in air and the necessary conditions for sparking have been established by Loeb. A more exhaustive discussion of the application of the theory will be given in an article to appear at some future date.

13. It can be shown that the theory leads to an explanation of the breakdown of unsymmetrical gaps where the field distribution is known, and that quantitative calculations can be made. The theory may be applied to either surge-impulse or static breakdown.

14. It is found that the self-propagating streamer mechanism, as modified for longer sparks, will adequately account for the pilot streamer in Schonland's mechanism[30] for the lightning discharge, and it clarifies the theory proposed by the writer[31] for the "stepping" observed in lightning and spark discharges.

The writer wishes to express his appreciation to Professor L. B. Loeb, whose original qualitative theory stimulated this work and whose suggestions and criticisms have contributed much to the development of the present theory. He also thanks the Commonwealth Fund for the grant of a Fellowship, during the tenure of which this work was carried out.

[30] B. F. J. Schonland, Proc. Roy. Soc. **A164**, 132 (1938).
[31] J. M. Meek, Phys. Rev. **55**, 972 (1939).

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Ferromagnetic Anisotropy, Magnetization at Saturation, and Superstructure in Ni_3Fe and Nearby Compositions*

EUGENE M. GRABBE†
Sloane Physics Laboratory, Yale University, New Haven, Connecticut

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The order-disorder transformation involving Ni_3Fe affects both the ferromagnetic anisotropy and the saturation magnetization. Iron-nickel alloys in the range 65 to 80 percent nickel have been investigated, using spheroidal specimens. With superlattice formation the anisotropy becomes more like that of pure nickel with ⟨111⟩ as the direction of easiest magnetization. The change is largest near Ni_3Fe. The saturation magnetization increases with ordering; the greatest observed increase was 5.8 percent for an alloy very near Ni_3Fe. Different rates of cooling from above the critical temperature (about 490°C) affect the saturation magnetization. These changes are attributed to changes in degree of local ordering effects. Long distance order, induced by baking for long periods, greatly influences both anisotropy and magnetization at saturation.

INTRODUCTION

IRON–NICKEL alloys in the composition range 65 to 80 percent nickel have unusual properties which are sensitive to heat treatment. They develop extremely high permeabilities when cooled rapidly from above 600°C. Baking below this temperature or cooling slowly does not produce uncommonly high permeabilities. Attempts to explain these characteristics in terms of an order-disorder transformation involving Ni_3Fe have long been hampered by the lack of conclusive evidence for the existence of this superlattice.[1]

Changes in resistance, which occur in these alloys with proper baking after quenching, are not as marked as in many order-disorder transformations. This is to be expected, however, since the differences in size and chemical properties between iron and nickel atoms are not great. Specific heat measurements have not been conclusive because the anomaly, due to the magnetic transformation, occurs near the critical ordering temperature. X-ray analyses have, until after the experiments here reported were com-

* Part of a dissertation presented to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.
† Now at the General Laboratories, United States Rubber Company, Passaic, New Jersey.

[1] O. Dahl, Zeits. f. Metallkunde **28**, 133–138 (1936); S. Kaya, J. Fac. Sci., Hokkaido Imp. Univ. **2**, 29–53 (1938); F. E. Haworth, Phys. Rev. **54**, 693–698 (1938).

pleted, given negative results. Small difference in x-ray scattering power between iron and nickel and the sluggishness of the transformation have probably been responsible for ambiguities.

The ferromagnetic anisotropy of single crystals affords an excellent means of examining this order-disorder transformation, even though the anisotropy of alloys of interesting compositions is small. Its high temperature coefficient indicates that it is sensitive to changes in lattice parameter, and lattice spacing usually decreases with ordering. Furthermore, anisotropy may be uniquely affected, since a regular arrangement of two unlike atoms having different magnetic moments may well modify the energies required to magnetize a single crystal in the principal directions. Calculations by McKeehan,[2] for purely magnetic interactions, predict such characteristic differences between ordered and disordered states.

The first reported measurements of changes with baking in the anisotropy and saturation magnetization of iron-nickel alloys near Ni_3Fe[3] have since been extended to other alloys in the range 65 to 80 percent nickel by weight. These data would be difficult to explain by other than an order-disorder transformation, since they indicate changes throughout a single crystal specimen primarily related to the crystal structure.[4] X-ray evidence presented since the experiments here reported[5,6] has proved that this superstructure occurs. Exposures as short as eight hours have now revealed superlattice lines from alloys baked for 500 hours in the temperature range 490°C to 370°C.[5] These lines were absent from similar exposures with quenched specimens.

Specimens

Large single crystals, of volume greater than 1 cm^3, were grown in a vacuum furnace by the slow freezing of melts in high purity magnesia crucibles. The stock materials used were homogenized castings containing about 0.15 percent of the usual impurities: principally sulphur, silicon, and cobalt, with traces of phosphorus, manganese, aluminum, and carbon.

Table I. *Description of specimens.*

Ni (weight percent)	80*	74.8	70.5	69.8	68.0(*a*)	68.0(*b*)	65*
Fe (weight percent)	20*	25.2	29.5	30.2	32.0	32.0	35*
Mass, 10^{-3} g	41.2	40.2	23.8	26.2	29.1	48.7	37.4
Diameter, 10^{-4} cm	5001	5106	4076	4495	4470	5364	5082
Thickness, 10^{-4} cm	360	305	302	274	297	323	356
Volume, 10^{-6} cm^3	476	470	280	309	343	578	444
Axial ratio	13.9	16.8	13.5	16.4	15.0	16.6	14.3
Demagnetizing factor							
(1) Observed	0.626	0.574	0.667	0.552	0.620	0.596	0.561
(2) Calculated	0.651	0.548	0.669	0.560	0.606	0.552	0.635

* Not analyzed.

Specimens were prepared in the form of oblate spheroids having an equatorial plane of the form {110}. This plane contains all three important magnetic axes of forms ⟨100⟩, ⟨111⟩, and ⟨110⟩, so that the anisotropy of a given alloy may be completely determined from one specimen. A slab of correct orientation is sawed out, and a disk, cut from this slab, is cemented to the shaft of a high speed motor. A highly magnified silhouette of the disk is projected on a vertical screen on which an ellipse of proper size and of the desired axial ratio has been carefully plotted. The disk, while rotating, is cut with fine files to match this contour.[7] Exceptional care was taken in preparing the samples, and their x-ray Laue patterns show that distortion by cold work was trivial. Departures of the equatorial plane from the {110} plane aimed at were not allowed to exceed a degree or two. The effect introduced by such deviations of the axes chosen for measurement from symmetry axes in the crystal should be negligible. In each spheroid, the axial ratio (diameter to thickness) was made large enough (greater than 12) to ensure a low demagnetizing factor. The volumes were calculated from densities based upon x-ray data. Table I gives the compositions, in weight percent, of the spheroids used in this investigation, their dimensions, volumes, axial ratios, and demagnetizing factors, as calculated from dimensions and as experimentally determined.

Measurements

Magnetic measurements were taken with an improved quinquefilar pendulum magnetometer. The weight was redistributed to increase the stability, and the sensitivity was greater than that of similar pendulums previously used.[7] The

[2] L. W. McKeehan, Phys. Rev. **52**, 18–30 (1937).
[3] L. W. McKeehan and E. M. Grabbe, Phys. Rev. **55**, 505 (1939); E. M. Grabbe and L. W. McKeehan, Phys. Rev. **55**, 1142(A) (1939).
[4] Order-disorder transformations in a single crystal are especially simple to analyze. Cf. W. G. Burgers and J. L. Snock, Physica **2**, 1064–1074 (1935).
[5] P. Leech and C. Sykes, Phil. Mag. **27**, 742–753 (1939).
[6] F. E. Haworth, Phys. Rev. **56**, 289 (1939).
[7] L. W. McKeehan, Rev. Sci. Inst. **5**, 265–268 (1934); L. W. McKeehan, R. G. Piety and J. D. Kleis, Rev. Sci. Inst. **7**, 494–497 (1936).

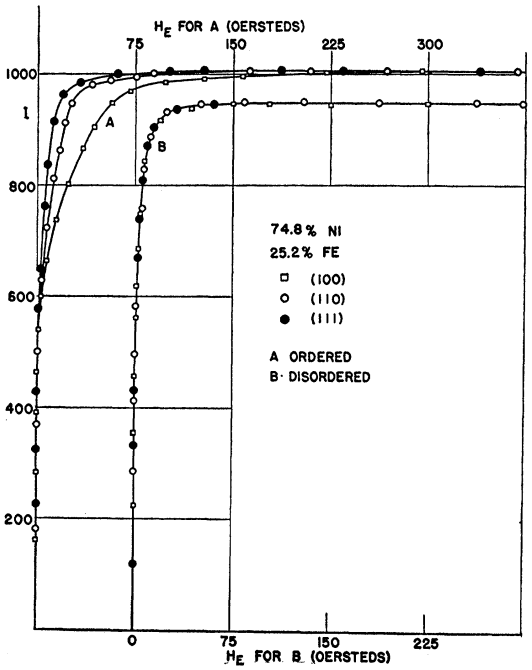

FIG. 1. *I vs. H* curves for 74.8 percent nickel.

most important modification was in the method of measuring deflections. A small square of a diffraction grating replica fastened to a thin glass plate was mounted on the pendulum beam with its rulings vertical and in the plane of permitted motion. This was intensely illuminated from behind by a platinum ribbon lamp, using circulating water in a cell to absorb heat radiation. Highly magnified images of several adjacent rulings were thrown on a translucent glass scale by means of a compound microscope. At magnifications of 1200 to 1500, the line images were quite sharp. No fixed fiducial line is used; any line image may be chosen as the zero point for the subsequent deflection. By adjustment of the field gradient the deflection can always be made an integral number of line spacings, so that the displacement of the pendulum is simply this number multiplied by the grating constant. There is then no correction for lens curvature, and the magnification need not even be known. Furthermore, the deflection range is large, and the character of the images is such that slight transverse displacements of the pendulum, vertical or horizontal, do not diminish the precision of measurements. Displacements of the order of 0.5 mm were measured to about 1 part in 1000 by this method.

The magnetizing field was supplied by a solenoid, previously described,[8] with compensating coils to level the field near the center. Two types of gradient compensating arrangements proved satisfactory; one with two series coils placed at the ends of the solenoid, the other utilized a single coil of 75 turns with reversed

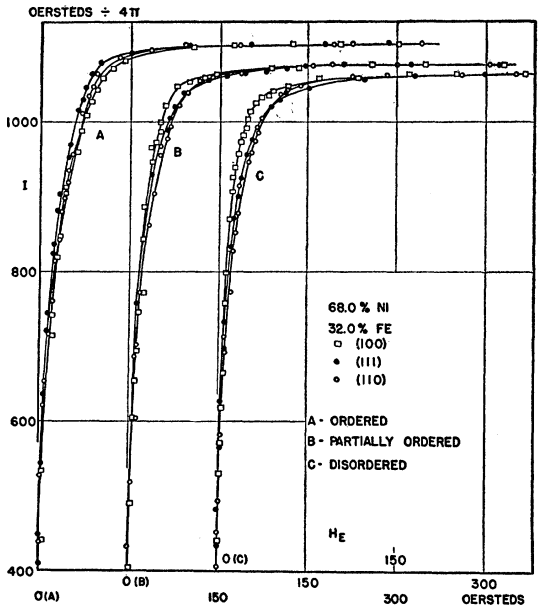

FIG. 2. *I*—*H* curves for 68.0 percent nickel.

current placed around the middle of the solenoid.[9] The field was made uniform to 1 part in 2000 for a distance of 8 mm along the solenoid axis. All the specimens saturated at low fields, and the scatter of points on the magnetization curves is small, indicating that the precision expected was attained.

HEAT TREATMENT

After shaping, the spheroids were annealed in hydrogen for 1 hour at 750°C to relieve strains. The cooling rate, attained by permitting the specimen to cool with the furnace after annealing, was about 300 degrees per hour. This cooling rate was slow enough to develop local order to a small degree. (See Results II.)

[8] L. W. McKeehan, R. G. Piety and J. D. Kleis, Rev. Sci. Inst. **7**, 494–497 (1936).

[9] L. W. McKeehan, Rev. Sci. Inst. **10**, 371–373 (1939).

In order to retain the disordered state at room temperature, a method for extremely rapid cooling was devised. The specimens were placed in the bend of a fused silica U-tube through which hydrogen at about atmospheric pressure was passed. This bend of the tube was lowered into a furnace with the ends projecting. When the temperature had reached 750°C (well above the critical temperature), the tube was quickly withdrawn and inverted. The specimens fell from the red-hot bend of the tube into a cool part of the tube. Due to its small volume and large surface, a spheroid ceased to glow while falling. The cooling rate was estimated to be 200 to 400°C per second. Maximum disorder was obtained by this drastic treatment.

The most favorable ordering temperature, in agreement with Kaya,[1] was found to be near 490°C. Specimens were baked at this temperature for at least a week in evacuated Pyrex tubes. Magnetic measurements were then made, and the spheroids were returned to the furnace and baked for another long period at a slightly lower temperature. If no changes occurred during the second baking period, it was assumed that equilibrium had been attained. It is probable that equilibrium was reached in all cases. In three instances there is additional ground for this opinion, since the same final condition was reached in consecutive programs of baking separated by a quenching process.

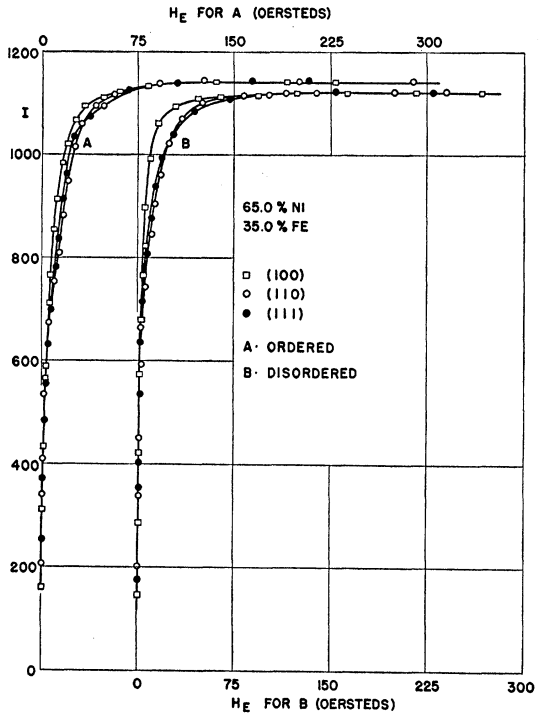

FIG. 3. *I vs. H* curves for 65.0 percent nickel.

RESULTS

I. Magnetic anisotropy

Baking for long periods at or below 490°C caused large changes in the ferromagnetic anisotropy of the crystals. For an alloy of 74.8 percent nickel and the remainder iron (very nearly the correct stoichiometric ratio for Ni_3Fe), the disordered state exhibited nearly zero anisotropy. In the ordered state the anisotropy observed, measured by the first anisotropy coefficient (K_1), was almost two-thirds that reported for pure nickel. The direction of easiest magnetization was [111], with [110] and [100] following in that order. Fig. 1 shows the magnetization curves for this spheroid.

For 80 percent nickel, the anisotropy after

TABLE II. *Magnetization energy differences.*

	Energies in 10^4 erg·cm^{-3} for following weight percents of Ni					
	80	74.8	70.5	69.8	68.0	65
$W_{110}-W_{100}$ Ordered	−0.31	−0.58	0.08	−0.03	−0.05	0.21
$W_{110}-W_{100}$ Disordered	−0.01	0.00	0.40	0.27	0.26	0.29
$W_{111}-W_{100}$ Ordered	−0.48	−0.83	−0.25	−0.34	−0.19	0.17
$W_{111}-W_{100}$ Disordered	−0.03	0.00	0.25	0.21	0.22	0.26
K_1 Ordered	−1.26	−2.30	0.31	−0.11	−0.18	0.83
K_1 Disordered	−0.04	0.00	1.60	1.07	1.04	1.16
K_2 Ordered	−1.75	−1.65	−9.52	−8.24	−3.55	−2.98
K_2 Disordered	−0.33	0.00	−7.76	−3.82	−3.40	−3.41

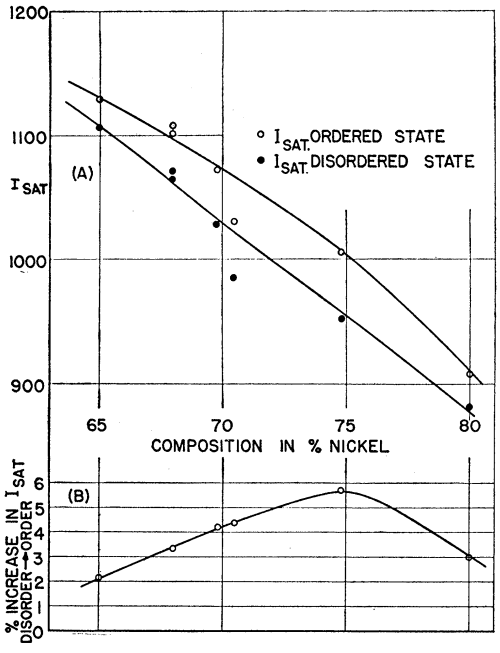

FIG. 4. (A) Saturation magnetization *vs.* composition for iron-nickel alloys. (B) Percent increase in $I_{SAT.}$ with ordering *vs.* composition.

quenching is very small, with [111] as the direction of easiest magnetization. Baking again develops a large anisotropy similar to that for the 74.8 percent alloy, but the change in K_1 is less.

For crystals containing less nickel than Ni_3Fe, the irregular order[10] of decreasing ease of magnetization [100], [111], [110] was observed at low fields for the disordered state. At higher fields, however, the [110] curve jumps to saturation, crossing the [111] curve. This crossover, which has not before been reported, was observed in the 65, 68, and 70 percent nickel alloys. In going over to the ordered state, a complete changeover occurs for the 68 and 70 percent nickel alloys. The [111] direction becomes the direction of easiest magnetization at all values of H. The [110] and [100] curves cross and recross, with [100] reaching saturation last. This crisscrossing is for almost coincident curves and may be due to errors in cutting the spheroids. That it is an inherent effect is, however, rendered more probable by the fact that it was observed to occur in three different specimens. Fig. 2 shows the upper part of the magnetization curves for a 68 percent nickel, 32 percent iron alloy for the ordered state, the disordered state, and an intermediate condition. The changes in anisotropy are small in comparison with those for the 74.8 percent alloy.

For 65 percent nickel, this complete changeover of magnetization curves does not occur. (See Fig. 3.) The irregular order [100], [111], [110] is observed for the disordered state, and the anisotropy merely decreases when the superstructure is formed. It follows that for some composition between 65 and 68 percent nickel, the anisotropy must be vanishingly small for the ordered state.

The changes in anisotropy between various degrees of disorder, induced in a specimen by the different cooling rates given above, were negligible. The large changes took place only after prolonged baking. Table II tabulates the anisotropy constants and the energy differences $W_{100}-W_{110}$ and $W_{111}-W_{100}$ for ordered and disordered crystals. The general effect of superstructure formation is to make the anisotropy more like that of pure nickel.

II. Saturation magnetization

The large changes observed in the saturation magnetization were unexpected. Considering the amount of work that has been done on the alloys in this composition range, it is surprising that such large effects have not been detected before.[11] The difference in saturation magnetization between ordered and disordered states was a maximum for the 74.8 percent nickel alloy. For

TABLE III. *Saturation magnetization values.*

Percent Nickel	Saturation Values (a) Ordered	(b) Normal* Cooling (Local Order)	(c) Drastic** Cooling (Disordered)	Percent Increase (b) to (a)	(c) to (a)
80.0	908	895	882	1.4	3.0
74.8	1007	963	952	4.6	5.8
70.5	1029	—	986	—	4.4
69.8	1071	1044	1028	2.6	4.2
68.0	1102	1080	1066	2.0	3.4
68.0	1108	1082	1072	2.4	3.4
65.0	1129	1117	1106	1.2	2.2

* 10°C to 100°C per minute (normally expected values).
** About 200°C per second.

[10] J. D. Kleis, Phys. Rev. **50**, 1178–1181 (1936).

[11] Confirmatory results have since been reported by P. Leech and C. Sykes, Phil. Mag. [7] **27**, 742–753 (1939) and by S. T. Pan, Phys. Rev. **56**, 933–936 (1939).

disorder attained by rapid or normal cooling, the change amounted to 4.6 percent, while for drastic cooling, the difference between ordered and disordered states was 5.8 percent of the saturation value for the disordered crystal. These values could be reproduced very accurately, regardless of previous heat treatment, and, therefore, the difference of 1.2 percent for different cooling rates is regarded as due to changes in the degree of short distance order.

For 65, 68, and 70 percent nickel, the changes with ordering, though marked, were smaller and decreased with increasing departure from Ni_3Fe. One of the specimens of composition near 70 percent nickel was difficult to magnetize to saturation and exhibited an abnormally low saturation value. The change with ordering, however, fits in with the other values. (See Fig. 4.) The increase in saturation magnetization with ordering falls off more rapidly on the nickel-rich side. At 80 percent nickel the maximum change observed was 3.0 percent, while near 70 percent nickel the shift amounted to 4.3 percent.

In line with this, it may be noted that abnormal magnetic properties extend over a wider range below 75 percent nickel than above this composition. This supports the view that the order-disorder transformation is responsible for permeability changes as well as for saturation changes.

The difference in the saturation magnetizations for different rates of cooling was of the same order of magnitude for all the alloys tested. Table III lists the saturation values obtained for different heat treatments.

The dissymmetry of the ordering forces, which is suggested by these facts, implies that the ordering forces which act below the critical temperature for order are greater if, at this temperature, the degree of ferromagnetic saturation is higher. The Curie point has its maximum near 70 percent nickel, and the magnetization at any selected temperature below the maximum Curie point has its maximum value at a still lower concentration of nickel, because the magnetic moment per atom rises with addition of iron. It is therefore suggested that ferromagnetic interaction promotes order in this series of alloys.

Curves plotted for the two ⟨111⟩ axes lying in the equatorial plane of the 74.8 percent nickel alloy proved to be identical. This test, suggested by Dr. R. M. Bozorth of the Bell Telephone Laboratories, shows that the effects are not determined by the accidental direction of a stray magnetic field present during baking, but are immediately related to the structure.

Discussion

The superstructure transformation involving Ni_3Fe is a sluggish one, with a critical ordering

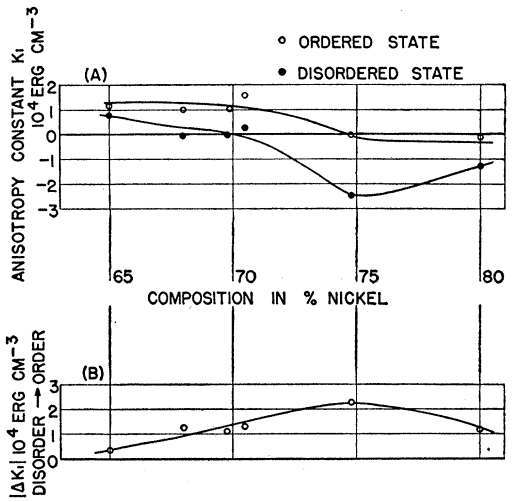

Fig. 5. (A) K_1 *vs.* composition for iron-nickel alloys. (B) Change in K_1 with ordering *vs.* composition.

temperature near 490°C. Baking just below this temperature was most effective in ordering.

Both the anisotropy and saturation magnetization are changed by baking for long periods below the critical temperature. Cooling at different rates produces appreciable changes only in the saturation magnetization. Hence, the anisotropy gives a measure of the long distance order, while the saturation magnetization change is related to local ordering, or the average magnetic moment for any one atom is determined by the nature of its nearest neighbors. Fig. 4 gives plots of magnetization at saturation *versus* composition and change in magnetization with ordering *versus* composition. The maximum is near the critical composition. Fig. 5 shows the change in the anisotropy constant K_1 by superstructure formation for different compositions. The maximum at Ni_3Fe is quite broad. The values for K_1 (disordered) are slightly lower than values

obtained by Kleis.[10] The second anisotropy constant K_2 becomes more positive with ordering except for the 65 percent nickel alloy.

The high permeability developed in these alloys by quenching is characteristic of the highly disordered state. A plausible explanation for the normal low permeability is that slow cooling forms small ordered regions which are frozen into an otherwise disordered lattice and give rise to strains. These strains increase the coercive force, and the permeability is low, while the highly disordered state is relatively strain-free and exhibits an extremely high permeability.

Cooling alloys in this composition range from above 500°C in the presence of a magnetic field also produces high permeabilities.[12] The effects of such heat treatment in a magnetic field may also be related to ordering. The critical temperature may be altered by the application of a field during cooling, if the ordering forces are in part of ferromagnetic origin. It does not appear, however, that the saturation value can be much affected by such treatment, as the following additional test indicates. Two specimens of 74.8 percent nickel and 68 percent nickel were each cooled slowly six times from 750°C with magnetic fields of 25 and 800 oersteds directed in turn along the three principal magnetic axes. The saturation magnetizations were the same as for cooling in the absence of a field, indicating, in accordance with the views expressed above, that these fields had no effect on the local order.

The addition of small amounts of the elements Mo, Mn, and Cu to these alloys increases the permeability to high values without the necessity of quenching or cooling in a magnetic field.[13] If the existence of local order is related to the permeability in these cases, the ordering forces are likely of a ferromagnetic nature, since ferromagnetic properties of pure alloys are easily disturbed by impurities in small quantities.

If the superstructure FeCo exists, indications are that it has an ordering temperature near 800°C, and it would be almost impossible to obtain the disordered state at room temperature.[14] In a preliminary test for such order, if it exists, one iron-cobalt specimen containing 56.3 percent iron (near FeCo) was repeatedly drastically quenched from temperatures ranging from 800°C and 900°C. The anisotropy and saturation value were not affected. The iron-cobalt spheroid had an axial ratio of about 20 to 1 and, consequently, saturated easily. Its magnetization at saturation was 1937.

Kaya[1] found that polycrystalline samples of compositions near Ni_3Fe were more difficult to saturate after they had been baked for long intervals. Much earlier than this, Elmen[15] had shown that such treatment greatly lowered initial permeability. This is in agreement with the results here presented, which show the appearance in the ordered state of one direction of very difficult magnetization.

As mentioned in the introduction, the reported changes in resistance with ordering are small, and so too are the possible changes in lattice parameter. It may be worth noting that the change in resistance is consistent in sign with increase in the number of free electrons and corresponding increase in the vacancies in the 3d electron group. The latter change corresponds to the observed increase in magnetic moment per atom.

McKeehan[2] has calculated the anisotropy constants K_1 and K_2 for Ni_3Fe as a disordered solid solution and as a superstructure, from magnetic multipole interaction. The quadrupole terms predict the correct sign for the change in K_1 accompanying the order-disorder transformation and are of the correct order of magnitude. For Ni_3Fe in the disordered state, K_1 (calculated) $=-0.18\times10^4$ erg·cm^{-3}, while for the ordered array, K_1 (calculated) $=-1.62\times10^4$ erg·cm^{-3}. These are to be compared with the experimentally observed values, zero and -2.30×10^4 erg·cm^{-3}, respectively. The computed sextupole part of K_1, and the computed K_2, which has no quadrupole part, do not change in the observed directions for superstructure formation.

The author wishes to express his sincere thanks to Professor L. W. McKeehan, who suggested this investigation, for his ready advice and for stimulating discussions during the course of the work.

[12] R. M. Bozorth, J. App. Phys. **8**, 575–588 (1937).
[13] S. Kaya and M. Nakayama, Zeits. f. Physik **112**, 420–429 (1939).
[14] A. Kussmann, B. Sharnow and A. Schultze, Zeits. f. tech. Physik **13**, 449–460 (1932).
[15] G. W. Elmen, J. Frank. Inst. **207**, 583–617 (1929), esp. Fig. 13.