percent silicon iron. The 400-oersted curve shows an initial cooling which is more or less linear with H, but this becomes less rapid as H is reduced to about -40 oersteds, when a pronounced cooling sets in, and this continues until H reaches a small positive value. The same features are reproduced in the opposite direction, i.e., heating instead of cooling, to give a curve which is moderately symmetrical about the Q axis. The over-all heating, corresponding to one-half the area of the appropriate hysteresis loop, is given by the position of the final point above the H axis on the right-hand side of the curve. The central portions of this curve are also seen in the 200- and 40-oersted cycles. The virgin Q, H curve, not reproduced here, follows closely that part of the Q, H curve of Fig. 1 for which H is positive, and lies entirely above the H axis.

In the case of the annealed 4 percent silicon iron specimen, Fig. 2, the curves for all three cycles show remarkably well how the cycles with the lower field ranges correspond with the central portions of the 400-oersted cycle. Once again the curves are fairly symmetrical about the Q axis, with a pronounced minimum in their central portions. It is interesting that if one superimposes Fig. 1 on Fig. 2, the curves of the former lie inside the latter.

The Q, H curves for the 0.5 percent silicon iron warrant rather more detailed treatment. The curve for the 40-oersted cycle for the annealed specimen, Fig. 3, shows an initial steady cooling with decrease in field, and this continues down to a field of -1 oersted, after which there is a rapid heating. The curve becomes less steep at about $+0.4$ oersted and is thereafter practically linear up to the final value of Q equal to the ordinary hysteresis loss. There appears to be a slight discontinuity at about $+0.2$ oersted. The same discontinuity is found in the Q, H curve for the untreated specimen, Fig. 4. Figures 3 and 4 are indeed in marked contrast.

The 400-oersted cycle Q, H curve for the annealed 0.5 percent specimen may be seen in Fig. 10, where it is labelled Q'. It is linear when H is large and has a dip at a small positive field; the virgin curve shows a slight cooling followed by a sharp heating, thus agreeing with the 400-oersted cycle at a positive value of the field. The 400-oersted cycle curve for the untreated 0.5 percent specimen gives the usual initial cooling with, in

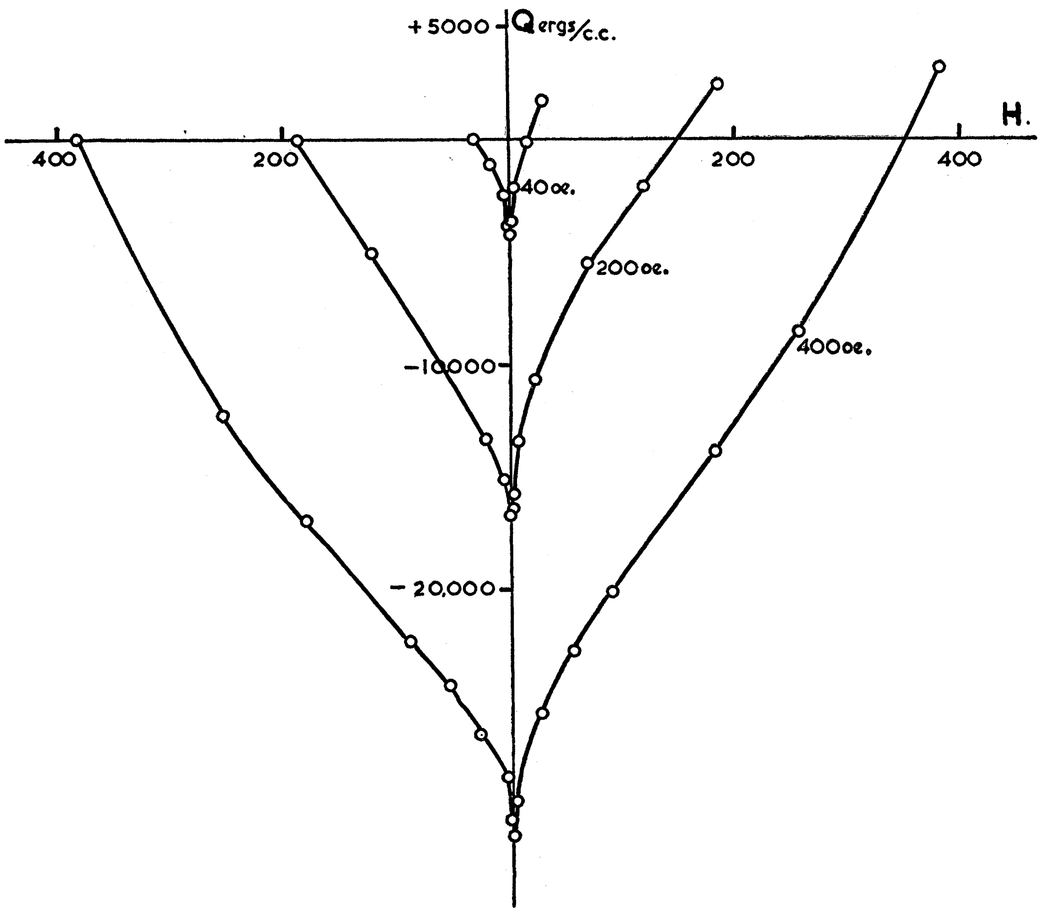

FIG. 2. Four percent silicon iron, annealed (specimen II). Q, H curves for $H_{max}=40$, 200, and 400 oersteds, approximately.

this case, a minimum at about -20 oersteds, as shown in Fig. 9. Thereafter there is a rapid heating, with a discontinuity at about $+1$ oersted, and then the heating becomes less rapid and increases linearly with H to the maximum value of the field.

Now, although the Q, H and the Q, I curves both

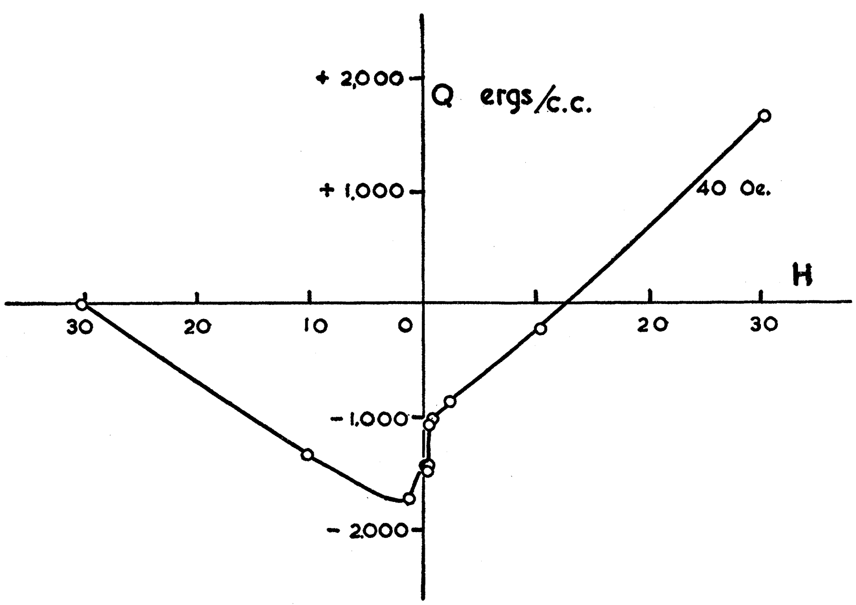

FIG. 3. 0.5 percent silicon iron, annealed (specimen IIIA). Q, H curve for $H_{max}=40$ oersteds, approximately.

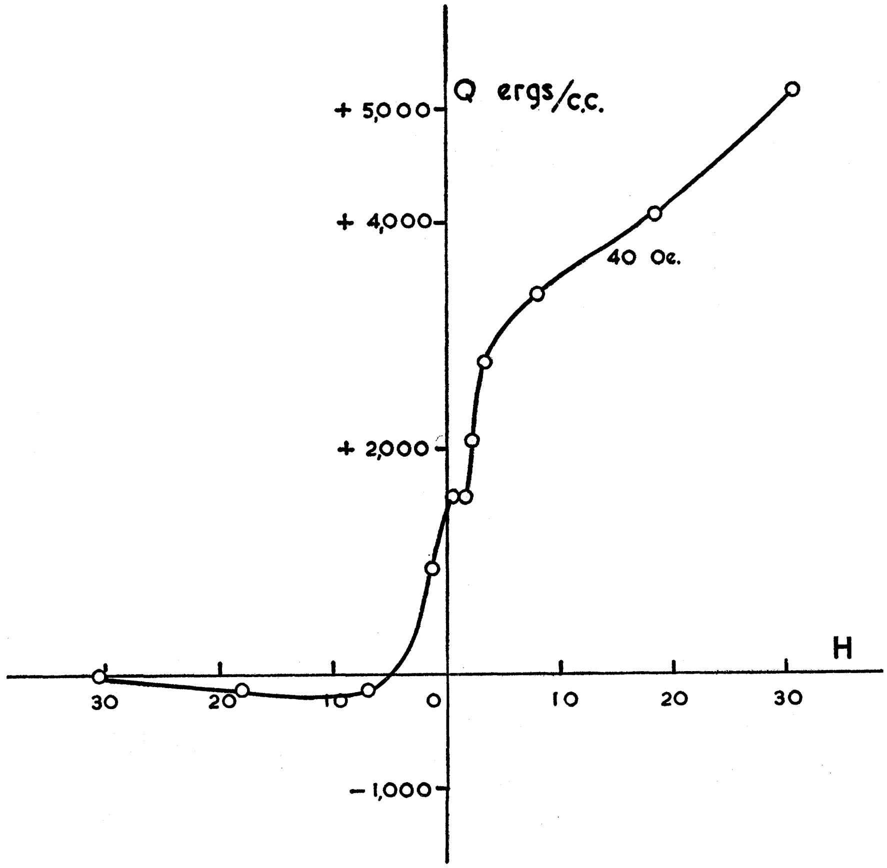

FIG. 4. 0.5 percent silicon iron, untreated (specimen III). Q, H curve for $H_{max}=40$ oersteds, approximately.

give the same information, the former are not as well suited for the illustration of energy changes occurring in the region of low field values, because I then changes rapidly with very small changes in field. Consequently, some of our results plotted as functions of I are reproduced in Figs. 5, 6, 7, and 8. All the Q, I curves for the larger cycles show a very pronounced initial cooling and corresponding final heating in the half-cycle, since large changes in field are needed to produce an appreciable change in I, except over a small field range near the origin of the hysteresis curve. Again, the curves for the 40- and 200-oersted cycles show remarkably well how the effects recorded in describing a cycle with a low maximum field are reproduced in the appropriate regions of the Q, I curve for the larger 400-oersted cycle.

In the case of untreated 4 percent silicon iron the curves for the three cycles have a rounded, symmetrical form with a minimum in the region of $I=0$, while in contrast the corresponding cycles for the annealed material are much steeper at the outer extremities with their central portions more flat. The results for the 0.5 percent specimens also show the distinction between the rounded type of curve characteristic of unannealed material and the angular type of curve for annealed material. The 40-oersted cycle curve (not reproduced here) for the annealed 0.5 percent specimen has two peaks around $I=-700$ gauss and $I=+300$ gauss, respectively. Our records show that these are also present in the 400-cycle curves although they are not visible on the latter graphs because of the coarse energy scale. Two marked changes in slope are also found both in the 40- and 400-oersted cycle curves for untreated 0.5 percent material, but actual peaks are not found.

VI. DISCUSSION OF RESULTS

In many of the earlier papers the equation

$$\sum\Delta E_M=\int HdI-\sum\Delta Q, \tag{1}$$

which is valid whether the thermal changes are reversible or irreversible, was used as a basis for the examination of results. In this equation, ΔE_M is the finite change in the magnetic as distinct from the change in thermal energy associated with a change ΔI in the magnetization. Accordingly, E_M was usually plotted against I in order to make clear those parts of a cycle in which the internal energy is changing and the extent of the changes.

We have examined the present results in this form, although the graphs are not reproduced here. It may be mentioned that the graphs of E_M for the 40- and 200-oersted cycles in all cases show the same features as the central portions of 400-oersted cycles. In the case of the

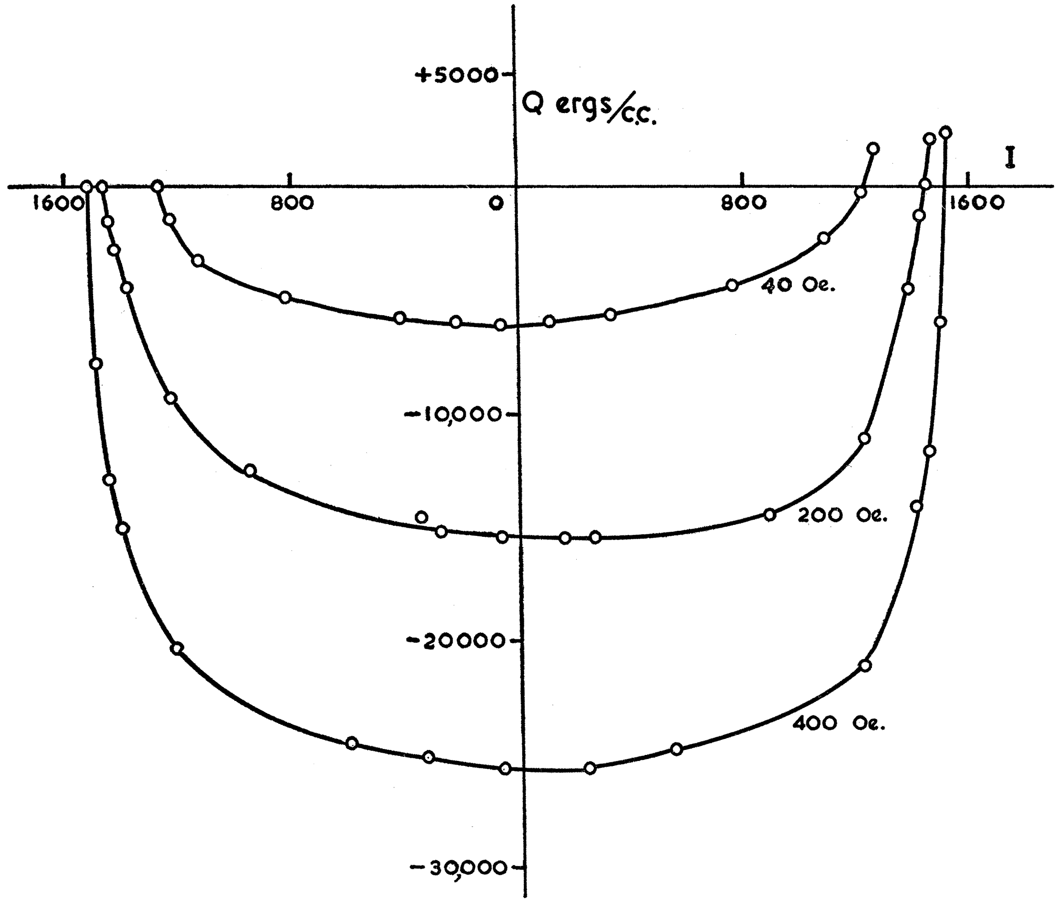

FIG. 5. 4 percent silicon iron, untreated (specimen I). Q, I curves for $H_{max}=40$, 200, and 400 oersteds, approximately.

larger cycles, at high field values $\int HdI$ is nearly always numerically larger than $\Sigma\Delta Q$, although both are negative, so that the E_M curves show a steep initial fall and a final rise. In most cases, the central portions of these curves are flat, although there are some interesting kinks well brought out when the 40-oersted cycle curves are plotted on a large scale. The E_M curves for the annealed 4 percent silicon iron specimen show a pronounced hump in the central portions which extends from $I=-1200$ to $I=+1200$ gauss.

In two papers[2,7] attempts were made to interpret the form of the thermal curves from the I, H curves of the specimen and certain other magnetic and thermoelastic data, etc. In particular, it was suggested that there was evidence that the energy supplied to each cm^3 of a specimen when its magnetization increases by dI is not HdI but $HdB/4\pi$. The same treatment was applied to the present results, and although the application is not easy, it can definitely be stated that it is of little or no value in the case of 4 percent silicon iron. The separate energy changes recorded by experiment were very much smaller than—less than half of—those predicted. In particular, the treatment did not lead to a prediction of the sharp cooling and subsequent heating which is found as the field is reduced to a small value and increased again; on the contrary, arising from a magnetostriction term, there was a very pronounced peak of about 250 00 ergs per cm^3 in the calculated curve, precisely in the field region where the dip is observed experimentally. Consequently, we do not reproduce the calculations here.

Probably the most important theoretical study of the thermal changes which accompany magnetization is that of Stoner and Rhodes,[12] who have attempted to interpret Q, H curves in terms of fundamental theoretical concepts, in particular those of intrinsic magnetization, rotation of domain magnetization vectors, and domain boundary movements. They were at pains to emphasize that Weiss and Forrer magnetocaloric phenomena could occur in weak as well as in strong fields and that they could be especially pronounced in the cases of alloys with low Curie points.

Following Stoner and Rhodes, we write

$$\Delta Q' = a\int d(IH) + b\int HdI, \qquad (2)$$

[12] E. C. Stoner and P. Rhodes, Phil. Mag. **40**, 481 (1949).

where $\Delta Q'$ is the heat liberated per cm³, $a=-T/I_0 \times(dI_0/dT)$, and $b=T/K(dK/dT)$; here K is an anisotropy constant which measures the variation of the potential energy of the system as a function of the orientation of the intrinsic magnetization I_0 with respect to the crystalline axis. The first term on the right-hand side of Eq. (2) represents the contribution arising from changes in the intrinsic magnetization of the domains, while the second term represents the contribution resulting from domain vector rotations. Thus, for the adequate testing of this theory we must have data for I_0, dI_0/dT, K, and dK/dT. Stoner and Rhodes showed that effects due to internal stresses and reversible boundary movements could be taken into account by modifying the coefficient b, and those due to the formation of new boundaries by modifying a.

If we now subtract from the observed heat changes those which may reasonably be attributed to changes in spontaneous magnetization, we have

$$Q''=\sum dQ'-a\int d(IH)=\int b''HdI. \tag{3}$$

In this equation, b'' formally corresponds to b, but we place it within the integral sign in case it should be found to be a variable coefficient which has to be calculated from the experimental results. Hence, $b''=1/H\,(dQ''/dI)$ or, if we wish to make perfectly clear what we do with the experimental results, we may write $b''=\Delta Q''/\Delta\int HdI$.

We thus see that the quantity b'' is of considerable interest, and it should be possible to find how it varies over a hysteresis cycle, always bearing in mind that it is expected to be equal to the calculated value b. Naturally, exact agreement between b'' and b cannot be expected, because we do not know the exact value of b, we have no means as yet of separating reversible and irreversible heat changes, and we do not know how to allow for the effects of internal stresses. The latter would require an accurate knowledge of the variation of the magnetostriction of the material with temperature. But, we would expect b'' to exhibit discontinuities in regions where irreversible processes are prevalent, as, for example, in the hysteresis region between coercive points.

Representative values of b and b'' now available, many of them calculated by Stoner and Rhodes, are

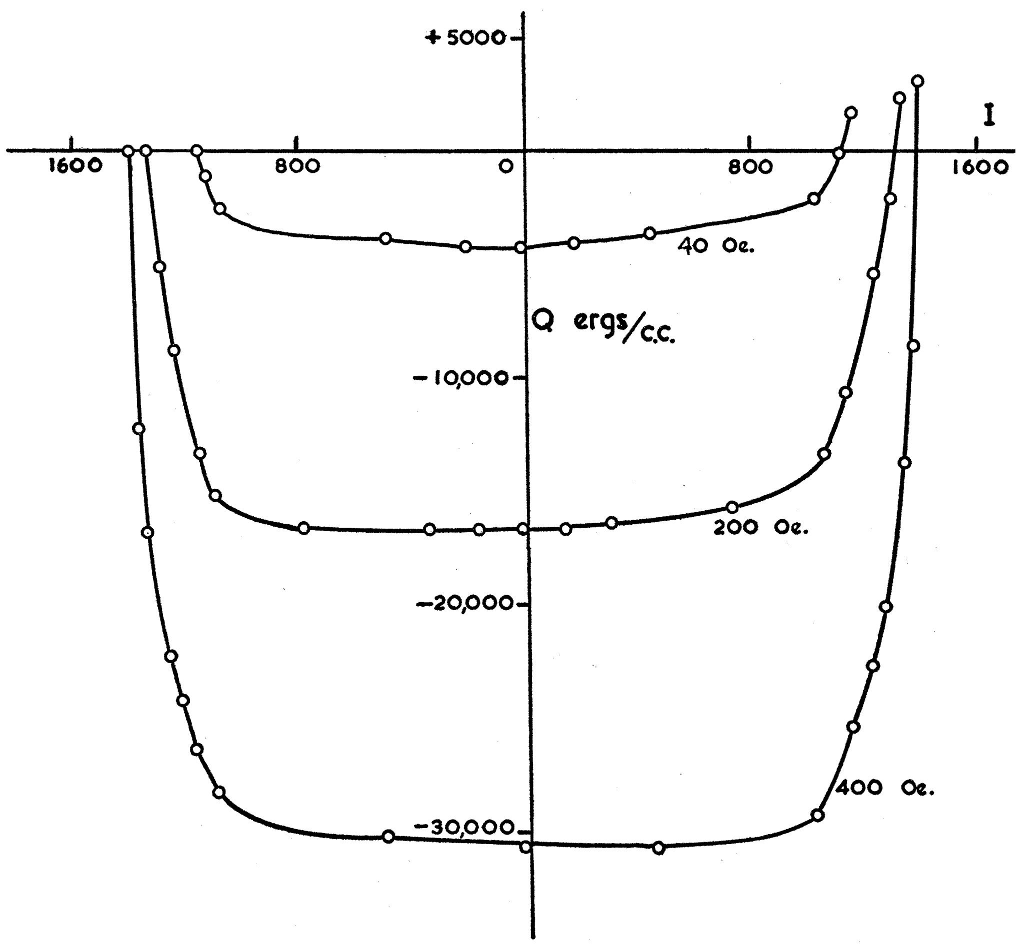

FIG. 6. Four percent silicon iron, annealed (specimen II). Q, I curves for $H_{max}=40$, 200, and 400 oersteds, approximately.

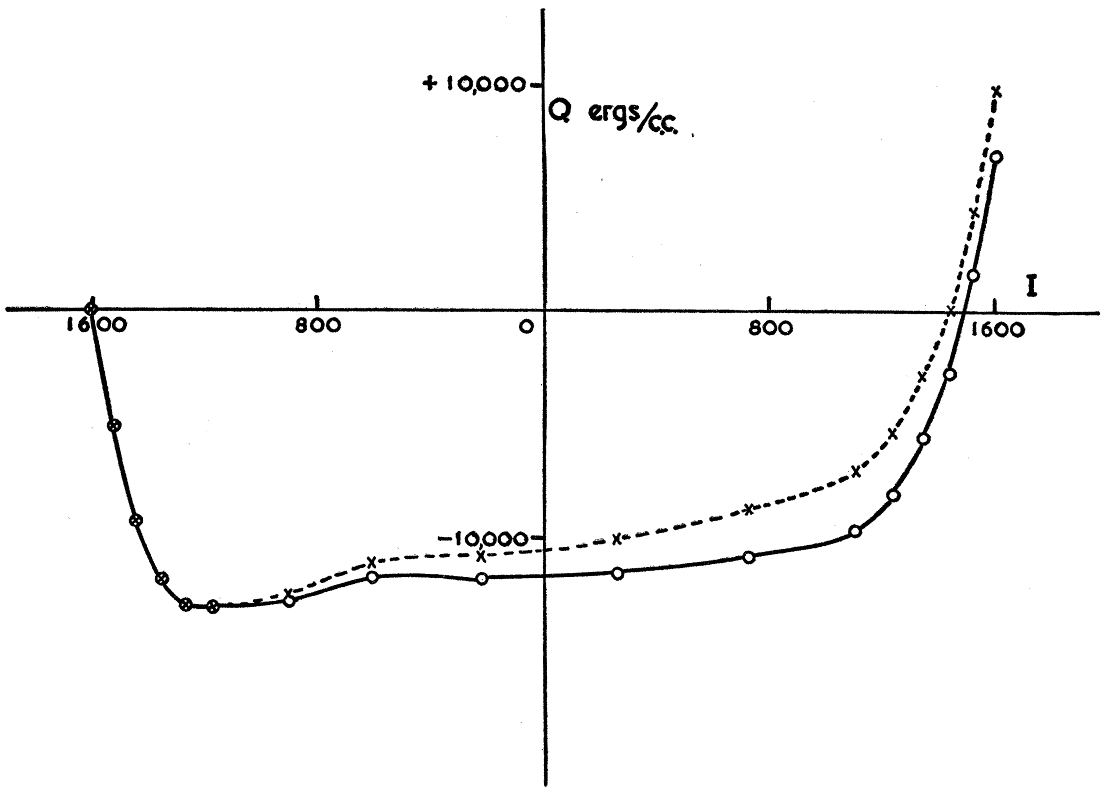

FIG. 7. 0.5 percent silicon iron, untreated (specimen III). Q, I curve for $H_{\max}=400$ oersteds, approximately. Uncorrected for eddy currents – – – –; corrected ———.

given in Table I, together with theoretical values of b. The curves of b'' as a function of H calculated by Stoner and Rhodes for iron, nickel, and cobalt, and for heavily strained nickel by Bates and Davis, are not reproduced here, although they are very instructive.

The Stoner and Rhodes treatment was now applied to our results for silicon iron. Referring to Eq. (3)we calculated the quantity $a\int d(IH)$ for the 400-oersted cycles for the two samples both in the annealed and untreated states; the 40- and 200-oersted cycles were not further examined in view of the fact that these merely reproduce the central portions of the largest cycle. The products (IH) for the several field increments used in the thermal measurements were readily found over the half-cycle from $-H_{\max}$ to $+H_{\max}$. The calculation of the coefficient a presented some difficulty. It is equal to $-T/I_0\ (dI_0/dT)$ where I_0 is the spontaneous magnetization in zero field at T°K. Now experimental values of I_0 and dI_0/dT are not yet known for silicon iron. Consequently, we estimated a in the following way.

The effect on the intrinsic magnetization at absolute zero of adding small quantities of silicon to iron is shown graphically by Bozorth.[13] Taking the value for pure iron to be 1740, the value for 4 percent silicon iron is computed to be 1583 emu per cm^3. Using the law of corresponding states and taking the Curie point of 4 percent silicon iron to be 1008°K (from Brailsford[14]), we found the value of dI_0/dT to be 0.19 cgs units per degree C for the temperature at which our experiments were made, namely, 290°K. Consequently, the value of a was 3.51×10^{-2}. In the case of 0.5 percent silicon iron there is likely to be little error in assuming the value 3.40×10^{-2} calculated by Stoner and Rhodes for pure iron.

The quantity $a\int d(IH)$ was then plotted against H with the Q', H graphs as in Figs. 9, 10, 11, and 12, where it is labeled M.C. (magnetocaloric effect). The difference between the ordinates of the two graphs gives the quantity Q'' which is also plotted on the same graphs.

To calculate the coefficient b'', we found it necessary to plot $\int HdI$ against H, and from this graph and the Q'' graph the increments $\Delta Q''$ and $\Delta\int HdI$ were found for stated increments of H, the latter increments usually being those actually recorded directly during the experiment. The ratio $\Delta Q''/\Delta\int HdI$ was then plotted against the mean value of H for each stated increment, except at very low fields where irreversible processes predominate and the values of b'' are meaningless.

Turning now to Figs. 9 to 12, we first note the shape of

[13] R. M. Bozorth, *Ferromagnetism* (1951), p. 79.

[14] H. D. Brailsford, *Magnetic Materials* (Methuen and Company, Ltd., London, 1951), p. 90.

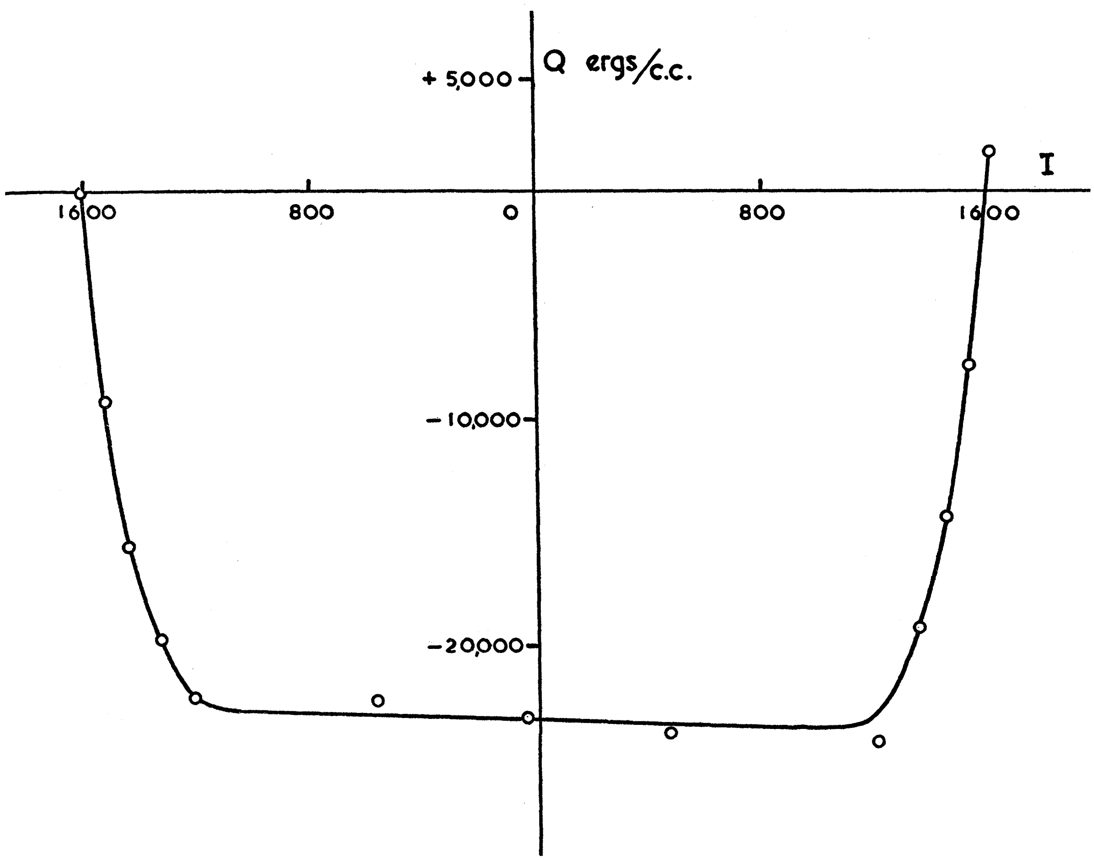

FIG. 8. 0.5 percent silicon iron, annealed (specimen IIIA). Q, I curve for $H_{max}=400$ oersteds, approximately.

the $a\int d(IH)$, H curve with the symmetrical heating and cooling effects associated with the negative value of dI_0/dT which are characteristic of the magnetocaloric effect. In the case of 0.5 percent silicon iron, both annealed and untreated, $\int HdI$ is considerably greater in magnitude than Q'; while for 4 percent silicon iron at the higher fields, $\int HdI$ is smaller in magnitude than Q', but is greater at low fields. The relative magnitudes of Q' and the magnetocaloric effect for the untreated material (Fig. 9) are such that the Q'' curve shows a steady heating as H is reduced from $-H_{max}$, corresponding to reversible rotations of domain vectors or reversible boundary movements. This persists until a field of -10 oersteds is reached, when the rate of heating changes sharply with the marked onset of irreversible changes. When H exceeds $+50$ oersteds, cooling from reversible processes predominates and continues almost linearly to $+H_{max}$. This is precisely what one would expect, and is very similar to the curve calculated by Stoner and Rhodes from the results of Hardy and Quimby on annealed Armco iron. Our untreated silicon iron specimen had a comparatively high coercivity (approximately 1.9 oersteds) and the irreversible heating, of some 7000 ergs per cm³, is much greater than is found for the other specimens. The reversible heat change which occurs between $\pm H_{max}=377$ oersteds

TABLE I. Values of b and b''.

	b	b''	Remarks	Author
Fe	0.58 (−0.63 ideal)	−0.30	Armco, annealed	a
		−0.26	Armco, annealed	b
		−0.20	Hilger H.S.	b
		−0.36	Armco, unannealed	b
		−0.38	Armco, unannealed	a
		−0.22	Armco, annealed	c
Ni	−4.5 (−5.9 ideal)	−3.70	Annealed, H_m 200 oersteds	a
		−4.20, −4.30, −3.70, −4.80	Annealed specimens with H_m 200 oersteds	d
		−1.40	$H_m > 200 < 400$ oersteds	d
		−4.00	H_m 400 oersteds	e
		−0.65, −0.84	Hard-drawn	d
		−0.40		f
		+0.37?	Unannealed	a
Co	−1.3	−2.0, −2.0, −2.4	Annealed	g
		−2.9, −3.3, −2.6	Unannealed	g
Silicon iron		−0.11	Untreated 0.5 percent	h
		+0.04	Annealed 0.5 percent	h
		−0.05	Untreated 4 percent	h
		+0.10	Annealed 4 percent	h

[a] Hardy and Quimby.
[b] Bates and Harrison.
[c] Bates and Healey.
[d] Bates and Weston.
[e] Bates and Davis.
[f] Davis.
[g] Bates and Edmondson.
[h] Bates and Marshall.

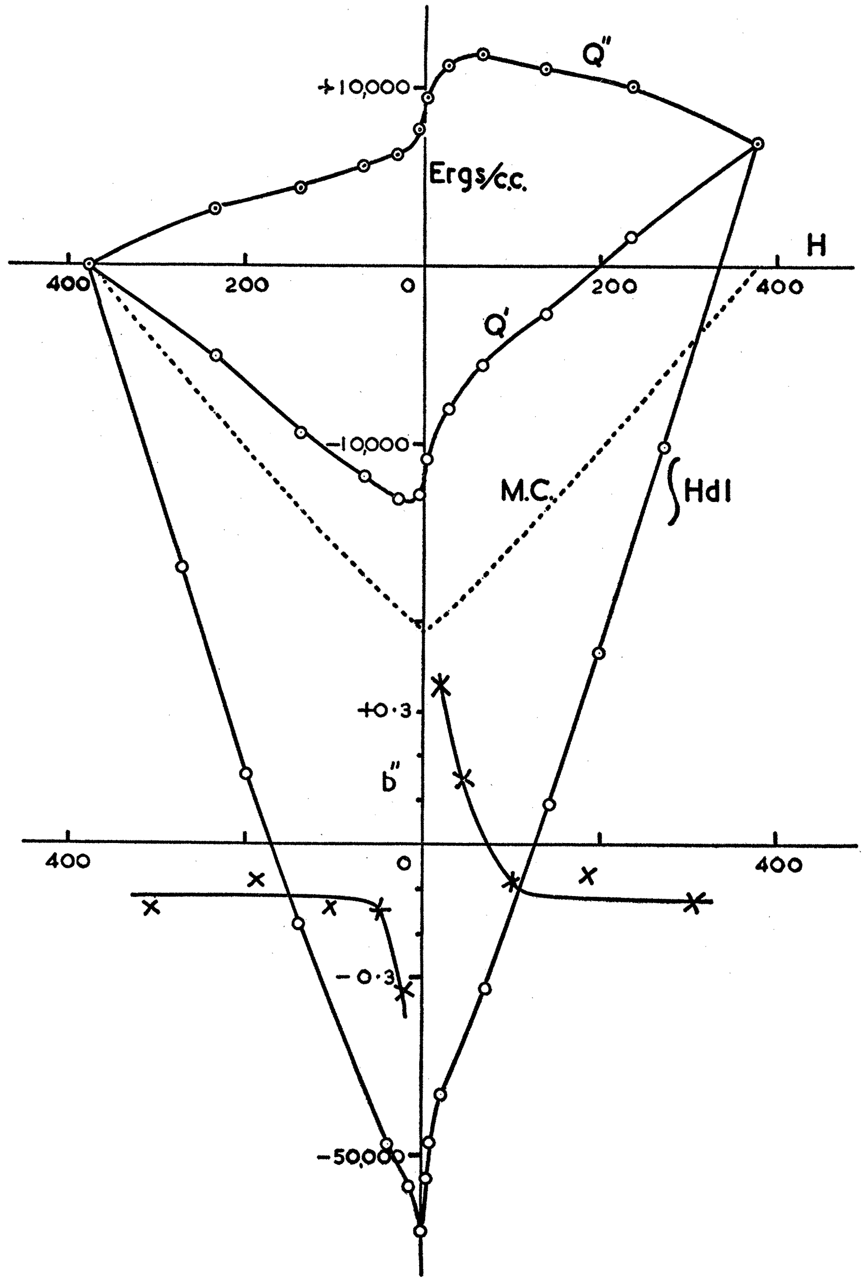

FIG. 9. 0.5 percent silicon iron, untreated (specimen III). Curves of Q', Q'', and b'' against H; $H_{\max}$ 400 oersteds.

and $H=0$ corresponds also to about 6 to 7000 ergs per cm³.

The values of b'' obtained as described above show some degree of scatter about the lines drawn through them since they are calculated directly from experimental points. As H is decreased from $-H_{\max}$ towards zero, b'' remains fairly constant until the region of irreversible processes is reached, when it rapidly assumes a large negative value. When H is subsequently increased to a positive value, b'' first takes a large positive value at low fields to fall to the same fairly constant value of -0.11 in high positive fields. This value may be compared with the values -0.26 and -0.22 given for Armco iron and Hilger iron, respectively (from Bates and Harrison[5]), and the value -0.30 for the Armco iron (from Hardy and Quimby[15]). (The estimated value for polycrystalline iron free from internal strains is -0.58; values for alloys of silicon and iron are not yet known.)

We consider next the results for the annealed specimen of 0.5 percent silicon iron. The curve of Q'' against H in Fig. 10, does not show the initial heating found with the untreated specimen when the field is decreased

[15] T. C. Hardy and L. Quimby, Phys. Rev. 54, 217 (1938).

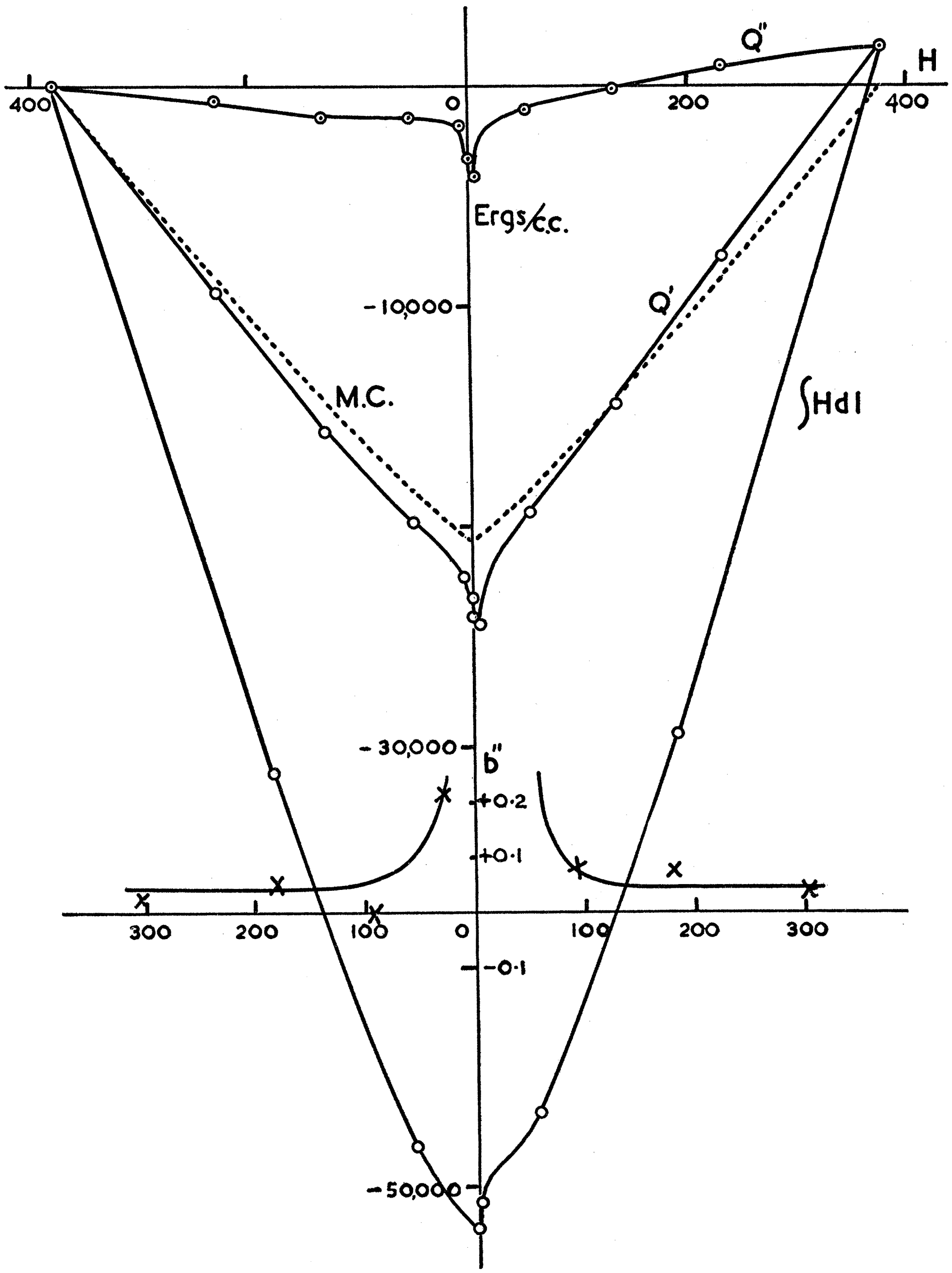

FIG. 10. 0.5 percent silicon iron, annealed (specimen IIA). Curves of Q', Q'', and b'' against H; H_{max} 400 oersteds.

from $-H_{max}$ towards zero. In contrast, there is a slight and almost linear cooling which persists until the field has a small negative value, whereupon there is a sharp dip or trough in the curve, some 2500 ergs per cm^3 in magnitude, which is followed by a more pronounced rise succeeded by linear heating up to $+H_{max}$. This behavior is remarkable, because the sharp dip in the curve occurs in a region where we would anticipate an irreversible heating effect. Since the Q'', H and $\int HdI$, H curves slope in the same direction, the values of b'' are now positive, and b'' has the value $+0.04$ in high fields and remains fairly constant until the region of the dip, where it takes a large positive value.

The Q'', H curve for untreated 4 percent silicon iron in Fig. 11 shows little energy change in the higher fields after allowance has been made for the magnetocaloric effect. There is actually a small cooling near $-H_{max}$, and one near $+H_{max}$, which gives way to a slight heating

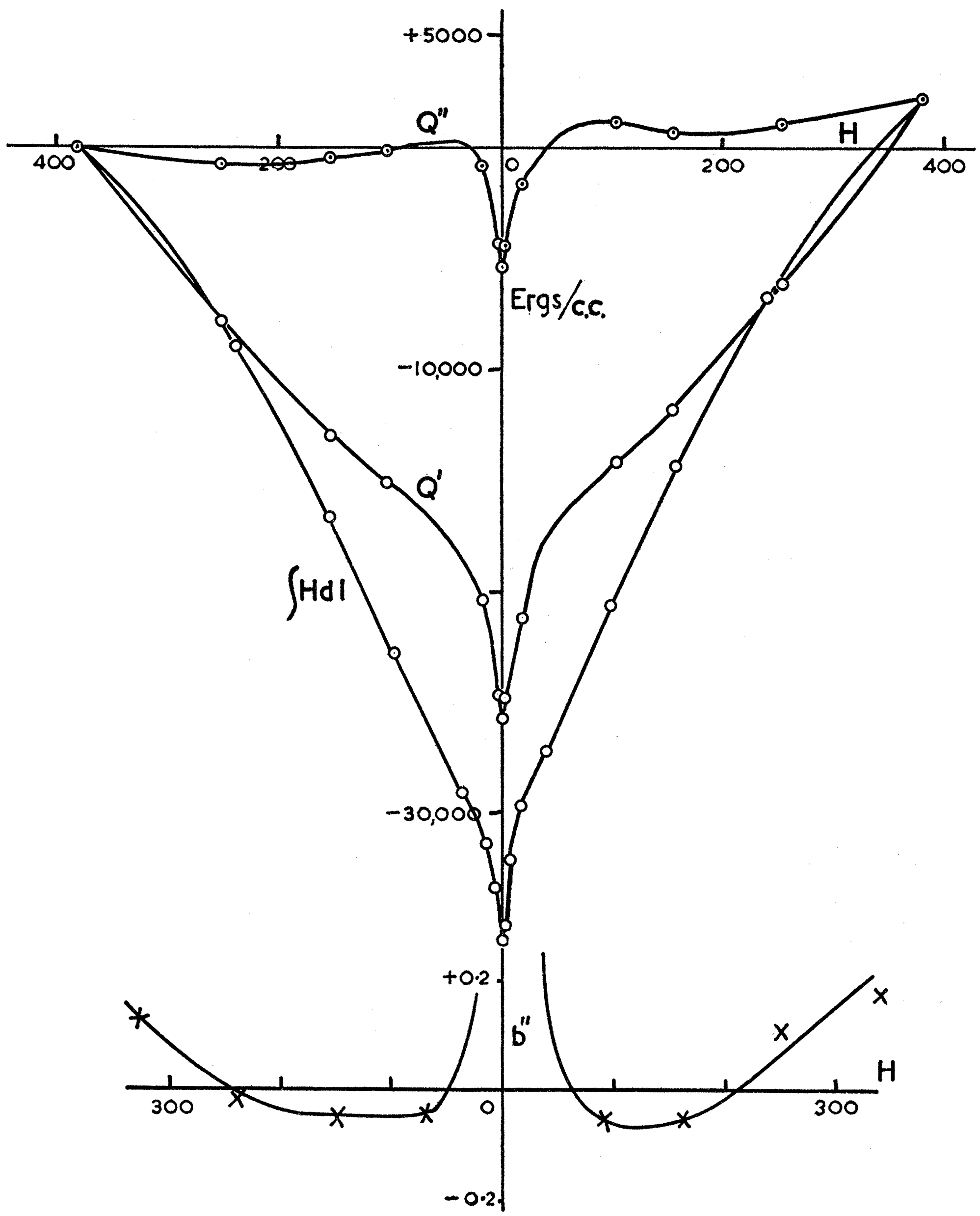

FIG. 11. Four percent silicon iron, untreated (specimen I). Curves of Q', Q'', and b'' against H; H_{max} 400 oersteds. (Note pronounced dip in Q'', H curve around $H=0$.)

which persists except in the field region between -50 and $+50$ oersteds approximately. In the latter region there is again a pronounced dip, of magnitude about 6000 ergs per cm^3, even greater than that with the annealed specimen. We note that b'' is initially positive near $-H_{max}$, but, as H is decreased, b'' falls to a negative value of -0.05, to remain constant until the region of irreversible processes is reached when it again becomes positive.

The curves for annealed 4 percent silicon iron in Fig. 12 are somewhat similar to those for the untreated specimen, but the magnitudes of the changes in the two cases are very different. In Fig. 12 the minimum values of Q' and of the magnetocaloric effect are about $-31\,000$ and $-19\,000$ ergs per cm^3, respectively, and the Q' curve is always below the other. Therefore as H is first reduced the Q'' curve shows a sharp initial cooling which becomes less pronounced until a field of -50 oersteds is reached, when we find the sudden dip recorded for the two previous specimens. When we increase the field to $+H_{max}$, the phenomena are repeated in the reverse order with an irreversible heating superimposed. The b'' curve has the same form as that for the untreated 4 percent silicon iron specimen, but b'' is

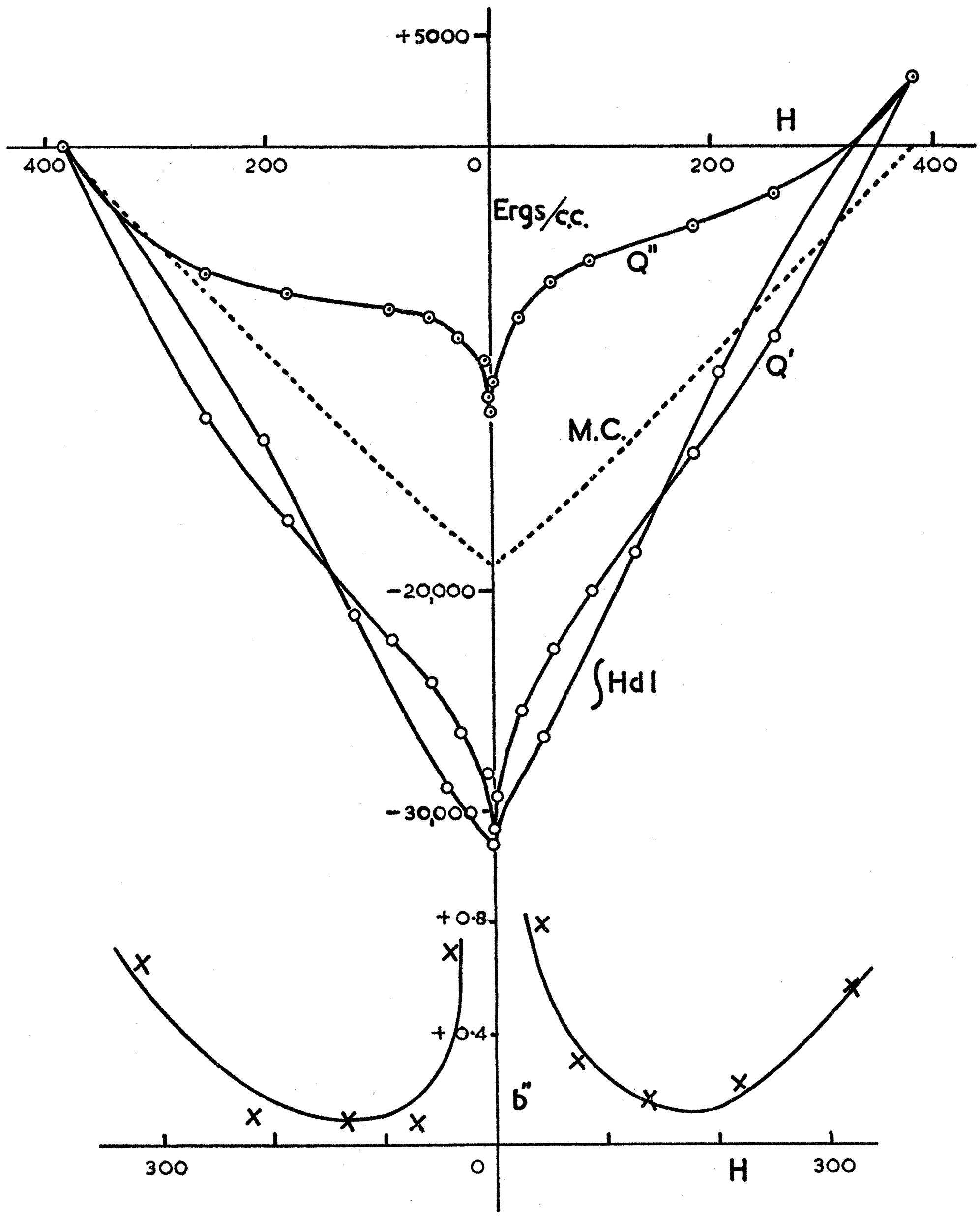

FIG. 12. Four percent silicon iron, annealed (specimen II). Curves of Q', Q'', and b'' against H; H_{max} 400 oersteds. (Note pronounced dip in Q'', H curve.)

now always positive with small regions round about $H=-150$ oersteds and $H=+150$ oersteds where it has a fairly constant value of 0.1.

Perhaps the most striking feature of the Q'', H curves for the last three specimens, the 0.5 percent annealed and the two 4 percent specimens, is the dip or trough described above. It should be mentioned that it was, of course, present in the 40- and 200-oersted cycles, although very different field increments from those employed in the largest cycle were used in these cases. This dip is most unusual, but Bates and Healey[6] made somewhat similar observations in a 100-oersted cycle for annealed Armco iron. They considered that the dip was a spurious effect, possibly the result of the effects of vibrations upon the measurements, and they avoided its appearance by changing the field in one operation from a small negative value to a small positive value, so that in their view the specimen did not remain in magnetostrictive contraction for an appreciable interval of time. It seems clear, however, that as the effect appears in the present curves in all the cycles whatever field steps were employed, it must be a real effect and characteristic of the material. Incidentally, the dips are clearly visible only on the Q'', H and not on Q'', I

curves, so emphasizing the importance of plotting thermal changes against both H and I.

A priori, one might think that the cause of the dip resided in the method of allowing for eddy-current heating. The latter is proportional to $(dB/dt)^2$ and is therefore very large in low field regions and comparatively small elsewhere, so that the correction described above is applied mainly in the region where the dip is found. Suppose now that the method of correction is unsound and that the actual correction applied in that region is too large. The effect would be to accentuate the cooling which is expected as H is reduced from $-H_{\max}$ towards zero and to decrease the apparent rate of heating as H is increased again, in fact, to give the form of Q'', H curve actually recorded. To test this suggestion, the curves for the three specimens showing the effect were plotted without correction for eddy-current effects. The curves for the two 4 percent specimens were only slightly changed in form and a pronounced minimum remained, so that the suggestion is here ruled out. The uncorrected curve for the 0.5 percent specimen was changed but still showed distinct traces of a dip, so that even in this case, inaccurate eddy-current correction could not be entirely responsible.

Again, the dip cannot be a result of inaccuracy in applying the correction for the magnetocaloric effect on the grounds that the Stoner and Rhodes treatment can only be approximate at low fields, for the order of magnitude of the correction rules out this explanation.

Now, the saturation magnetization of iron decreases with increase in temperature, so that dI_s/dT is negative and there is a cooling on decreasing the field. But, in the hysteresis region where reversible rotations of domain vectors and reversible movements of boundary walls are important, dI/dT is normally positive because magnetic anisotropy decreases with temperature. Hence, when the cooling due to change of intrinsic magnetization has been subtracted from the observed thermal changes, there should remain only a heating on decreasing the field. Consequently, the question arises as to whether the sign of dI/dT can be negative in low fields.

A mechanism by which the sign of dI/dT could be rendered negative in low fields was suggested by the work of Dr. E. W. Lee. It is based on some work by Bozorth[16] who tried to account on the domain theory for the very low remanence exhibited by certain alloys, which may be as low as 0.07 I_s for a certain Permalloy after heat treatment. Bozorth put forward several ways in which such low values might arise.

The most likely explanation takes into account a possible departure from normal domain structure in materials of low crystal anisotropy. On such crystal surfaces, Bitter powder patterns are not successfully formed, because the Bloch walls between domains must be so wide, if they exist, that the stray fields above them must be too weak to act upon the colloid particles used to form the pattern deposits. Now, Kittel[17] suggested that under these conditions the flux in comparatively large regions of the material forms closed paths when the material is in the demagnetized state. On the application of a magnetic field these closed lines will be broken, but they will reform on its removal. In other words, the material tends to demagnetize itself and the remanence falls to less than the old theoretical value. This process is clearly the more favored the less the magnetostriction and crystal anisotropy, and as both decrease with rise in temperature, the field remaining constant, the flux-closing process occurs more easily and the magnetization is further reduced. In other words, $(dI/dT)_H$ is negative.

Some evidence regarding the sign of dI/dT for silicon iron has been provided by Spooner,[18] who measured the temperature coefficient of permeability of a number of specimens of low and medium silicon electric sheet material at various temperatures from $-20°$C to $+46°$C over a wide range of induction. The main conclusions relevant to the present discussion were that 4 percent silicon iron on the average has a large negative temperature coefficient of permeability at all inductions up to 15 000 gauss, though individual samples show considerable variations. The coefficient becomes more negative with increasing silicon content, and the shape of the curves also seems to be a function of the induction rather than of the field, since a maximum negative coefficient is found, whatever the silicon content, at about 10 000 gauss.

Returning to the Q'', H curves for the annealed 0.5 percent specimen, shown in Fig. 10, there appears to be no heating between $-H_{\max}$ and zero, but simply a faint cooling over the whole field range. Again, as H is increased from zero to $+H_{\max}$, we find a slight evolution of heat apparently in addition to that produced by irreversible processes. We might take this to indicate that boundary formation is taking place at high as well as at low values of field as the latter is reduced.

As the field is reduced from the saturation value, domain boundaries must be formed. Initially they are of low energy per unit area of boundary surface, since they then separate domains in which the domain vectors are almost parallel. The boundary pattern becomes more and more complex as the field is further reduced, and since its formation requires energy, there will be a cooling associated therewith.

The very slight cooling observed at high field values with the untreated 4 percent specimen as the field is reduced, and the slight heating on increase to $+H_{\max}$, is probably to be explained on the same lines as for the annealed 0.5 percent specimen. The cooling is much more pronounced in the case of the annealed 4 percent specimen and extends over the whole range from $-H_{\max}$

[16] R. M. Bozorth, Z. Physik **124**, 519 (1945).

[17] C. Kittel, Revs. Modern Phys. **21**, 541 (1949).

[18] T. Spooner, Phys. Rev. **30**, 136 (1927).

to zero field. It seems difficult to account for these large thermal changes in the opposite direction to what one would normally expect purely on the basis of Bozorth's flux-closure hypothesis. But some Bitter patterns recently recorded on the surface of a single crystal of some 3 percent silicon iron by D. H. Martin may throw some light on the problem. The crystal was exposed to a high field which was subsequently reduced to zero, and during the course of the experiment it was noted that closure domain daggers shot across the surface and that strange domain boundaries were formed in a perfectly regular sequence. Some of these boundaries separated domains whose vectors appeared to meet head-on, just as if the page before us was divided into two portions by a boundary running across it more or less parallel to the lower edge of the page. In the upper portion we may imagine the domain vectors to be parallel to the long edge of the page and directed downwards, and in the lower portion to be likewise parallel and directed upwards. But the boundary is not now the normal straight and clear-cut boundary as frequently recorded in Bitter figure work. It twists and wriggles in an extraordinary way as if it were trying to counteract the formation of free poles on its surfaces. If we have here the type of flux closure postulated by Bozorth and Kittel, then at the boundary the flux must turn either upwards or downwards into the surface of the page on both sides of the boundary. The latter is, however, so serrated and so narrow that considerable energy must be associated with it, and one feels that here is the most likely explanation of the observed cooling.

VII. ACKNOWLEDGMENTS

We are indebted to Mr. A. E. De Barr (now at Elliott Brothers), and Dr. R. J. Wakelin of Guest, Keen, and Nettlefolds Research Department for the provision and treatment of the silicon iron samples used in this work; one of us (G.M.) thanks the Department of Scientific and Industrial Research for a maintenance allowance which made the work possible.

DISCUSSION

G. Rathenau, *N. V. Philips Gloeilampen Fabrieken, The Netherlands:* The number of domain walls formed by thermal demagnetization may be much larger than the number formed by demagnetization in an alternating current field of decreasing amplitude at room temperature. These additional walls may be in metastable equilibrium at room temperature and give rise to nonequilibrium configurations.

L. F. Bates, *University of Nottingham, England:* The results of measurements of Bitter figures have shown very little change in magnetization patterns with the temperature ranges from solid CO_2 to about 150°C. We have found that "wriggly" boundaries appear on specimens which have been demagnetized by heating.

C. A. Fowler, Jr. (with **E. M. Fryer**), *Pomona College, Claremont, California:* By employing the longitudinal Kerr magneto-optic effect, photographs of domains in the (100) surface of a large crystal of silicon iron have been obtained. A series of such pictures clearly shows the characteristic movement of domain walls as the sample is carried through an initial magnetization curve to saturation. A second series of photographs, taken as the originally saturated sample has its magnetization gradually reversed to saturation in the opposite direction, reveals the sudden appearance of a single narrow antiparallel domain which proceeds to grow, with increasing reverse field, until it covers the entire crystal surface. Preliminary results have been described[1] and photographs of these effects are attached (see Figs. 1 and 2).

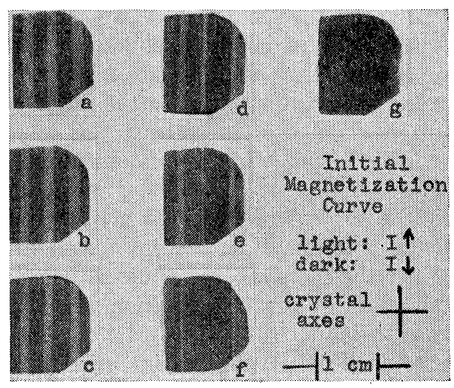

Fig. 1.

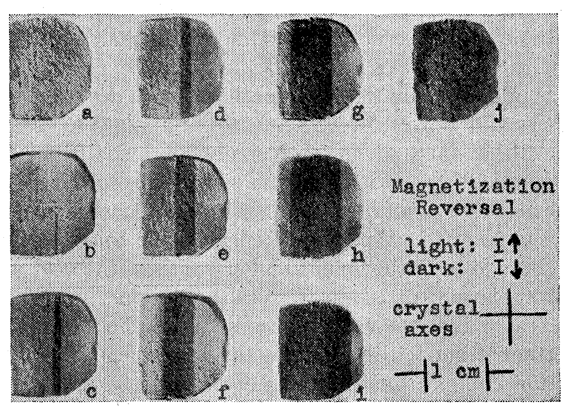

Fig. 2.

[1] C. A. Fowler, Jr., and E. M. Fryer, Phys. Rev. 86, 426 (1952).