are listed in Table VII. Eq. (40) was applied to these data with the assumption that N_0 for skeleton films on chromium was the same as for normal films. The value of n_W which was required to satisfy Eq. (40) when $N/N_W=0.7510$ and $i=80°$ was $n_W=1.295$. Thus the method of building films simultaneously on glass and chromium affords a useful means of making two independent determinations of n_W which cover a range of i from 14° to 80°.

After the data given in Tables VI and VII were obtained, films were built on seven microscope slides, each film having steps of 333, 343, 353 layers. All were soaked in benzene for 1 min. Measurement of the angles i at which these films reflected the minimum $m=7$ gave the result $n_W=1.32$. It frequently happens that after a water solution has stood in a trough for several hours the values of n_W which are then obtained are slightly higher than the initial values. This is probably due to a gradual accumulation in the solution of substances dissolved from the trough or taken up from the air.

The slides were stacked in a pile and the birefringence of the total of the seven films was measured by means of a quartz wedge compensator using transmitted light. The relative phase retardation of the R_s and R_p rays corresponded to $\lambda/4$ for sodium light at $i=48°$ and $\lambda/3$ at $i=54°$. The total thickness Nt_W of the 2471 layers was 59,800A, taking $t_W=24.2$A. Therefore the factor $5752t$ in Eq. (28) was replaced by 59,800. For $\Delta l=1473$A at $i=48°$ it was found that when $n_1=1.32$ the value of n_3 which gave terms which satisfied Eq. (28) was $n_3=1.390$. For $\Delta l=1964$A at $i=54°$ the calculated value was $n_3=1.391$.

A measurement of Brewster's angle made after these films were built gave the result $i_B=51°\,17'$. Substituting $i_B=51°\,17'$ and $n=1.32$ in Eq. (34) we obtain $n_3=1.383$. The refractive indices of the normal films built at pH $=7.0$ were $n_1=1.491$, $n_3=1.551$ from Eqs. (12) and (25). The skeleton films having $n_1=1.32$ and $n_3=1.390$ or 1.383 have therefore approximately the same value of n_3-n_1 as the normal films.

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Properties of the Surface Magnetization in Ferromagnetic Crystals

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The magnetic powder patterns found on polished iron crystals (which may contain a few percent of silicon) have been studied more carefully by using a macroscopic model and by investigating the forces on the powder particles. Reasons are given for preferring one of two simple models to explain the patterns; some interesting implications of the proposed model are then considered. Experiments are described which indicate that the structures under discussion originate during the polishing operation, but that other than magnetic causes must be responsible for the remarkable regularity of the patterns.

A SMALL magnetic field applied normal to the *polished* surface of a silicon-iron single crystal will cause magnetic powder in a colloid suspension placed on it to collect into regular patterns related to the crystal symmetry. To explain these patterns, which resemble mazes with paths about 4 microns wide on a (100) surface but consist of lines parallel to a [110] axis on a $(1\bar{1}0)$ surface, McKeehan and Elmore[1] assumed the surface to contain blocks about 2 microns on a side spontaneously magnetized along <100> or <110> axes in the surface, with opposing magnetizations at about one-half

[1] L. W. McKeehan and W. C. Elmore Phys. Rev. **46**, 226 (1934) W. C. Elmore and L. W. McKeehan, Trans. A. I. M. E. **120**, 236 (1936).

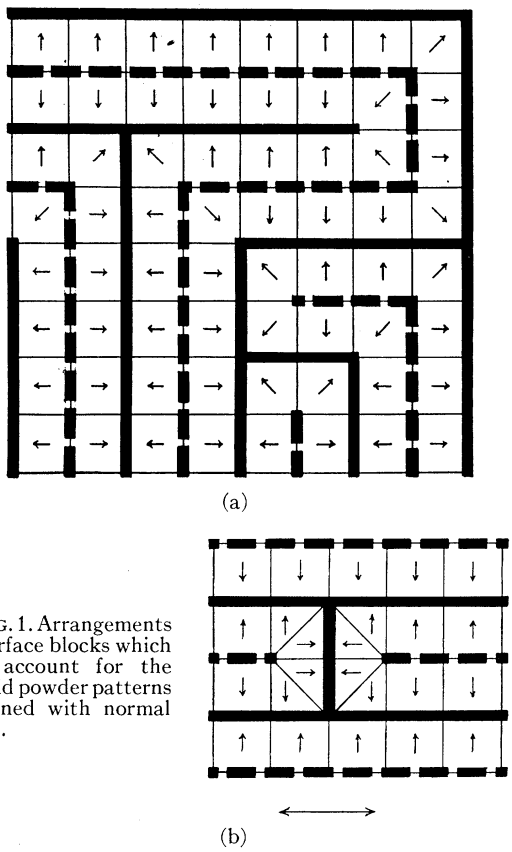


FIG. 1. Arrangements of surface blocks which will account for the colloid powder patterns obtained with normal fields.

of the block boundaries. The blocks with diagonal magnetizations were considered necessary to account for corners and for the abrupt endings of some of the maze pattern lines, illustrated in Fig. 1a. In this diagram, which shows a typical proposed arrangement of the block magnetizations, the heavy solid lines represent the colloid pattern which would be found upon applying a magnetic field normal to the specimen and directed outward. Upon reversing this field the colloid would migrate from the solid lines to the heavy broken lines. This change in pattern constitutes the shifting effect. It was also reported that a no-field pattern, less distinct than these patterns, appeared to be a *superposition of them*, that is, a double pattern of lines occurring at all of the block boundaries separating opposing magnetizations. Very careful observation under higher magnification (1500×) has since revealed that the no-field pattern lines always occur *halfway between those of the superposed double pattern*. Realization of this fact has led to a more careful analysis of the patterns, and to the construction of a macroscopic model. It is proposed to discuss this model, its connection with the iron patterns, and some interesting properties of the magnetic structure which seems best suited to account for the patterns. Brief mention will be made of a few points of experimental technique.

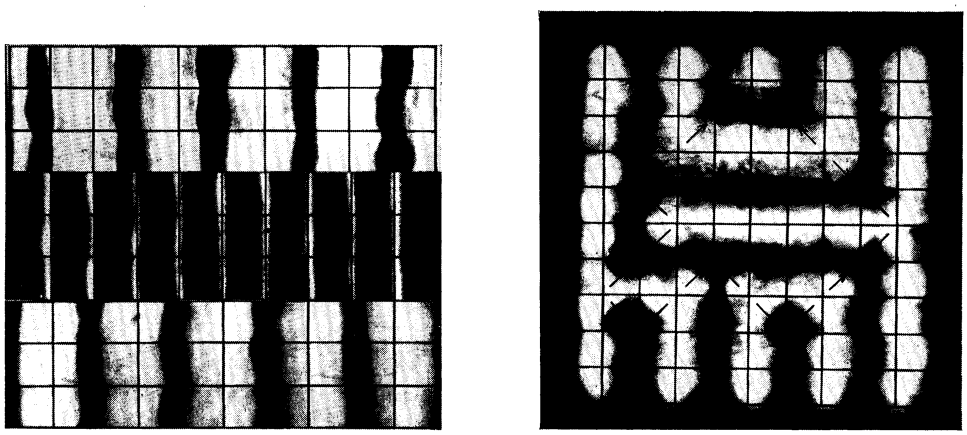
THE MACROSCOPIC MODEL

The model consisted of 100 one-half inch cubes of hardened steel packed together in square array. Each cube was permanently magnetized in one direction and various characteristic patterns simulated by suitably arranging the cubes. Exploration with iron filings of the field surrounding individual cubes indicated a satisfactory uniformity of magnetization. Fig. 2a shows a composite photograph of the simplest parallel line patterns for no field and for small normal fields of both signs. For this pattern the blocks were magnetized parallel to edges and arranged in rows which had the same polarity on adjacent faces. The no-field distribution of powder is seen to occur in lines along the middle of the blocks in the same position with respect to the field-selected lines as observed under high magnification for the colloid distributions.

That the no-field pattern does not occur at the block boundaries at first seemed puzzling, for intuition, confirmed by mathematical analysis of the field above the blocks (by the method of conformal mapping using the complex transformation $x+iy=-(id/\pi)\ \ln\ \mathrm{sn}(U+iV)$),[2] indicated that the force on a single powder dipole, $\mathbf{F}=\mathbf{M}\cdot\nabla\mathbf{H}=M(H)\mathbf{H}\nabla\cdot\mathbf{H}=\frac{1}{2}M(H)\nabla H^2$, would move it to the nearest block boundary. It is now realized that this discrepancy chiefly comes from neglecting the mutual magnetic interaction of large numbers of the powder particles. The following consideration will reveal the important part played by this interaction when there is no normal applied field.

Regardless of the actual distribution of surface magnetization responsible for the parallel line pattern, as long as it is periodic, the local field above the specimen can be derived from the

[2] J. J. Thomson, *Recent Researches in Electricity and Magnetism* (Oxford, 1893), p. 239.



(a) (b)

FIG. 2. Patterns obtained with the steel cube model. (a) shows the no-field and the two normal field patterns of parallel lines; (b) shows a typical maze pattern obtained when diagonally magnetized blocks are used.

potential

$$V=\Sigma A_n e^{(-\pi n y)/d}\cos(\pi n x/d)$$
(summed with $n=1, 3, 5, \cdots$),

where x and y are distances measured in and normal to the surface, respectively; $2d$ is the smallest distance in which the surface distribution of magnetization does not repeat itself; the A_n are constants depending only upon the model of surface magnetization assumed, and, in general, decreasing with increasing n. For $y>0$ this series converges very rapidly, in fact the first term is a good approximation when $y \doteqdot d/2$. Consequently, the vector $\nabla H^2=\nabla\{(\partial V/\partial x)^2+(\partial V/\partial y)^2\}$ in the expression for **F**, the force on a dipole, is nearly independent of x, that is, **F** is everywhere directed towards the surface. With the same approximation, however, the dipoles will make angles with the x axis given by $\theta=(\pi/d)(x+d/2)$. Fig. 3 shows schematically a cross section of the surface and the oriented particle dipoles. The layer L (drawn to be about 0.5 micron thick) represents a protective film of lacquer and a possible surface layer of the metal, damaged to such an extent by polishing that it does not take an active part in the production of surface stray fields. It is obvious from a simple consideration of energy that this arrangement of particles is not the most stable one. If the particles avoid positions near $x=0, \pm d, \pm 2d, \cdots$ and concentrate near $x=\pm d/2, \pm 3d/2, \cdots$ their mutual potential energy will be less, with little or no increase in their potential energy with respect to the local field. Accordingly, it is this latter arrangement which should be found, a result which does not depend upon a particular model of surface magnetization.

If a uniform magnetic field $\pm H_N$ normal to the surface is superposed on the unchanged local field H derived from V, then $\nabla H^2=\nabla\{(\partial V/\partial x)^2+(\partial V/\partial y)^2\}\pm 2H_N\nabla(\partial V/\partial y)$ in which the second term will correctly explain the shifting effect. It gives lines at $x=0, \pm 2d, \pm 4d, \cdots$ or at $x=\pm d, \pm 3d, \cdots$ depending on the sign of H_N. The mutual particle interaction, so important for the no-field pattern, simply tends to broaden these bands without affecting their mean position.

The above analysis shows, in addition, that there are many possible periodic magnetic structures which might account for the patterns.

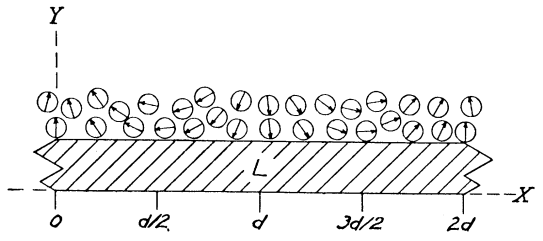


FIG. 3. Distribution of powder dipoles above the surface when mutual dipole interaction is neglected. An arbitrary periodic arrangement of surface magnetization is assumed.

Another *simple* structure is one in which blocks are magnetized normal to, rather than parallel to, the surface. Müller and Steinberg[3] proposed a somewhat similar model of layer magnetization for magnetite. Experiments with the macroscopic model have indeed shown that patterns similar to the three colloid patterns can so be obtained. The blocks were lined up with magnetization outward along the lines of one of the denser maze patterns, and inward along the lines of the corresponding reciprocal maze. The block boundaries then coincided with the less distinct no-field pattern. There are a number of reasons, however, for preferring the first model, in addition to some reasons to be discussed later in connection with diagonal magnetization. (1) The first model permits a qualitative interpretation of the effect on the patterns of preferential polish and of previous magnetic saturation. (2) The second model would seem to imply the frequent occurrence of patterns resembling a checkerboard. (3) The no-field patterns on iron have been compared with those on the basal plane of cobalt. The local stray fields of the latter crystal were found to be much greater than those of iron. Since the hexagonal axis in cobalt is the only direction of easy magnetization, it seems likely that the local magnetization must here be perpendicular to the basal plane. Consequently, the comparison of the stray fields favors the first model for iron. (4) Perhaps the best argument for the first model is the fact that only parallel line patterns are found on a polished (110) face with lines in the direction of traces of (001) planes. If the block magnetization were normal to the (110) surface or pointing out at an angle of 45°, there is no apparent reason why maze patterns should not be found. The first model can account for the (110) patterns very simply by employing block magnetizations in the surface parallel to the [001] axis. (5) Finally, the surface can have a small net residual magnetization parallel to itself if the surface magnetization resembles that of the first model.

An attempt has been made with the steel cube model to obtain ells, tees and other details of a maze pattern by using only blocks magnetized parallel to an edge and arranged in accordance with the first model. Additional short segments of powder and also gaps in the pattern lines appeared in a manner that has never been observed in hundreds of colloid patterns. When blocks more or less uniformly magnetized parallel to a diagonal were placed at appropriate positions in the model, the patterns were very similar to the colloid maze patterns, as may be judged from the photograph, Fig. 2b. The postulation of *uniformly* magnetized diagonal blocks, however, is open to question. It is well known that in iron axes of form <100> are directions of easiest magnetization; other directions in the crystal require more energy for magnetic saturation. Hence, instead of having the diagonal block uniformly magnetized, it seems better to have its magnetization divided between two <100> directions by a diagonal plane, as, for instance, in Fig. 1b. It would be difficult to decide between the two types of diagonal block by use of the macroscopic model; in what follows the second one will be assumed.

Some Properties of the Proposed Model

The model which is being proposed to account for the patterns on polished iron possesses a number of interesting properties. If patterns on paper are constructed by placing arrows indicating directions of magnetization in a network of squares, it is found that the arrows in the diagonal blocks must form continuous chains with pairs of arrows pointing to and from common corners (see Fig. 1a). The pattern lines change to their other possible direction as they pass such a chain. Accordingly, these chains of arrows (or the diagonal block divisions) divide the surface into a number of regions differing in the prevailing direction of magnetization. It is clear that the chains (or *diagonal lines*, as they will be called hereafter) must start at the edge of the pattern or close on themselves. Furthermore, they may be locally modified without changing the pattern other than locally. Geometrically, the diagonal lines completely determine the pattern.

Further analysis reveals that consecutive diagonal lines cutting any line in the surface cannot be chosen arbitrarily. The details of permitted choices, which depend essentially upon dividing diagonal lines into four classes and

[3] N. Müller and D. Steinberg, Tech. Phys. U. S. S. R. **1**, 205 (1934).

establishing a cyclic order for these classes, are easily worked out. Once the class of such a line is determined, its exact course is arbitrary with the exception that two diagonal lines cannot, in general, cross one another. The positions of the lines, however, determine the amount and direction of a small residual magnetization associated with the pattern. This remanence for any given pattern is easily computed.

The relation of magnetostriction to the patterns leads to an interesting speculation. The magneto-mechanical properties of iron crystals are well known and have been correlated by a formal theory.[4] For instance, an iron crystal magnetized along an axis of form $<100>$ increases its length in that direction, and, conversely, the crystal can be magnetized most easily along a $<100>$ axis which is, at the same time, the direction of an applied tension. If the tension is replaced by compression, then the other two axes of form $<100>$ become directions of easiest magnetization. Since magnetostriction is essentially related to the spontaneous magnetization of the ferromagnetic, it is correct to apply these results to the magnetization of the blocks. Hence it is realized that the diagonal lines have more than a geometrical significance: they represent boundaries in the surface between regions in which the magnetostrictive strain axes, always lying in the surface, differ in direction by a right angle.

From the converse point of view it can be argued that, during the polishing operation, the surface is stretched or compressed in various places in a more or less random fashion. These regions of positive and negative strain must be distributed so that the distortion of the surface as a whole is small. From the brief discussion of the magneto-mechanical interaction it is clear that the resulting regional stresses must tend to control the direction (not the sense) of the local magnetization. If the proposed model is correct, the diagonal lines must be the approximate boundaries between these regions. To summarize, the magnetization of the blocks will arrange itself not only to produce a nearly complete demagnetization of the surface of the crystal, but in addition to decrease the magnitude of the stresses set up in the surface by the polishing operation. The diagonal lines have been drawn on several photomicrographs of which Fig. 4 is typical. One set of regions marked out by the lines has been shaded. The direction of magnetization in the shaded and in the unshaded parts differs by a right angle.

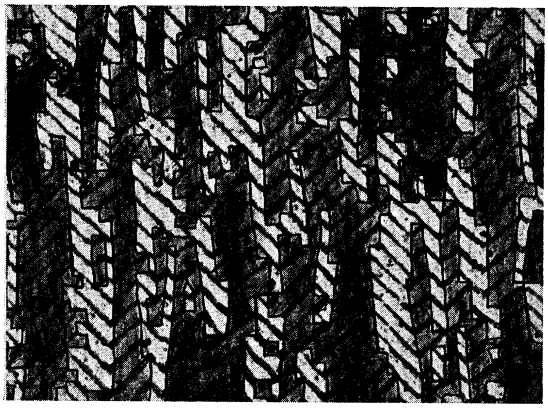


FIG. 4. A maze pattern in which the diagonal lines discussed in the text have been drawn. The direction of magnetization in the shaded parts is perpendicular to that in the unshaded parts.

The diagonal lines have further use in the interpretation of local pattern changes which occur upon the application and removal of a field parallel to the surface. These changes have already been sufficiently described[1] although they require subjective observation for a full appreciation. (Plans are under way to take motion pictures of these and other changes in pattern.) The local pattern changes were shown to be consistent with the view that the blocks retain their identity, with only their direction of magnetization changing. Such changes involve local modification of a diagonal line, in fact it can be considered that they consist of the motion of this line from one stable position to another. Only rotations of the net block magnetizations through angles of 45° would then be involved and the diagonal line boundary itself would progress by rotation of electron spins through angles of 90°. The following local pattern change which was observed on one specimen of silicon-iron is simple enough to be described in words. The cross bar of an "*H*" occurring in a maze pattern was found to be quite unstable with respect to the variation of a field applied parallel to the surface and to the sides of the "*H*."

[4] E. C. Stoner, *Magnetism and Matter.* (Methuen & Co., London, 1934), p. 395.

By slightly increasing and then decreasing the field, which was not very uniform, the cross bar could be made to run back and forth along the sides of the "*H*." The neighboring pattern showed no changes unless the field was considerably increased. Fig. 1b shows the arrangement of magnetization which will account for the pattern; the two-headed arrow indicates the motion of the cross bar.

Nature of the Block Structure

The analysis of the maze patterns presented so far has been based on the assumption of unit blocks, uniformly magnetized, uniform in size and geometrically fixed in the surface. The character of this structure requires further elucidation.

At first it was thought that the structure extended throughout the crystal in a manner suggesting Zwicky's regular secondary structure,[5] and not depending upon the presence of a polished surface layer. This conclusion was drawn chiefly from a study of patterns found on various cuts of the same crystal. It is now recognized that polishing plays an all-important role, and that the position of the block boundaries, as far as the patterns are concerned, is fixed during the polishing operation, but probably not by causes deriving from magnetism.

The evidence is fairly conclusive. Patterns formed on a very smooth unpolished strip of silicon-iron, as well as on unpolished pieces of Cioffi iron,[6] did not resemble the maze patterns under discussion. They resembled, rather, the more widely spaced parallel line patterns discovered by Bitter.[7] An entire set of these lines could be made to move continuously across the microscope field by changing the applied magnetic field which, for the effect, had a component parallel to the surface and perpendicular to the lines. No sign of the maze patterns could be found. The behavior of the colloid while the applied normal field was increasing from zero to a small value suggested that, if such a structure be present, it is too fine for resolution. Detailed study of the Bitter lines has been retarded by the difficulty of obtaining mirror-like surfaces suitable for high power microscopic examination, without recourse to mechanical polishing. This difficulty has been very recently met by extending to iron the Jacquet electrolytic method of polishing.[8] A specimen of silicon-iron polished by this method, which yields unstrained surfaces of extreme local smoothness, gave only the Bitter parallel line pattern. It is expected to continue the study of these patterns and their relation, if any, to the finer scaled maze patterns.

Further evidence about the maze patterns was obtained by making a broad shallow scratch on the Cioffi specimen. Colloid deposited by normal field formed a portion of a perfect maze on the scratched region, whereas the neighboring undamaged surface contained only a broadly spaced parallel line pattern, very sensitive to changes in magnetic field. In another experiment a piece of silicon-iron strip magnetized practically to saturation by a small Alnico horseshoe magnet was subjected to the customary metallurgical polishing. Upon removing the magnet and applying a normal field, the usual maze pattern was found. This experiment shows that magnetostrictive strains in undamaged demagnetized crystals probably do not play an important part in the origin of the maze structure during the cold working of the surface. To account for the regularity of the magnetic structure produced by polishing, it seems necessary to suppose that cold working of the surface merely serves to enhance some sort of nonmagnetic structure already present in the crystal, perhaps by the formation of block crystal fragments.

Electron diffraction[9] indicates that a polished surface consists of, first, an amorphous or microcrystalline layer 30 or 40A thick (the Beilby layer); next, a relatively thicker layer of larger crystal fragments; finally the parent crystals. A recent optical investigation of copper, polished mechanically and then electrolytically,[10] indicates that polishing cold work extends to a depth of 13 microns or more. Since silicon-iron is

[5] F. Zwicky, Phys. Rev. **43**, 270 (1933).
[6] P. P. Cioffi, Nature **126**, 200 (1930). The specimens used were kindly furnished by Mr. P. P. Cioffi and Dr. R. M. Bozorth of the Bell Telephone Laboratories, New York.
[7] F. Bitter, Phys. Rev. **38**, 1903 (1931); **41**, 507 (1932).
[8] P. Jacquet, Comptes rendus **201**, 1473 (1935); **202**, 403 (1936).
[9] For a general discussion see Trans. Faraday Soc. **31**, 1043 (1935).
[10] H. Lowery, H. Wilkinson and D. L. Smare, Phil. Mag. [7] **22**, 796 (1936).

harder than copper, it is likely that the depth of the damage in the former is more nearly comparable with the size of the magnetic blocks. With the addition of a block regularity to the crystal fragments underneath the Beilby layer, the present picture of a polished iron surface is consistent with these views. The aim of speculation and future experiment must be to account for the regularity in the cold worked crystal.

Before the part that polishing plays was realized, it was suggested that the magnetic structural regularity and stability might be due to the segregation of foreign atoms in the necessary planes. Such a segregation seems now to be a reasonable, if not the only, pre-polishing structure (assuming that such a structure is really necessary) which could lead to a regular fragmented block structure through cold working. If it be supposed that at high temperatures the foreign atoms are uniformly distributed in solid solution but that at lower temperatures they are most stably located as a two-dimensional array in <100> planes (rather than forming three-dimensional particles) the very regular distribution called for may represent an attained equilibrium. Only 0.02 atomic percent of impurity would be required to populate single planes at the observed intervals.

Notes on Technique

Colloid similar to that used to form patterns in this and in previous investigations may be prepared quite simply. The author is greatly indebted to Dr. O. Baudisch[11] for the following formula:

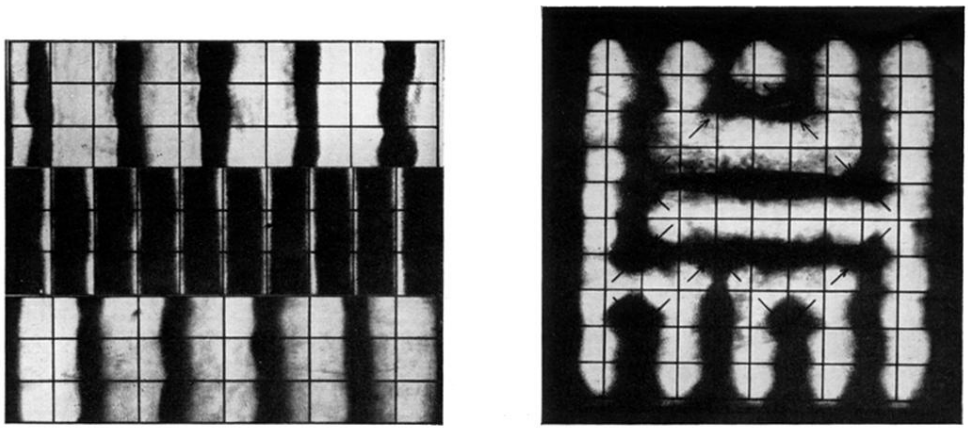
100 grams gamma Fe_2O_3, or siderac
200 grams white Schering-Kahlbaum dextrin (puriss)
0.66 grams HCl
1 liter distilled water.

These constituents are to be run through a colloid mill until the siderac is in a colloid state. If the colloid is to be kept for some time it will be found necessary to add a small amount of preservative to prevent bacterial action.

An improvement in the technique of producing patterns consists in coating the clean surface of the specimen with a thin layer of water-proof lacquer. For this purpose a small amount of lacquer dissolved in amyl acetate may be brushed on the surface which is then held in an air blast. The resulting film, thin enough to show interference colors, will prevent the colloid from sticking to the metal and will also protect the specimen from rusting. The sticking of the colloid, formerly prevented by a thin grease film, is no doubt due to the electrical discharge of the colloid particles by the metal surface. The layer of lacquer does not interfere with the formation of patterns.

In conclusion the author wishes to thank Professor F. Bitter and the Department of Mining and Metallurgy for placing at his disposal certain facilities for conducting the experimental part of this work. He is greatly indebted to Professor Bitter and to Professor L. W. McKeehan of Yale for discussing many of the ideas which have been presented. The colloidal siderac used in recent experiments was kindly furnished by Sharp and Dohme of Philadelphia.

[11] Director of Research, Saratoga Springs Authority. For a discussion of magnetic and other properties of iron oxides, see L. Welo and O. Baudisch, Chem. Rev. **15**, 45 (1934).



(a) (b)

FIG. 2. Patterns obtained with the steel cube model. (a) shows the no-field and the two normal field patterns of parallel lines; (b) shows a typical maze pattern obtained when diagonally magnetized blocks are used.

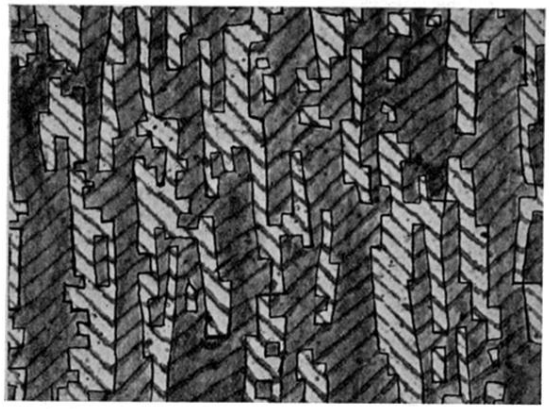


FIG. 4. A maze pattern in which the diagonal lines discussed in the text have been drawn. The direction of magnetization in the shaded parts is perpendicular to that in the unshaded parts.