Spontaneous Magnetization—Techniques and Measurements

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Measurements on the temperature variation of spontaneous magnetization by both the magnetothermal and magnetic methods have hitherto been confined to nickel; the extension of these measurements, calling for greater sensitivity, is discussed. To the direct method devised by Weiss and Forrer has been added a direct current amplifier, which allows a small magnetocaloric rise of temperature to be measured accurately. The original ferromagnetic balance devised by Sucksmith has been improved and now is capable of wider application to measurements of magnetic intensity in fields which are due to either air core coils or electromagnets. The method is not complicated by the presence of any image effect so that measurements of $d\sigma/dH$ in high fields can be made with considerable precision.

Measurements on a copper-nickel alloy (27.5 percent Cu) have been made, and it is shown that the two methods give identical results except in the immediate neighborhood of the Curie temperature, where the thermal measurements give a steeper descent to the temperature axis with little "tail," while the magnetic data indicate a higher Curie temperature with a significant tail. Below the Curie temperature the linear relationship between the magnetocaloric rise of temperature and the square of the intensity magnetization is found as in nickel and iron; above this temperature there is pronounced curvature.

Measurements have also been carried out on a mixed ferrite ($MgO\ ZnO\ 2Fe_2O_3$). Satisfactory agreement between the results by the two methods are obtained, both curves differing markedly from the law of corresponding states for the ferromagnetic elements.

INTRODUCTION

THE magnetization of a domain in zero applied field is known as the spontaneous magnetization (σ_{0T}) and is a quantity of fundamental significance. Its change with temperature, from the absolute zero to the Curie temperature, plays an important part in the formulation of ferromagnetic theory. In spite of this importance, our knowledge of this variation, is extremely limited. Of the three ferromagnetic elements, only one, nickel, has been the subject of adequate investigation. The experimental determinations are not a straightforward matter, since the spontaneous magnetization does not, in general, admit of direct observation, and it can only be obtained by indirect use of the magnetic isothermals in high external fields. At the lowest temperatures, there is usually no difficulty, since at high values of the field, the magnetization increases so slowly and linearly that simple extrapolation of this to the axis of zero field can be carried out with accuracy. With increasing temperature, however, the rate of increase of magnetization with field becomes more rapid and nonlinear, so that the accuracy decreases as the Curie point is approached. It is in this region that two methods, both developed by Weiss and Forrer,[1] were successfully applied to nickel. The first method is exclusively derived from the magnetization isothermals, and curves are plotted giving the field as a function of temperature for constant values of the magnetization. These curves were found by the authors to be linear for the higher values of the field, and extrapolation to zero field gives the temperature which corresponds to the value of σ employed. The second and better method for determining the spontaneous magnetization comes from the magnetocaloric effect. The increase of temperature ΔT on magnetization, at first increases only very slowly until "saturation" is reached, after which it increases linearly with the square of the observed magnetization. Theoretical considerations show that extrapolation to the axis $\Delta T=0$ gives the spontaneous magnetization and Weiss and Forrer considered that the two methods gave identical results, the Curie temperatures obtained differing by not more than 1°C. It is necessary to draw attention to the fact that the former, purely magnetic method, becomes less accurate as the Curie point is approached, while the magnetocaloric determinations increase to a maximum accuracy at this temperature. This consideration, therefore, offsets in some degree the significance of the agreement between the two methods.

Unfortunately, this complete investigation has not been reproduced for any other ferromagnetic material, probably owing to the severe experimental difficulties which confront accurate measurements by both methods Potter,[2] succeeded in making simultaneous magnetic and magnetothermal measurements on iron in the elevated temperature range from 523°C to 826°C (Curie temperature about 770°C). Up to the present, this work is the only attempt to make measurements on the magnetocaloric effect other than that of the originators, Weiss and Forrer.

Recently, Myers and Sucksmith[3] made magnetic observations on cobalt (earlier investigations by Bloch[4]), where the high Curie temperature (1120°C) makes magnetocaloric measurements virtually impossible. In this case, there are difficulties attributable mainly to the abnormally high crystalline anisotropy which makes the approach to saturation of the polycrystalline material very slow. In addition, at ordinary tempera-

[1] P. Weiss and R. Forrer, Ann. phys. **5**, 153 (1926).

[2] H. H. Potter, Proc. Roy. Soc. (London) **A146**, 362 (1934).

[3] H. P. Myers and W. Sucksmith, Proc. Roy. Soc. (London) **A207**, 427 (1951).

[4] O. Bloch, Vierteljahrsschrift naturforschende Ges. Zürich. **56**, 415 (1911).

tures, polycrystalline cobalt exists as a mixture of hexagonal and face-centered cubic structures, which at about 370°C becomes wholly cubic. For accurate measurements it was necessary to use single crystals and utilize the properties in the direction of easy magnetization in the low temperature hexagonal state, while above the transition range, this breaks down to the ordinary polycrystalline cubic material and, therefore, suffices.

These three researches constitute the total information on spontaneous magnetization available on the three ferromagnetic elements. It now is necessary to review briefly the comparison of these results with existing theory. The simple quantum modification of the Weiss theory predicts that the variation of the ratio σ_{0T}/σ_{00} (the latter being the spontaneous magnetization at absolute zero, i.e., the absolute saturation moment) with T/θ (where θ is the Curie temperature in degrees absolute) is dependent only on the quantum number j. For the ferromagnetics we put $j=\frac{1}{2}$, and thence it follows that the variation of spontaneous magnetization with temperature should be the same for all ferromagnetics, i.e., the quantum version of the Weiss' Law of corresponding states. For the case of nickel, when the reduced magnetization (σ_{0T}/σ_{00}) is plotted against the reduced temperature (T/θ), there are slight but definite divergences from the theoretical curve. For small values of T/θ the experimental values are slightly below, and for T/θ approaching unity, more markedly above the calculated curve. Potter's results for iron in the lower temperature range agree approximately with those of Weiss and Forrer for nickel, his results cutting the theoretical curve at $T/\theta\cong 0.6$, but above this temperature, the values are in excess of the nickel data, thus showing greater divergence from the theoretical $j=\frac{1}{2}$ curve. It should be noted that Potter used only the magnetothermal method of determining the law for iron. The purely magnetic results obtained by Myers and Sucksmith fall naturally into two parts, the portion below the phase change, in which the structure is close-packed hexagonal, and the range above this temperature where the structure is face-centered cubic. The former portion, extending to $T/\theta=0.5$ where σ_{0T}/σ_{00} falls only to 0.94, is too short to admit of accurate comparison with theory, although the experimental accuracy in this range is high. In the face-centered cubic phase, the range is adequate for comparison with the previous results, and the trend is identical with that of nickel. In other words, both face-centered cubic structures agree within experimental error, yet differ from the quantum modification of the law of corresponding states. It would appear that, at least to some extent, the law is structure sensitive.

Although a considerable amount of work on magnetic alloys has been carried out, there is comparatively little which admits of spontaneous magnetization data being extracted from the experimental results. Two exceptions are the early papers of Bloch[4] on cobalt-nickel alloys and papers of Alder,[5] who carried out measurements on copper-nickel. The reduced magnetization-temperature curves for the former system are almost coincident over the range extending from pure nickel to the cobalt rich alloys, and an extrapolation to 100 percent cobalt is employed rather than the interpretation of the slow approach to saturation of the mixed hexagonal and face-centered cubic polycrystalline material. While this is a somewhat hazardous procedure, the later results of Myers and Sucksmith discussed above provide justification. When we come to the results of Alder on the copper-nickel alloys, it is evident that with increasing dilution, the departure from the trend both for theory and for pure nickel becomes very marked in that the curves become less concave towards the origin. The method of determination of the spontaneous magnetization is of an arbitrary type, and as such open to criticism. The intensity values at 10 000 and 5000 oe are extrapolated linearly to $H=0$. Many other cases of experiments on alloys assume that the saturation intensity is an adequate measure of the spontaneous magnetization.

It will be appreciated from the foregoing discussion that the determinations on nickel are the only ones which can be regarded as satisfactory, and in view of the importance of the quantities involved, it seems desirable to extend the field of reliable determinations, particularly for ferromagnetic materials other than the three elements. Furthermore, the assumption that both the methods are equally valid rests only on the observations on nickel, and verification of this assumption for a selection of other ferromagnetics is called for. For these reasons it was decided to initiate measurements by both methods on representative materials. The copper-nickel series, which has played an important role in the development of the theory of ferromagnetic solid solutions is an obvious subject for investigation, and an alloy, chosen so as to afford the maximum range for profitable measurements, has been used. The ferrites have recently become prominent in ferromagnetic researches, and there are drastic differences from ordinary ferromagnetics in the intensity-temperature relationships of some of these substances. Experiments have also been carried out on a suitable ferrite. The present paper gives an account of the measurements which have been already carried out on one each of these types of ferromagnetics.

The experimental problem consists of the measurement of the magnetization in high fields together with the small reversible rise of temperature (ΔT) owing to the magnetization. In previous work these determinations have been made in a single apparatus, but in the work described here this has not been attempted and two distinct pieces of apparatus have been used. The resulting freedom in the design of the experimental arrangements renders a high degree of accuracy at-

[5] M. Alder, thesis, Zürich (1916).

tainable in the separate determinations. The magnetocaloric technique has been sufficiently improved to enable measurements of the rise of temperature, which is much smaller than in previous investigations, to be made accurately over an adequate range of reduced temperature. The ferromagnetic balance designed and used earlier by one of us[6] was originally employed for the intensity measurements and was, indeed, used for the earlier observations, but during the course of the work an improved form was developed which possesses considerable advantages over the original, particularly for measurements such as where the greatest possible accuracy is required for the rate of increase of magnetization with field.

THE MEASUREMENT OF THE MAGNETOCALORIC EFFECT

In principle, the method is simple and consists in measuring the temperature change in a specimen placed between the poles of an electromagnet of which the field is switched on or off.

The specimen was spherical in shape and 0.6–0.7 cm in diameter. The thermocouple was inserted in a small hole of diameter about 0.05 cm and held firmly in position in good thermal contact with the specimen.

THE THERMOCOUPLE

A thermocouple of high thermoelectric power is required for the experiment. The conflicting requirements are for low electrical resistance in order to secure high sensitivity and low thermal conductivity to minimize the heat losses. Since the thermal conductivity of copper-nickel is very much greater than that of the nonmetallic ferrite, the couple appropriate to the specimen has to be selected with some care. This feature will be dealt with in connection with the appropriate materials below.

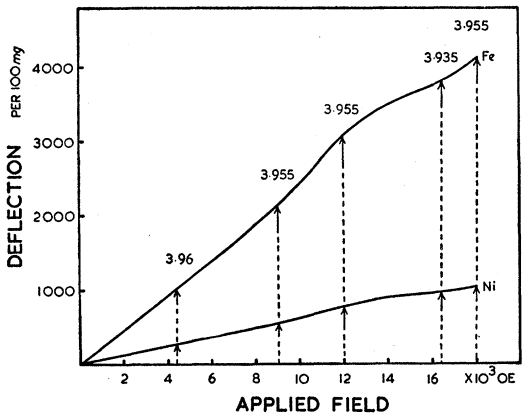

FIG. 1. Graph showing the relationship between the deflection per 100 mg of iron or nickel to the applied magnetic field in the original Sucksmith ring balance for ferromagnetics.

THE GALVANOMETER SYSTEM

The maximum magnetocaloric effect, even at the Curie point, is only about 0.35°C, and with even the sensitive thermoelements described above, together with a suitable low resistance galvanometer of short period to give adequate quickness of response, it is clear that some form of amplification must be employed in order to measure the effect accurately over a wide range of both magnetic field and temperature. A galvanometer amplifier employing a high degree of negative feedback similar to that of Preston[7] was constructed. This employs two photovoltaic cells connected in parallel with the input signal in order to secure a low input resistance. The primary galvanometer had resistance 15 ohms, period 4.5 seconds, and current sensitivity 193 mm/μA. In the secondary circuit, a short period galvanometer of period 2 seconds, resistance 26 ohms, and current sensitivity 150 mm/μA was used. The over-all sensitivity of the arrangement using maximum feedback was about 30 mm/μv corresponding to about 1100 mm/°C for the copper-constantan thermocouple. If necessary, this could easily be increased by reducing the feedback.

THE POTENTIOMETER

It was essential to reduce extraneous thermoelectric emf's as far as possible. The commercial potentiometers which were used in the initial stages exhibited these spurious emf's to such an extent as to make accurate measurements impracticable. It was found necessary to construct a special potentiometer in which the electrical circuit was composed entirely of copper and a special resistance alloy "minalpha" which has a low thermal emf against copper, i.e., 0.9μv/°C. The potentiometer itself was completely immersed in an insulating oil in order to minimize changes of ambient temperature. These precautions proved to be highly successful.

THE ELECTROMAGNET

A Weiss type electromagnet with 10-cm diameter poles was employed. The pole pieces were conical truncated to a plane pole face diameter of 2.0 cm, with a gap of 1.72 cm. With an excitation of 55 000 ampere-turns a maximum field of 20 000 oe was produced.

EXPERIMENTAL PROCEDURE

The potentiometer described above was used to balance the main emf of the thermocouple and thus gave the mean temperature at which observations were being taken. After recording the general slow drift of the galvanometer at 10-second intervals, the magnet was switched on, the magnetocaloric rise of temperature being shown by the out of balance deflection. The heat produced is dissipated in various ways, and a cooling curve is observed, observations still being taken at 10-second intervals; after about a minute the magnet field is switched off, and the same procedure followed

[6] W. Sucksmith, Proc. Roy. Soc. (London) **A170**, 551 (1939).

[7] J. S. Preston, J. Sci. Instr. **23**, 173 (1946).

during the cooling. Immediately after this, a calibrating emf producing the same order of deflection is injected into the circuit, and a similar procedure followed during the switching on and later during the switching off. These four readings insure adequate accuracy in determining the magnetocaloric ΔT.

Eddy current effects due to the magnetic field can be shown to be too small to be observable. Radiation loss is kept as low as possible by carrying out the experiments in vacuum. The chief source of error is probably that owing to thermal conduction down the thermocouple leads; and by deliberately increasing the extrapolation time, it was shown satisfactorily that this source of error must be less than 10^{-3}°C for the nickel-copper specimens. The procedure for the points is dealt with below, along with the measurements on that material.

THE MEASUREMENT OF THE INTENSITY OF MAGNETIZATION AT VARIOUS VALUES OF THE MAGNETIZING FIELD

The intensities of magnetization were, in the initial stages, obtained by the method developed by Sucksmith.[6] During the coarse of the work, an improved apparatus was developed, and since the method is particularly suitable for this type of measurement, it is described in some detail. In order to appreciate the significance of the modifications, some reference to the original method is necessary.

THE ORIGINAL BALANCE METHOD

This is a traction method, and the principle is that a ferromagnetic material placed in a inhomogeneous magnetic field experiences a force according to the equation

$$F_x = \sigma m dH_y/dx. \quad (1)$$

The magnetic field H can have any direction, but by far the majority of applications find it most convenient to employ a field whose direction is perpendicular to the direction of the force.

This force is measured by the ring balance, in which the displacement of the small specimen, very highly magnetized, is linearly proportional to the force which amounts to a few grams weight. The field must be sufficiently large for the requirements of the investigation, while the gradient must be constant over the working volume and involving only a small change in the absolute value of the field. To achieve this, stepped pole faces were employed such that a region of constant (and maximum) gradient existed. The balance is only intended for fields of some thousands of oersteds and upwards, and calibration is effected by comparison with a standard iron specimen, whose moment is assumed constant in fields above about 5000 oe at liquid air temperature. This assumption is fully justifiable for the maximum absolute accuracy claimed ($\frac{1}{4}$ percent). Comparison results for nickel and iron, together with sample ratios obtained at different fields, are given in Fig. 1. The field gradient which varies between 140 oe/cm to 600 oe/cm at the maximum magnetizing field of 18 000 oe was, of course, not separately controlled, and efforts were made to replace this with a coil system, a problem in which the suitable disposition and sensitivity of which presents the chief difficulty. Finally, the following improved arrangement for the field and field gradient was found satisfactory and adopted.

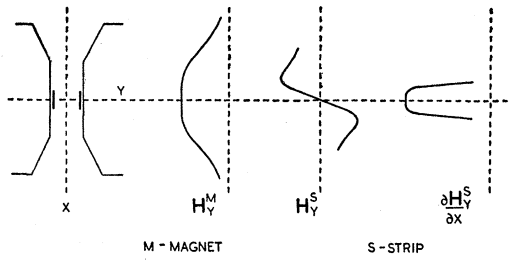

FIG. 2. Variation of magnetic fields and field gradient in gap of magnet.

A uniform field is employed throughout, and an electromagnet of similar type to that previously employed is used. The 10-cm pole pieces are truncated with a pole face diameter of 5.0 cm, and the gap width is 2.2 cm. To produce the field gradient, two horizontal copper strips 1.0×0.15 cm mounted symmetrically along, but insulated from, the face of the magnet poles (see Fig. 2) carry currents in the same direction being mounted in series so that the field due to these currents at the midpoint is zero. The variation of this field along the x axis together with the gradient is also shown in Fig. 2. The gradient at the center is shown as a flat maximum with variation less than 1 part in 2000 over the central 1.0 mm. Perpendicular to this, the gradient is a minimum the the center, so that in so far as horizontal displacement is concerned, the specimen will be in a position of unstable equilibrium. On the other hand, the flat spirals, preventing motion other than in the x direction, easily make this equilibrium quite stable. The gradient is directly proportional to the current, and for the dimensions employed the constant of proportionality is close to 0.5 when the current is measured in amperes. This means that since currents up to about 60 amperes were used the forces vary between 5 percent and 20 percent of those for the original balance. As stated above, the earlier form was concerned with forces up to a few grams weight so that no serious difficulty is presented by this change. Since the deflection produced is directly proportional to the current in the gradient strips, this must be measured accurately, and accordingly the usual potentiometer method is employed.

If measurements are restricted to high fields, i.e., those appreciably in excess of likely demagnetizing fields, accurate shaping of the specimens is unimportant, but for reasons which will be discussed below, ellipsoids of revolution were used for most measurements. The length was fixed at 5.0 mm, the diameter ranging from 1.25 to 2.50 mm, according to the intensity of magnetization.

Any nonuniformity of the field will be shown by a

TABLE I. Relation between deflection (in units of 10^{-2} mm) and applied field for two specimens.

H in oe	Fe[a]	Ni[b]	Ratio[c]
4600	2678	2483	3.972
8600	2677	2486	3.966
10 900	2678	2487	3.966
14 150	2679	2489	3.964

[a] Deflection for specimen of iron, weight 64.8 mg, strip current 36.00 amp.
[b] Deflection for specimen of nickel, weight 143.2 mg, strip current 60.00 amp.
[c] Ratio of the deflection per unit mass of iron to that of nickel.

deflection when the field is switched on, even in the absence of current through the gradient strips. Even with the utmost care in choice of material and machining of the pole tips, it was impossible to reduce this to a negligible magnitude. This residual effect, however, is not difficult to eliminate. The double deflection when the current through the gradient strips is reversed is always used. This procedure eliminates the error due to magnet field nonuniformity, the actual "zero" being unimportant and not figuring explicitly in the observations.

Table I shows a sample set of measurements on a nickel and an iron specimen. It will be seen that the ratios per unit mass of iron to nickel are in good agreement with the generally accepted ratio (Weiss and Forrer[8]). There is no correction for the image effect, and deflections expressed per unit mass have only to be multiplied by an instrumental constant for conversion to mass intensity. The double deflection is accurately proportional to force up to about 5000 scale divisions (1 division=0.01 mm), which represents ± 0.15 mm movement of the specimen, over which the gradient does not change perceptibly. This feature promises a high relative accuracy in estimating dH_y/dx, a precise knowledge of which is particularly important in determinations of the spontaneous magnetization. In order to test this, high field measurements were carried out on ellipsoidal single crystals of nickle cut with their easy directions of magnetization along the long axis of revolution of the specimen. In no case was there any determinable increase in σ between 5000 and 15 000 oe, i.e., $d\sigma/dH$ $\geqslant 0.04\times10^{-4}$. On the other hand, a specimen of polycrystalline nickel increased from 2483 ± 1 at 4600 oe to 2489 ± 1 at 14 100 oe, (see Table I). This gives $d\sigma/dH$ as 0.14×10^{-4}, whereas the value given by the results of Weiss and Forrer[8] for room temperature is 0.2×10^{-4}.

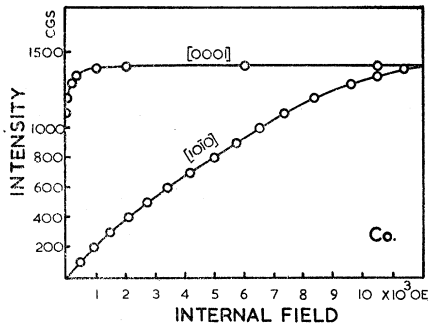

FIG. 3. Anisotropy of cobalt as measured in new ring balance (high fields).

While it is not strictly within the purview of spontaneous magnetization to deal with measurements in the low fields below saturation, it would seem not out of place in a Congress on Magnetism, in which experimental techniques are included in the program, and this extension is, therefore, included. There is no *a priori* reason why a pair of air core coils should not replace the electromagnet, while the same strips are employed to produce the field gradient. Two coils were, therefore, disposed Helmholtz fashion to give calculable uniform fields at their mid-point. These coils cover the range up to about 2000 oe, and the measurement procedure does not differ from that employed for high fields. (There are no complications due to stray nonhomogeneity of magnetizing field.) Both electromagnet and air core coils are disposed so as to be capable of horizontal translatory motion in a direction perpendicular to their fields, so that a continuous series of measurements from the lowest fields to the highest can be carried out. Calibration is effected by one measurement only at a selected high field. The standard calibration material was an ellipsoid of pure iron, whose intensity of magnetization at 15 000 oe and 15°C is taken as 217.7 per unit mass. This single calibration is in contrast with the previous balance where comparison at all the high field values employed was necessary.

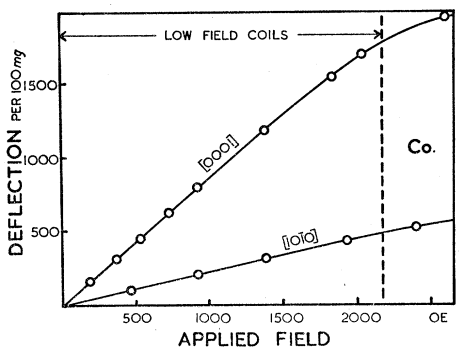

FIG. 4. Air core field measurement on single crystals of cobalt.

To illustrate the adequacy of the method for the complete range of fields, the measurements on two single crystal ellipsoids of cobalt cut along the easy and difficult directions of magnetization are included. Figure 3 gives the results of measurements (corrected for demagnetizing field), while Fig. 4 on a larger scale shows the data as obtained for the lower range of magnetizing fields. As with the earlier form of the balance, measurements can be carried out at all temperatures up to about 1600°C without any modification or disturbance of the moving system.

[8] P. Weiss and R. Forrer, Ann. phys. **12**, 279 (1929).

THE SPONTANEOUS MAGNETIZATION OF A COPPER-NICKEL ALLOY

The alloy, chosen so as to afford the maximum range over which both methods could be applied with accuracy contained 27.5 atomic percent copper. From magnetic measurements below room temperature, σ_{00}, the spontaneous magnetization at absolute zero, was found to be 31.0 units, in satisfactory agreement with the results of Alder (see reference 5). The magnetic intensity-temperature measurements were carried out for small temperature intervals up to 150°C (Curie temperature ~100°C) and exhibit the characteristic that the linearity at high fields persists to much higher (reduced) temperatures than is the case for pure nickel. Even above the Curie temperature there is marked linearity. This property allowed linear extrapolation to zero field, as well as the employment of the curves of constant intensity, to determine the spontaneous magnetization; and there is little if any difference between the two methods of extrapolation.

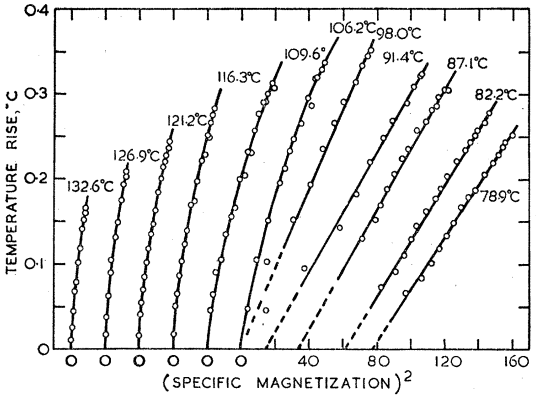

FIG. 5. Variation of magnetocaloric rise of temperature for 27.5 percent Cu-Ni alloy with square of intensity of magnetization per unit mass.

The magnetocaloric rise of temperature plotted against field shows the same features as those previously noted by Weiss and Forrer, i.e., linearity for low temperature with concavity towards the temperature axis developing with increasing temperature. The maximum ΔT is 0.35°C as compared with about 1.25°C for nickel and about twice this value for iron, while the variation with temperature is very similar to the previous results, though the half-width of the peak extends over a larger temperature range than in these cases. When we examine the variation of ΔT against the square of the magnetization (see Fig. 5), there are new features. Below the Curie point the linearity previously observed is reproduced, but above this temperature there is pronounced curvature, i.e., the relationship $\Delta T = A\sigma^2$ is not followed, and to express the variation a term involving a higher power of σ is required.

It is now necessary to compare the values of the spontaneous magnetization obtained by the two methods, and this is summarized in Fig. 6. For values of T/θ between zero and about 0.9, there is satisfactory agreement between the purely magnetic and the magnetothermal methods. Above this temperature, however, the curves diverge, and the Curie temperature deduced from the magnetothermal data is some 5.5°C below that determined from magnetic data alone.* Furthermore, the "tail" is much less pronounced in the case of the magnetocaloric effect, with a corresponding decrease in the uncertainty of extrapolation.

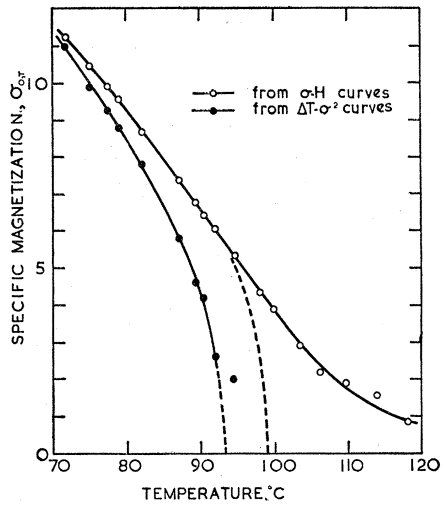

FIG. 6. Comparison of spontaneous magnetization for a 27.5 percent Cu-Ni alloy determined from the magnetic measurements and from the magnetocaloric effect.

Finally there is the comparison of these curves with the shapes previously obtained, and with the theoretical $j=\frac{1}{2}$ curve. This is shown in Fig. 7. It is quite evident that the departure from the theoretical curve is quite firmly established.

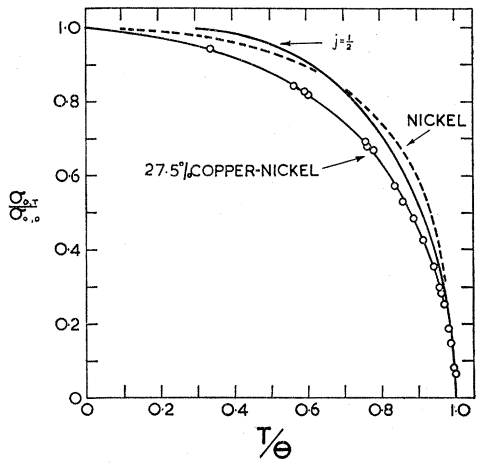

FIG. 7. Spontaneous magnetization of 27.5 percent Cu-Ni alloy compared with nickel and with theory.

* The Curie point determined from paramagnetic measurements was 111°C, i.e., about 12°C higher than the ferromagnetic Curie temperature.

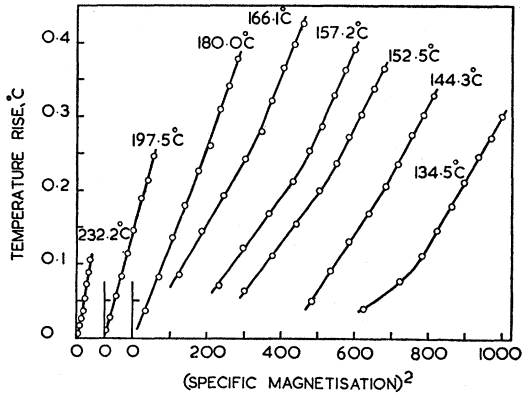

FIG. 8. Variation of magnetocaloric rise of temperature for magnesium zinc ferrite with square of intensity of magnetization per unit mass.

THE SPONTANEOUS MAGNETIZATION OF A FERRITE

As previously stated, the ferrite chosen was $MgO \cdot ZnO \cdot 2Fe_2O_3$. The reason for the employment of this particular material was twofold: the low Curie temperature combined with the departure of the saturation intensity-temperature curve from the conventional type [see Snoek, *New Developments in Ferromagnetic Materials* (Elsevier Publishing Company, Inc., Houston, 1947), pp. 87–90]. No further difficulty was presented in the magnetic determinations, but serious reconsideration of the thermal measurements was necessary on account of the low thermal conductivity. In this connection Stoner[9] has drawn attention to the error in the results of Weiss and Forrer owing to neglect of the thermal capacity of the thermocouple. In order to minimize this, various thermo-elements of different thermal conductivities and appropriate cross sections were employed for test experiments. Any heat loss will be proportional to the product KA for each element, where K is the thermal conductivity and A the cross-sectional area of the element of the couple. Table II gives the observed value of ΔT for a particular set of conditions plotted against ΣKA. It can be seen that such error as remains for materials of low conductivity can be easily corrected for.

The intensity-field relationships are quite similar to those already obtained for other substances, though with increasing temperature, the linear portions in the curves of constant intensity become shorter, until at $\sigma=5$ there is virtually no linear portion, whereas even at $\sigma=1$ the copper-nickel alloy displays linearity. On the other hand, the magnetocaloric rise of temperature, in general, follows the same trend as the ferromagnetic elements and is shown in Fig. 8. It is noteworthy that above the Curie temperature there is no evidence of the curvature characteristic of the copper-nickel alloy (see Fig. 5).

TABLE II. Variation of rise of temperature (ΔT) with material of thermoelements for different cross-sectional areas and thermal conductivities.

$\Sigma KA \times 10^5$	ΔT(deg C)
1.4	0.1590
2.1	0.1593
4.3	0.1573
9.9	0.1493
31.9	0.1399
31.9	0.1416

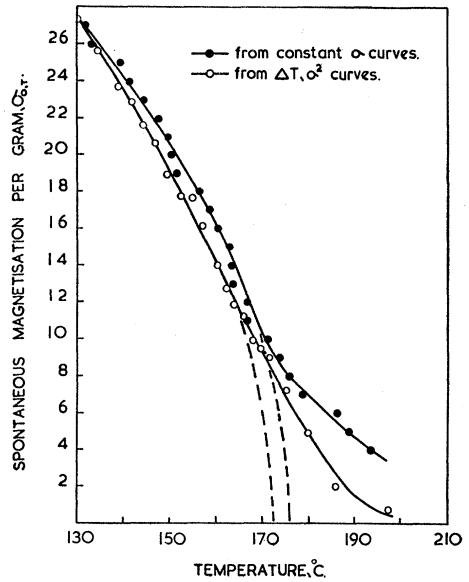

FIG. 9. Comparison of spontaneous magnetization for a magnesium zinc ferrite determined from magnetic measurements with that from the magnetocaloric effect.

[9] E. C. Stoner, Trans. Roy. Soc. (London) **A235**, 165 (1936).

When we consider the variation of spontaneous magnetization with temperature, we find satisfactory agreement by the two methods until the immediate neighborhood of the Curie temperature is reached. Above 130°C ($T/\theta>0.9$) there is a slight but definite divergence, the curve derived from the magnetocaloric rise of temperature being lower as is the case with the copper-nickel alloy (Fig. 9). The difference is, however, quite small, being only about 3°C, and the "tail" is markedly less than for other ferromagnetics. Finally in Fig. 10, σ_{0T}/σ_{00} is shown, together with the magnetocaloric ΔT for comparison. (The difference between the two curves of Fig. 9 is too small to be indicated in the figure.) It is quite evident that the variation of the reduced magnetization with temperature lies well inside the quantum-theory modifications of the law of corresponding states even for the largest values of j. The lowest temperatures employed were around 90°K, and the figure shows linear extrapolation to zero temperature. Guillaud (*Grenoble Conference on Ferromagnetism and Antiferromagnetism*, pp. 91–103) has shown that this linearity in ferrites may persist at least to the neighborhood of 20°K, so that probably little error is involved in this extrapolation. Measurements of the paramag-

netism above the Curie temperature are in progress, so that the method devised by Néel[10] for the law of variation of intensity with temperature can be calculated. Comparison with existing data for other ferrites indicates that there is likely to be substantial agreement between the theoretical and experimental curves.

CONCLUSIONS

It is clear that the two methods hitherto employed for the determination of the spontaneous magnetization are justified over a wide range from the lowest temperature to within the neighborhood of the Curie point. In this region the two methods diverge at the point where T/θ is greater than about 0.9. The tail is not so extensive as had been expected and is smaller for both materials when deduced from the magnetocaloric measurements. This feature prompts a re-examination of the results for nickel; and this suggests that the absence of tail is not so certain as these writers have supposed (e.g., see Potter, reference 2, for comments on this point).

The magnetocaloric experiments on the nickel-copper alloy show that there is substantial deviation from the $j=\frac{1}{2}$ curve, and it may be that the explanation is to be found in Stoner's collective electron theory,[11] but the values do not correspond with those suggested by Wohlfarth.[12] The new property of nonlinearity between the magnetocaloric rise of temperature and the square of the magnetization above the Curie temperature may be a characteristic of a diluted ferromagnetic, but this point calls for experiments on other alloys.

[10] L. Néel, Ann. phys. **3**, 137 (1948).
[11] E. C. Stoner, Proc. Roy. Soc. (London), **A165**, 372 (1938).
[12] E. P. Wohlfarth, Phil. Mag. **40**, 703 (1949).

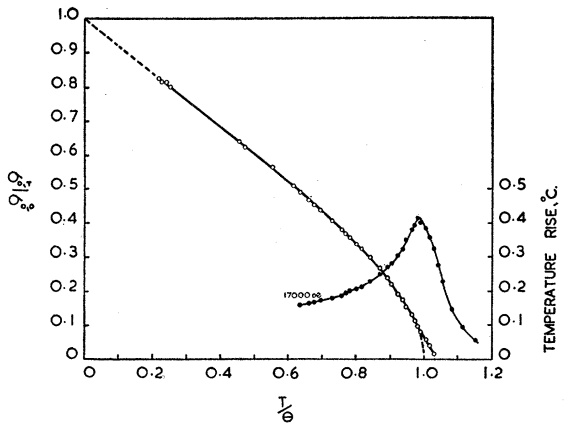

FIG. 10. Curve showing variation of spontaneous magnetization with temperature for a magnesium zinc ferrite. The magnetocaloric effect for a high value of the magnetic field is also shown.

The most marked feature of the experiments on the ferrite is the very close agreement between the magnetic and magnetothermal measurements. This is all the more striking in the mixed ferrite where deviations could reasonably be attributed to the nature of the material. When paramagnetic data is available, it is to be expected that a satisfactory correlation between theory and experiment will be available.

It should be emphasized that the results presented do not represent a completed work, and, therefore, detailed discussion would be premature. Further experiments, both on diluted ferromagnetics and on ferrites are planned or in progress.

DISCUSSION

C. J. GORTER, *Leiden University, The Netherlands:* Does not the fact that in the Cu-Ni alloy the ΔT is not proportional to σ^2 above the Curie temperature indicate that there the susceptibility must depend on the field? Then we would not have to do with paramagnetism proper. In view of the inhomogenity to be expected, a tail of ferromagnetism in the paramagnetic region is no wonder.

A. ARROTT, *Carnegie Institute of Technology, Pittsburgh, Pennsylvania:* We have used for the measuring of paramagnetic susceptibilities a method similar to that of Shoenberg which we think could be used with several modifications to measure saturation magnetization of ferromagnets. The motion of a paramagnetic cylinder in a uniform magnetic field may be picked up by a pair of detector coils connected in opposition in order to cancel out signals induced by fluctuations of the field. A zero pitch solenoid may be wound on the cylindrical surface of the paramagnet so that, with the proper current flowing, the movement of the sample plus solenoid will cause no pick up by the detector coils. The current then is a measure of the magnetization. This works for weak paramagnets, but with ferromagnets the solenoid's field affects the magnetization of the sample in no small way. If, as suggested by J. Osborne, the sample is a needle with a cross section much smaller than the solenoid, it is possible for both to have the same magnetic moment without the solenoid's field being large enough to influence the sample. The equality of the magnetic moments can be detected by placing pick-up coils some distance from the sample where both the needle-like sample and the solenoid will approximate extended dipoles. The advantages of the measurement are in the use of a uniform field and negligible demagnetizing effect and in the absence of image effects.