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H. A. McTAGGART**

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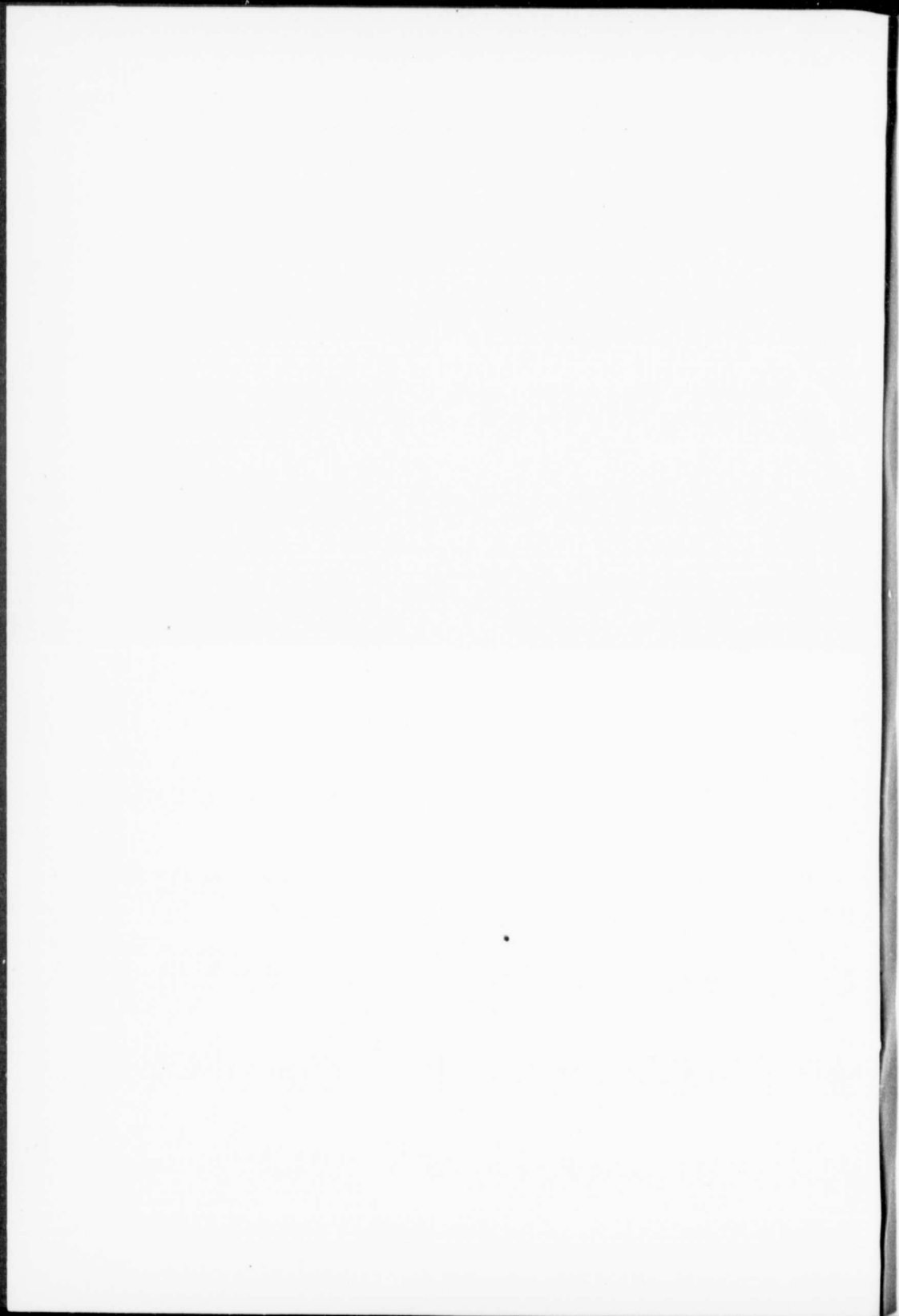
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University of Toronto Studies

ON THE CONSTITUTION AND PROPERTIES OF
HEUSLER'S ALLOYS, INCLUDING A STUDY
OF THEIR MICROSTRUCTURE

BY

H. A. McTAGGART, M.A.



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I. INTRODUCTION

It is now some years since the ferromagnetic alloys composed of aluminium, manganese, and copper were discovered by Heusler,* and in the period which has elapsed since this discovery many of their physical properties have been investigated.

Permeability.—Amongst others, Heusler, Starck and Haupt,† Fleming and Hadfield‡ have studied the permeability of these alloys. By increasing the percentage of manganese present in them, these investigators found a steady increase in the permeability until the manganese and aluminium were present in the ratio of their atomic weights (aluminium 27.11 = manganese 55.00). With still higher percentages of manganese, the permeability gradually decreased and approached a low value. The highest magnetization as yet obtained with these alloys is about one-third of that of the best iron.

In addition to what has been done elsewhere, the permeability of various castings of these alloys in the form of rings and of rods has been studied in the Physical Laboratory of the University of Toronto by Miss L. B. Johnson and by the writer in collaboration with Mr. J. K. Robertson, and a few curves are given in Diagram 1 to show the comparative permeability of five selected specimens. They were cast in the form of rods about 20 cm. long and 8 mm. in diameter, and numbered 1a, 2, 3, 3a and 4, to distinguish them. Those numbered 3 and 3a had the same percentage composition and were poured from the same melt, while the others had different compositions. The percentages of the constituents in each casting, as well as the relative weights of manganese and aluminium, and the atomic ratios of these two metals, are shown in Table A.

* Verh. d. Deut. Phys. Gesell., 5, 219 (1903).

† Marburg Schriften, 1904, 237.

‡ Electrician, June 16, 1905.

TABLE A.

No. of Alloy.	Percentages of Composition.			Ratio of Al. to Mn. by weight.	Atomic ratio of Al. to Mn.
	Al.	Mn.	Cu.		
1a	8.0	32.1	59.8	.250	.51
2	9.7	25.6	64.6	.378	.77
3 and 3a	14.3	28.6	57.1	.498	1.01
4	15.9	23.9	60.3	.683	1.392

The more magnetic alloys, whose magnetization is indicated in curves 3 and 3a (Diag. 1), contained manganese and aluminium very nearly in the proportions discovered by Heusler. No. 4, which was also highly magnetic, did not, however, reach such a high saturation value as Nos. 3 and 3a, while Nos. 1 and 2 were capable of magnetization only to a comparatively small extent. From the observations of different experimenters it appears to be evident that the copper serves no other purpose than to make the alloys—otherwise very hard and brittle—soft enough to be cast and handled.

Hall Effect and Allied Phenomena.—In addition to the permeability of these alloys, the Hall effect and their thermo-magnetic properties have been examined by Zahn and Schmidt.* These effects are more evident in magnetic than in other metals, with the exception of tellurium and bismuth. The coefficient of the Hall effect, represented by R , and that of the thermo-magnetic effect, represented by Q , were measured by these investigators for a number of Heusler's alloys. Their values (approx.) for the alloys are shown in Table B, and, for comparison, the corresponding values of these coefficients for the separate constituents, manganese, aluminium and copper.

TABLE B.

Metals.	$R \times 10^5$.	$Q \times 10^6$.
Heusler's Alloys.....	+ 1300 (approx.)	- 500 (approx.)
Mn.....	- 93	- 15
Al.....	- 40	+ 20
Cu.....	- 50	+ 90

* Verh. d. Deut. Phys. Gesell., March, 1907.

As the table shows, R and Q are much larger for the alloys than for the constituent metals.

Electrical Resistance.—The resistance of these alloys or bronzes, as they are sometimes called, was also examined in the Laboratory at Toronto by the writer in collaboration with Mr. J. K. Robertson. Owing to limitations of time, it was not found possible to determine the specific resistance for a large number of temperatures, but values were obtained at the temperature of liquid air, about -185° C., of carbonic acid snow mixed with ether, about -77° C., of melting ice, of boiling water, and of paraffin heated to 160° C. Eight rods in all were examined. The rod marked 1a had the same composition as that given in Table A; the rods marked 2 and 2a had the same composition as No. 2 in that Table; the rods 3, 3a and 3b had the same composition as Nos. 3 and 3a given in that Table; the rods marked 4 and 4a had the same composition as No. 4 in Table A. The five values determined for each of these rods are plotted in Diagram 2.

From an examination of the curves it will be seen that alloys Nos. 3, 3a, 3b were most regular, the resistance of each being practically a linear function of the temperature. Alloys 4 and 4a approximate closely in their behaviour to Nos. 3, 3a, 3b, while the least magnetic ones, 1a, 2, and 2a, show considerable irregularities. This probably indicates a greater homogeneity in Nos. 3, 3a, 3b, whereas in the others the absence of uniform change in the resistance may possibly be due to the superposition of distinct effects arising from the variations in the resistances of the different constituents.

Magnetostriction.—The phenomenon of magnetostriction has also been examined in connection with these alloys, and in a paper by Professor McLennan* the results of a number of measurements are given. In this paper attention is called to three factors in the elongation effect: (1) a change in the length of the alloy followed a change in the field; (2) the value of the elongation for a certain strength of field was not the same when the field was being increased as it was when being decreased; in other words, a hysteresis effect or lag in the elongation occurred

* Phys. Rev., 24 (1907).

when the field was gradually removed; (3) in some cases a continual shortening was noticed when the specimen was left for some time in a strong field.

The first and second effects are well shown in Diagram 3, where the curve represents a cycle of measurements taken with alloy 3a mentioned above, after it had been newly cast. The curve shows a steady elongation as the field increases, but as the field was diminished the elongation passed through a series of values greater than those accompanying the increasing field, the rod finally ending with a length greater than it had at first. In contrast with this the curve in Diagram 4 shows the behaviour of the same rod when taken through a cycle after it had been magnetized and demagnetized a number of times. Here a small lag was also observable, but the final length of the rod was the same as that at the beginning. From this investigation it would seem that the structure of a new alloy is more or less unstable, and that a condition of stability is reached by magnetizing and demagnetizing the specimen or by ageing it.

Heat Treatment.—These alloys have been studied from still another point of view, namely, that of noting the effect (1) of heating the more permeable of them for varying lengths of time and slowly cooling them, and (2) of raising them to various temperatures and then quenching them in water or mercury. The results of continued heating and gradual cooling were examined by Gumlich,* who heated a specimen for 102 hours at 110° C., and again for 544 hours at the same temperature. He found a considerable increase in the permeability of the alloy to result from this treatment, and the effect is shown graphically in Diagram 5. Another experimenter, B. V. Hill,† examined two specimens, one of which was successively heated and cooled while its magnetization was tested. Its behaviour is shown by the curve in Diagram 6. In continuation of this work‡ four other alloys were examined in this way, carried to still higher temperatures. The results of these experiments pointed to an apparent law that the permeability at ordinary

* Ann. d. Phys., 16, 535 (1904).

† Phys. Rev., 96, 335 (1905).

‡ Ibid., 23, 498 (1906).

temperatures depended on the temperature from which the alloy had been cooled. As this temperature was raised the permeability decreased to a minimum and then rose again.

Further interesting results have been found by Take* on the transformation points of these bronzes, using both a ballistic and a dilatometric method. A similar research has been carried out by Asteroth† recently with two specimens, one a casting allowed to cool in the usual way, the other a casting heated red-hot and plunged into water. A series of observations was made on the influence of various kinds of cooling after the specimen had been heated above the transformation points, which were about 195° C. and 220° C. respectively. Both samples were heated to the transformation point and allowed to cool slowly for three-quarters of an hour, when they were aged at 140° C. They were then taken through a cycle of readings to examine their magnetization, and with this treatment the values showed a considerable hysteresis. A second trial in the same way, except that the cooling occupied three hours, gave a small increase in the magnetic hysteresis.

Again both samples were raised to the magnetic transformation point and then plunged into cold water. The magnetic properties were so small that they were scarcely observable. The castings were then aged for 12 hours in boiling xylol and put through a cycle of readings. With a field of $H = 150$ the ordinary casting showed a value for the induction of $B = 2300$, the other casting a value of $B = 2500$ C.G.S. In this instance the magnetic hysteresis had almost vanished. It appears, then, that the cooling has some effect on the structure of the metal so far as its magnetic properties are concerned. Cooling slowly from the transformation point leaves a hysteresis effect, while quenching at that point produces a change which practically eliminates this property. Indeed, Asteroth found it almost possible to increase or decrease the hysteresis between certain limits at will.

From these investigations, and particularly those on temperature effects, it would appear that we have to do with phase

* Verh. d. Deut. Phys. Gesell., 7, 133 (1905).

† Ibid., Jan., 1908.

changes of some kind, and it is possible that a parallelism may exist between the crystallographic structure and the physical properties of the bronzes. This possibility seems to be borne out by the facts cited in the brief sketch of the properties of the alloys just given. The peculiar behaviour of the resistance of the less magnetic samples and their apparent lack of homogeneity; the instability of fresh castings as shown by the dependence of their magnetostriction phenomena upon their previous history and treatment; and finally the remarkable and almost complete control, within certain bounds, that an experimenter has over their permeability and magnetic hysteresis by suitable methods of heating and cooling, all point to a parallelism between the magnetic phenomena and the molecular or crystalline arrangement of the metals in the castings. As one of the most interesting and instructive ways of studying these phase changes, it was decided to begin a series of investigations on the microstructure of the alloys in the hope of throwing some light on their magnetic properties, and an account of the work done up to the present will now be given.

II. METHOD OF RESEARCH

The method employed in the study of the crystalline structure of the alloys was that of examining under the microscope a polished surface of the metal suitably etched by a reagent. This mode of proceeding was initiated by Sorby in the study of the microstructure of iron and steel as far back as 1864, and has been developed more recently in the case of alloys other than those of iron by Haycock and Neville, Osmond, Stead, and others. The specimens examined in this research were eight in number, cast in the form of rods, and were those mentioned in other parts of the paper as distinguished by the marks 1a, 2, 2a, 3, 3a, 3b, 4, 4a. Sections were made in the workshop of the Physical Laboratory both along the axes of the rods and at right angles to them so as to make the observations as complete as possible. In addition to examination by etching, the surfaces were also studied to some extent by heating them in order to give oxidation colours. The patterns or characteristic appear-

ances of the different surfaces as they were seen in the microscope were occasionally photographed for reference, but, in general, sketching with a pencil a portion of the field was found to be more expeditious and useful. The various processes of polishing, etching, photographing, sketching, etc., will now be described in detail.

Cutting and Polishing.—The alloys being too hard to be cut by a file or by lathe tools, the samples examined were cut of the desired length from the rods and ground into shape on an emery wheel. Eight pieces were cut from the rods (1a, 2, 2a, 3, 3a, 3b, 4, 4a) mentioned before, about 1½ cm. long, the ends being ground flat at right angles to the axis. Eight others were cut in this way from the same rods, but a surface was ground on each, parallel to the axis. The rough surface left by the emery wheel was then made smoother by grinding on flour emery applied to a lead disc. This disc was cast from lead in the workshop and then turned down to a diameter of 20 cm. and a thickness of about 2 cm., and fitted to the shaft of an emery machine. To obtain the best results the wheel was slightly dampened with a light oil, and the emery flour was then rubbed on; this gave a surface which was fairly dry without being pasty, and which was found to cut clean and rapidly. When more flour was needed it was found best to stop the wheel and rub the flour on with a cloth or some waste while the wheel was at rest. Grinding in this way gave the specimen a smoother surface than could be obtained by using emery. To get a still smoother surface, another disc was made of brass smaller than the last, of about 12 cm. diameter and 3 or 4 mm. thick. This was turned to fit a small adjustable bench motor arranged so that the shaft could be set at any angle. One side of the disc was covered with strong cotton cemented on with shellac. This when covered with tripoli rubbed on from a cake consisting of the powder and mutton fat melted together produced a smoother surface in the specimen. In the case of manganese itself, which is very hard and brittle, polishing on tripoli in this way was often sufficient to give a fairly good surface for examination under the microscope, but in most cases a final polishing was necessary. For this the opposite side of the brass disc, which could be reversed

on the shaft, was covered with a soft, firm cloth such as broad-cloth, cemented on as before. Instead of tripoli, rouge in a cake such as jewellers use was rubbed evenly on this cloth. Polishing in this way with rouge usually gave a satisfactory surface in the case of the alloys. A higher polish could be obtained by running the disc at a fairly high speed. Occasionally scratches across the surface were made by dust on the disc or some other cause, but these did not interfere materially with the patterns observed in the microscope, there being an abundance of area quite smooth and large enough to fill the field under a power of 300 or 400. It may be added, however, that this series of grindings and polishings did not give with the softer metals, such as copper, aluminium, or iron, as good a surface as could be desired. A final series of powders must be used in these cases to get the most satisfactory results.

Etching.—The principal acids used in the process of etching the alloys were acetic, hydrochloric, and nitric, diluted to suit the needs of the case. Some other reagents were found useful and convenient, but these were the most important, and in endeavouring to bring out the characteristics of any of the alloys they were used, as a rule, in the order mentioned above. If acetic acid is used first it will attack only the manganese—at least, presumably so, for it will not dissolve aluminium or copper in the ordinary state. If then hydrochloric acid is used, it will attack the manganese present, and in addition any free aluminium that may exist in the alloy, but it will not dissolve the free copper. To etch the copper we must finally resort to nitric acid. By following this sequence the presence of the elements may be detected in order.

When a surface is ready to etch, the concentration of the reagent used, the method of applying it, and the time during which it is applied become questions of importance in order to obtain the best results. If a light etching was desired, a dilute reagent applied for a suitable length of time was best as a rule, but sometimes a more concentrated solution applied quickly gave a better definition. In applying the acid the writer found it convenient sometimes to hold the surface in the acid, sometimes

to place a drop of the acid on the surface, but for lighter etching it was necessary to touch the surface to parchment or blotting-paper wetted in the solution. At this stage it was often difficult to dry the surface and leave it bright and in the condition produced by the acid. If it was not quickly dried the surface often became coloured or corroded in consequence of the oxidation of the surface. A solution of weak acid in alcohol as an etching reagent sometimes helps to prevent this result, or the surface may be quickly rubbed over with a piece of chamois leather dipped in benzene. Frequently, also, the stronger acids leave some of the dissolved material on the surface, and this, if not removed, interferes with the examination of the surface by the aid of the microscope. Washing quickly in weak acetic acid with a bit of absorbent cotton helps to produce a clear surface.

In addition to the reagents mentioned, picric acid and a mixture of hydrochloric acid and ferric chloride were also used. The former offered no special advantage over acetic acid, but the latter served as a good substitute for hydrochloric or nitric acid in the case of the alloys when a slow rate of etching was desired.

Heating.—The surfaces of the specimens were examined after they had been heated, to distinguish, if possible, the presence and appearance of the constituent metals or compounds by their characteristic observation colours. For this purpose they were placed on a thin plate of firebrick or a sheet of mica over a Bunsen flame and heated to the extent desired.

The Microscope.—Since the specimens were opaque they could not be examined by transmitted light as in the ordinary microscope. Reflected light had to be used, and for this purpose a vertical illuminator was employed. This was a thin circular glass plate mounted in a short tube so as to turn about a horizontal diameter. The tube had a circular hole in the side and was screwed into the bottom of the microscope tube; when attached it could be turned about its axis, thus communicating a second movement to the illuminator for purposes of adjustment. At the lower end of the illuminator tube the various objectives were attached. In this way light projected horizontally through a condenser, and focussed on the glass plate set at

the proper angle, was thrown down vertically upon the surface under examination and reflected back through the eye-piece. In most cases this vertical light could be used, but sometimes the etching brought into relief a crystalline arrangement which threw the light off in various directions from the vertical, so that it did not reach the eye. In such cases light was thrown upon the surface from the side by means of a suitable lamp. For vertical illumination a Nernst lamp was found to serve very well. A single vertical filament gave an abundance of clear, steady light without the sputtering and shifting which are so frequent in an arc light. If the light became too severe on the eye in the study of the more brilliant surfaces a filter of potassium bichromate of suitable concentration was used. The specimens, which were of convenient size, were held by a rubber band with the polished face against a microscope cover glass mounted in a small iron frame. The frame rested on the microscope table, which could be rotated as well as moved laterally. For coarse adjustment the table was moved up or down, while finer adjustment was made by moving the tube. By this means the light from the Nernst lamp was kept focussed on the illuminator. Three objectives and two eyepieces were used, giving the power shown in the Table attached.

EYE PIECES.		OBJECTIVES.
2 in. (50 mm.)	1 in. (25 mm.)	
Magnification.		
18	34	37.0 mm. ($1\frac{1}{2}$ inch)
41	87	16.0 mm. ($\frac{2}{3}$ inch)
205	385	4.2 mm. ($\frac{1}{6}$ inch)

Sketching.—The figures or patterns observed on the surfaces were traced on paper by the aid of a camera lucida. This instrument increased the actual magnification recorded on the drawings by about two diameters, because of the fact that it was not found convenient in tracing to hold the paper at the position of the image. All the sketches, however, are drawn

under the same conditions, so that the size of the various patterns may be accurately compared.

Photography.—Very little time was spent in photographing the specimens, because the photographs did not give the detailed pattern so clearly, and also because of the limited time at the disposal of the writer.

III. OBSERVATIONS MADE

An account will now be given of the observations made in connection with the microscopic study of the alloys and their component metals. Since the writer had never before attempted any work of this kind it was thought advisable to make a trial first with some metal whose structure had been fully examined and described by other experimenters. For this purpose iron and steel were chosen. After overcoming a number of difficulties as to polishing and etching, results were obtained which corresponded with drawings and photographs published by various experimenters. Fig. 1 is a sketch of a piece of steel as seen after etching with a mixture of dilute hydrochloric acid and ferric chloride.

Copper.—This preliminary trial having been made by way of a test, the constituents of the alloys were examined in turn, beginning with copper. With this metal the etching was done at first with nitric acid. A drop or two was applied for a moment to the polished surface, which was then quickly washed in dilute acetic acid and dried. Later on, the nitric acid was discarded for a solution of hydrochloric acid and ferric chloride. With this reagent the rate of etching was fairly slow, and the process could be stopped at any desired stage. Gently washing the surface with a bit of absorbent cotton soaked in the solution brought out crystalline areas of changing illumination quite visible to the naked eye. These when viewed under the microscope were seen to present a certain degree of regularity, the boundaries often being straight lines. When side light was used for illumination, the surface, as it was rotated under the objective, gave the appearance of a floor made of tiles of changing brightness. This characteristic appearance, illustrated in Fig.

2, soon becomes familiar to the experimenter, and though the crystals have not all the same size or shape, yet they can be distinguished at once from those of other metals. The drawing in Fig. 2 was made from the surface of a piece of sheet copper.

Aluminium.—The next constituent examined was aluminium. Of the acids hydrochloric alone will act upon it at ordinary temperatures, and this reagent alone was used, diluted to nearly one-half its full strength or even less. Several pieces of the metal cut from a casting such as is sold by dealers were studied, surfaces being polished on the outside of the casting as well as on sections made through it. The appearance of the etched surface of aluminium is quite different from that of copper. Large areas can be seen with a magnification of only 34, and these show a variation in illumination which is best seen with side light. If an ordinary filament lamp be moved about from side to side around the surface these areas change their illumination, one now shining out brilliantly, then gradually darkening, while another brightens as the light strikes it at the right angle. This effect, seen also in copper, is evidently due to the tactical arrangement of the elements of each crystal. If we liken these elements to bricks, then in any crystal the bricks are all laid in one direction, while in the neighbouring crystal they have all one direction, but a different one from the last. The acid tears down the surface of this masonry, so to speak, and leaves the bricks exposed, thus giving a set of areas from which the light is reflected as described. These areas, however, did not have the same general shape in the interior of a casting as they had near the surface. Fig. 3 indicates the shape of the areas near the surface of a casting, and, from the magnifications used, allows a comparison to be made as to the size of aluminium and copper crystals.

Manganese.—Of the three metals manganese is by far the hardest and is very brittle. It is difficult to get a surface of any size free from holes, but areas quite large enough for examination can be made very smooth, though the process of grinding takes some time. Any acid, and even hot water, will attack this metal, so that for light etching weak acetic acid was used. Later on, however, it was found that alcohol, applied to a smooth

cloth polishing disc, not only hastened the polishing, but gave at the same time a beautifully etched surface free from any oxidation colours. The surface presented the appearance shown in Fig. 4, which was characteristic of a surface taken in the middle of a lump of the metal. In this case the reagent, instead of indicating fairly regular distinct crystals as in copper, or uncovering large areas of varying illumination as in aluminium, attacked at first certain areas only. Continued etching deepened these areas, the surface after a time presenting the appearance of a collection of pyramidal prominences of different sizes and shapes.

Alloy 1a.—Familiarity with the appearance under the microscope of each component when treated in the way described having been gained, the least magnetic of the alloys, No. 1a, was chosen next for examination. Acetic acid had apparently no effect upon a polished surface of the alloy. Hydrochloric acid, slightly dilute, was then tried, the specimen being left in the acid for some hours. Large areas, each of uniform illumination, but some brighter than others, appeared, as in the case of aluminium, though the brilliancy of the various areas was not nearly so marked. A magnification of 385 diameters showed each area to be covered with short lines or ridges of metal of some kind scattered irregularly over the surface (Fig. 5). The writer had not a higher power with which to examine them more closely, but they appeared to be narrow elongated crystal elements mixed with aluminium as a conglomerate. Etching with nitric acid gave a similar effect to that produced by hydrochloric acid. The section, which was in this case perpendicular to the axis of the rod, did not present the same characteristics in every part, but seemed to vary in structure more or less, as if the metal had not combined uniformly throughout the rod.

Alloy 2.—The next least magnetic alloy, No. 2, was then examined. In this case the most noticeable characteristic of a freshly polished surface was a number of curiously-shaped openings or crevasses curled about in the way shown in Fig. 6. They were not numerous, but occurred fairly uniformly all over the section. Acetic acid did not seem to affect the surface except to make these peculiar figures a little darker and better defined.

Hydrochloric acid attacked the whole surface to some extent, giving a glistening appearance when a side light was moved about, as if small crystals, of aluminium possibly, were scattered throughout the alloy. It will be remembered that in pure aluminium the various areas were quite brilliant and well defined. In Alloy 1a these areas appeared again, but neither so bright nor so well defined along the edges, while here no definite areas were seen, though the changing brightness was noticeable. The application of nitric acid revealed the presence of crystalline formations of a type quite different from Alloy 1a. The sketch in Fig. 7, taken after using nitric acid, shows the characteristic appearance of the surface. The crystals have some semblance of individuality, but not the strikingly clear-cut boundaries of the crystals in a homogeneous piece of copper. They look as if they had begun to form in a definite way, but were unable to complete the process. This alloy, then, presents two features that distinguish it from the first: (1) The absence of different areas of changing illumination, (2) the formation of a distinct type of crystal structure.

Alloy 2a.—The next alloy taken up was No. 2a, which had the same percentage composition as No. 2. The section examined shewed considerable variation, crystals similar to those in No. 2 appearing in places, while several large patches quite brilliant in the light were seen surrounded by a mixture of a different kind. The linear arrangement of dots shown on etching with hydrochloric acid was here first observed. They occurred only in some places, possibly because of want of uniformity in the alloy, but they appeared to indicate boundaries to what under more favourable circumstances would have been individual homogeneous crystals.

Alloy 3.—One of the three most magnetic specimens (3, 3a, 3b), namely, No. 3, was now examined, the results obtained being characteristic of the three. On polishing the surface and looking at it in the microscope without etching, there were seen, scattered everywhere, sometimes dots, sometimes larger areas nearly always arranged in a sort of fern-like formation, often with one or more long branches and side branches running out. This was seen without etching, because the metal composing it

was a little darker in colour than the rest of the surface. On washing the surface with weak acetic acid this darker metal was at once eaten out, and hence it may be reasonably concluded that these figures were made of pure manganese in some crystalline form. The conclusion would be made more certain, however, by testing the acid residues for manganese.

The pattern when first seen suggested at once the process of crystallization that may be observed by putting a concentrated solution of ammonium chloride on a glass plate and projecting it on the screen by the aid of a lantern. With this salt long crystals are observed to shoot out which develop a number of branches from their sides. In such an experiment the process is confined to one plane, but in the alloy three dimensions are available, and on looking at a polished surface we may see a whole section of such a branch with its side shoots, or, again, only the ends of some that have been cut off by the plane under examination. If the surface thus etched by acetic acid is ground down on the polishing disc the openings from which the manganese has been removed gradually diminish in size, and finally look like short lines. The acid is thus seen to follow the manganese down to some depth.

Hydrochloric acid was used next. It brings out fine distinct lines which mark out regular individual crystals. These lines had occasionally been suggested by the action of acetic acid, but they consisted only of rows of dots here and there. The hydrochloric acid, however, brings them out regularly all over the surface. Under a magnification of 87 they look quite even and continuous, but a power of 385 reveals a sort of ragged or barbed appearance, as if some attempt at crystallization has taken place in the metal constituting these lines.

Fig. 8 is a sketch showing the large crystals as well as the fern-shaped aggregations of manganese. Figs. 9 and 10 show two of these fern-shaped crystals as they appear with a power of about 1400. The crystals themselves in general shape suggest those of copper, but they are larger, as may be seen by comparing the magnifications used. Nitric acid at once develops these lines, and continued etching with it lowers the metal all around the crystals and gradually eats away the crystals themselves.

We have here, then, at least two distinct characteristics not found in any of the slightly magnetic alloys, Nos. 1a, 2, 2a—(1) the occurrence of what appears to be manganese crystallized in a peculiar manner, (2) the presence of large regular crystals quite distinct from each other without that interlocking found in Nos. 2 and 2a. The crystals are apparently a homogeneous mixture of copper and aluminium enclosing bodies of crystallized manganese.

Alloy 3a.—The second alloy of the same composition as No. 3, namely 3a, was etched in a similar way by using (1) acetic acid, (2) hydrochloric acid, (3) nitric acid, and the process brought out the same characteristics as those possessed by No. 3. The hydrochloric acid not only removed the material taken out by the acetic acid, but also brought out fine lines around the larger crystals. Continued etching with hydrochloric acid made no further change, and it was necessary to resort to nitric acid to bring out any new effect. It appears, then, that the main body of the large crystal is a mass of some homogeneous material different from the material found along its edges or from the tree-like crystals found irregularly scattered about it. It may be noted that the latter were not always found in the interior of the larger crystals, but often occurred along the boundaries, as the sketch shows.

Alloy 3b.—The third of the three most magnetic alloys having the same composition, namely 3b, showed similar results characteristic of the other two, with one or two new features. Here the bounds of the large crystals were brought out quite clearly with a low power by using acetic acid as a reagent, while in the others hydrochloric or nitric acid was necessary to show them. A power of 385 showed these lines to be made up of separate dots of different shapes grouped along the borders.

Again, hydrochloric acid outlined wide paths between the crystals, and attacked slightly the surface of the crystals themselves. In the other two magnetic alloys this intercrystalline material occurred in narrow lines, while here it seemed to exist in considerable quantity. Light etching seemed to attack first the borders of the crystals on both sides, and only after first acting upon the crystals for some time did the acid eat away this

intercrystalline layer. In this case, then, we have the same features as in Nos. 3 and 3a, with the addition of the presence of a wider layer of material between the crystals whose composition does not seem to be the same. This variation may be due to the influence of cooling in some way, and suggests the necessity of examining the alloys from this point of view.

Alloy 4.—The next alloy taken up was No. 4, which with 4a was somewhat less magnetic than 3, 3a, and 3b. With this alloy acetic acid developed boundaries to large crystals, dots over the surface, and figures not exactly like those in 3, 3a, and 3b described as fern-like, but having a rosette or somewhat modified star shape. Hydrochloric acid gave the same effect, while nitric acid ate deeply round the crystals and attacked the crystals themselves. Fig. 11 is a sketch showing the effect of hydrochloric acid on a polished surface. The larger crystals as well as the smaller compact patches of manganese are seen. Fig. 12 is a sketch of one of these patches made by using a power of 1400.

Alloy 4a.—The last alloy, No. 4a, showed no characteristics distinctly different from the other magnetic alloys. Acetic acid developed figures similar to those in No. 4, though perhaps not so marked. Hydrochloric acid carried the etching no farther, and recourse was necessary to nitric acid to make any additional impression. It may be noted here that in all cases when the alloy was left in weak acetic acid for some time the surface layer gradually changed colour and seemed to become softer. The writer did not investigate this to any extent.

Oxidation Colours by Heat.—Time has not permitted up to the present to make as complete an examination as desired of various surfaces by heating to observe oxidation colours. In the more magnetic alloys, however, Nos. 3, 3a, 3b, the fern-like figures which we have considered to be manganese were all brought out in dark brown or black colour against a field of lighter appearance which seemed to be fairly uniform everywhere. Alloys Nos. 1 and 2, on the other hand, showed a mottled appearance, having at least two colours, as though the metals were not well mixed together.

IV. DISCUSSION.

In glancing over the observations made one is impressed with the striking difference in the crystalline structure exhibited by the highly magnetic in contrast with the feeble magnetic alloys. The latter exhibited either a lack of homogeneity or a sort of interlocking crystalline mass often containing bodies of a single material. The former showed distinct crystals apparently homogeneous and containing presumably free crystalline manganese. It may be concluded that the magnetic properties accompany this form of manganese, or that they accompany this type of crystal enveloping the manganese, or both together. If the property of magnetism depends upon an allotropic form of the metal the thought is at once suggested that we may have the manganese here in just that form.

The work done so far, however, is merely a beginning, and further investigation along this line is needed to give definite results. The following may be suggested as likely to yield valuable data: 1. Examination of acid residues; 2. Examination of structure of the same specimen after various methods of heat treatment; and 3. Examination of structure of the specimen after being used as cathode or anode terminal in a discharge tube. The research is still being continued, and it is hoped by following the methods suggested to obtain some additional interesting and instructive information regarding the structure of the alloys.

The writer wishes to express in this place his thanks to Professor McLennan for his kindness in placing at his disposal the necessary apparatus, and for his many helpful suggestions, given from time to time during the investigation.

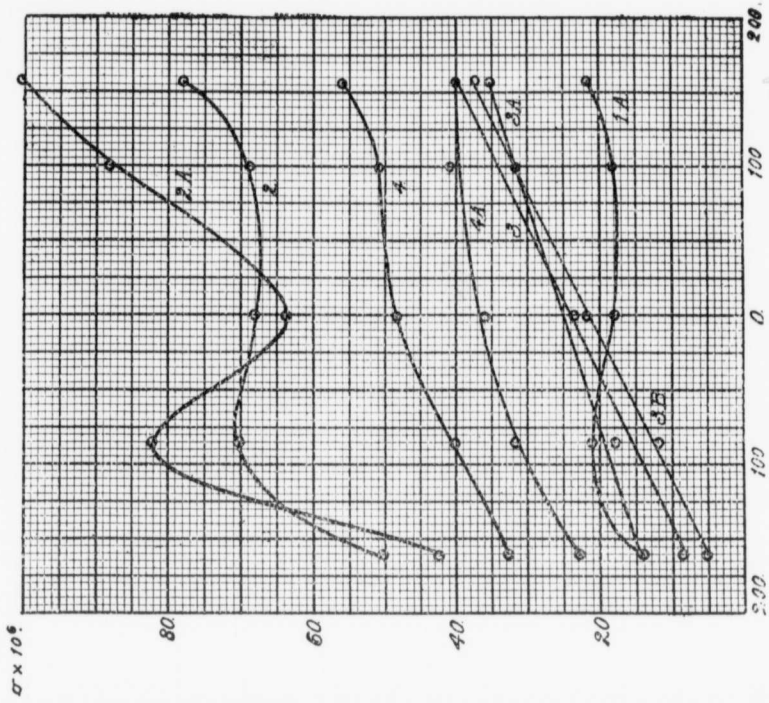


DIAGRAM 1.

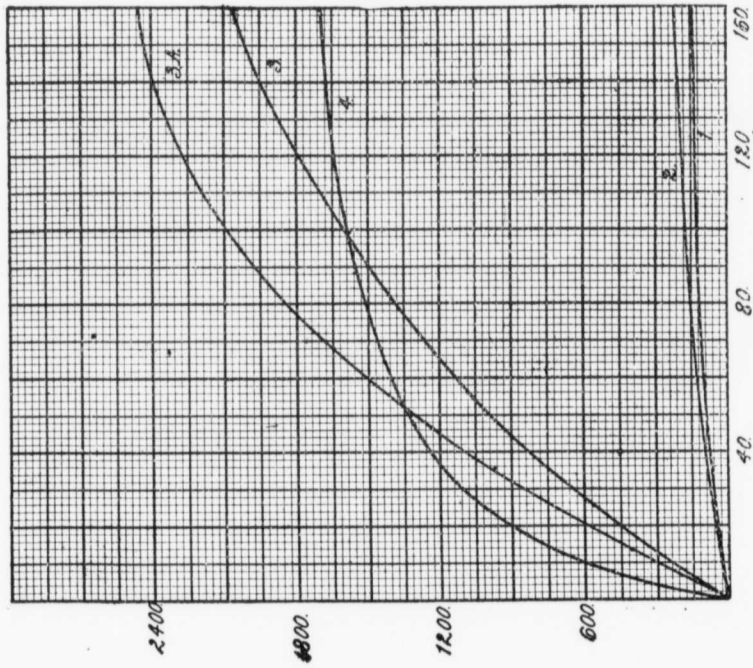


DIAGRAM 2.

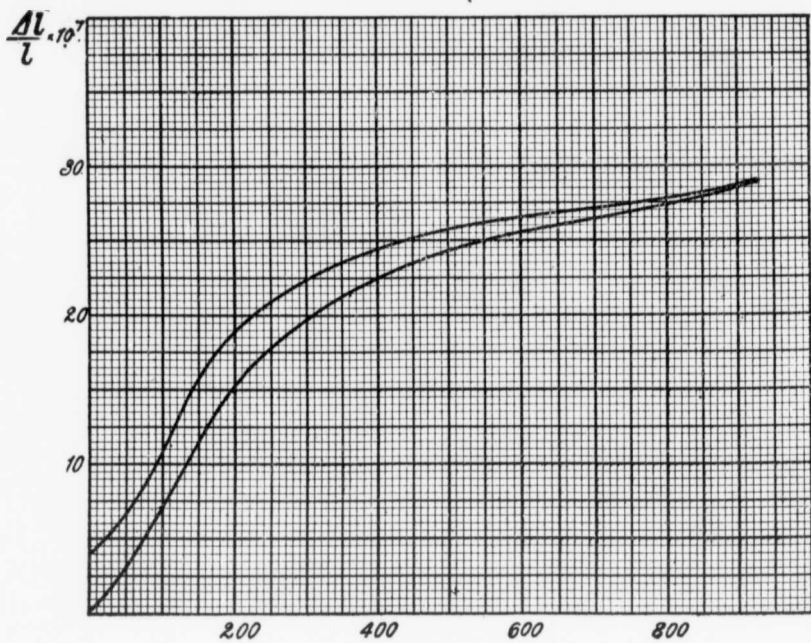


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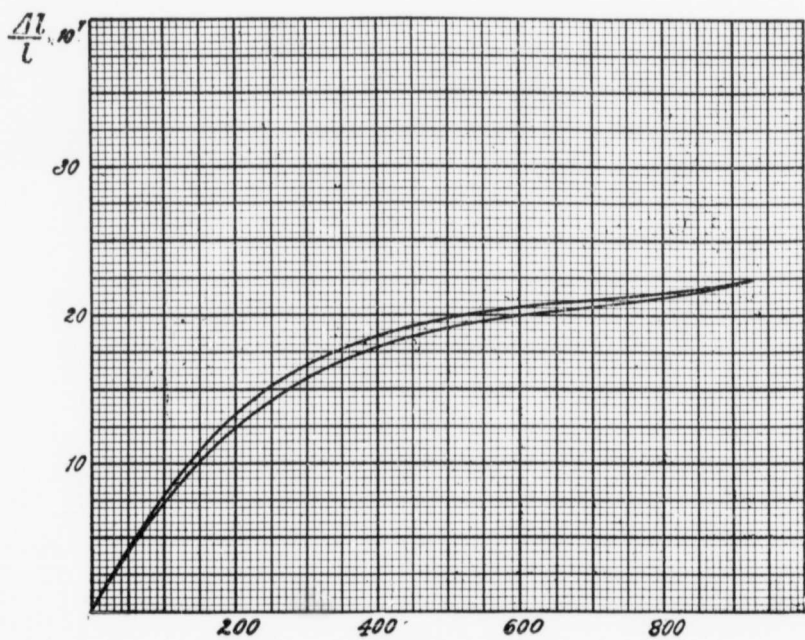


DIAGRAM 4.

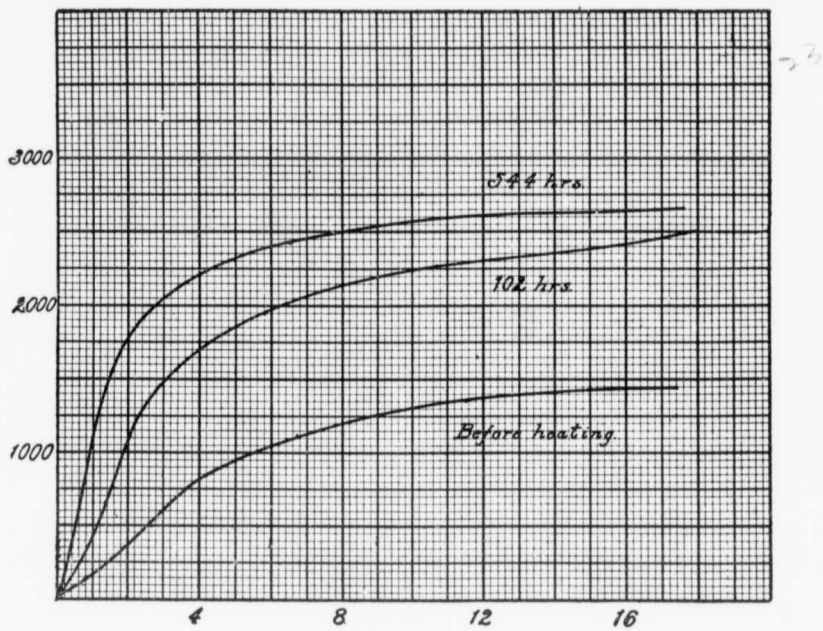


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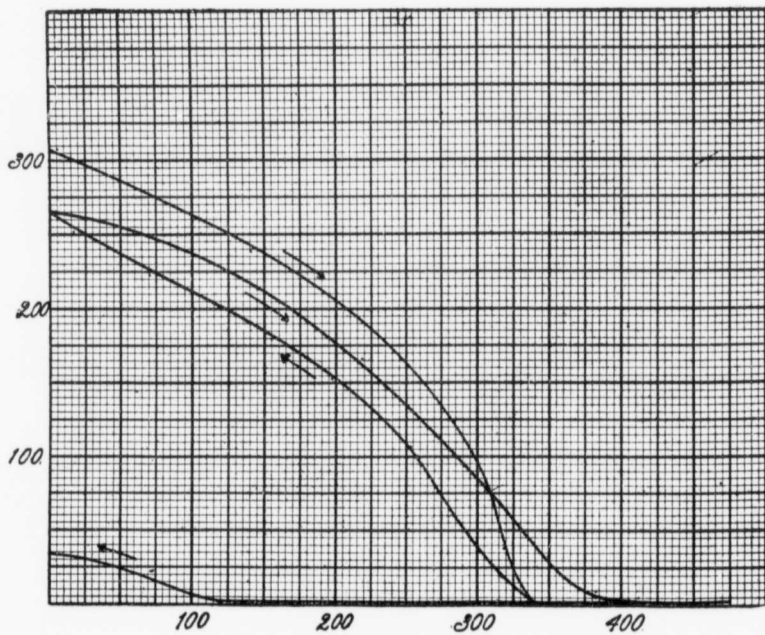
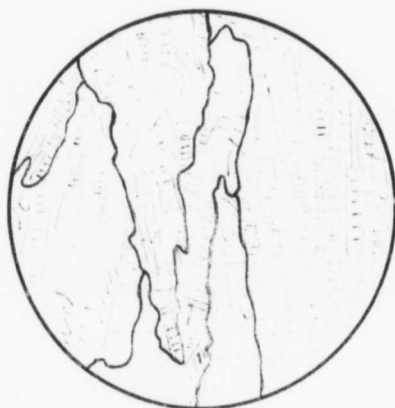
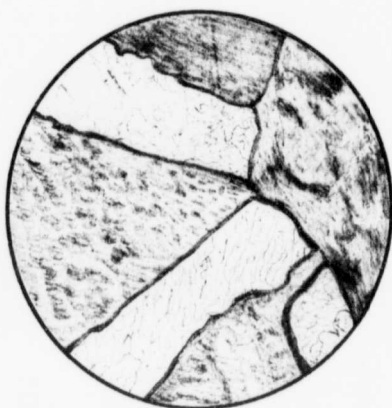
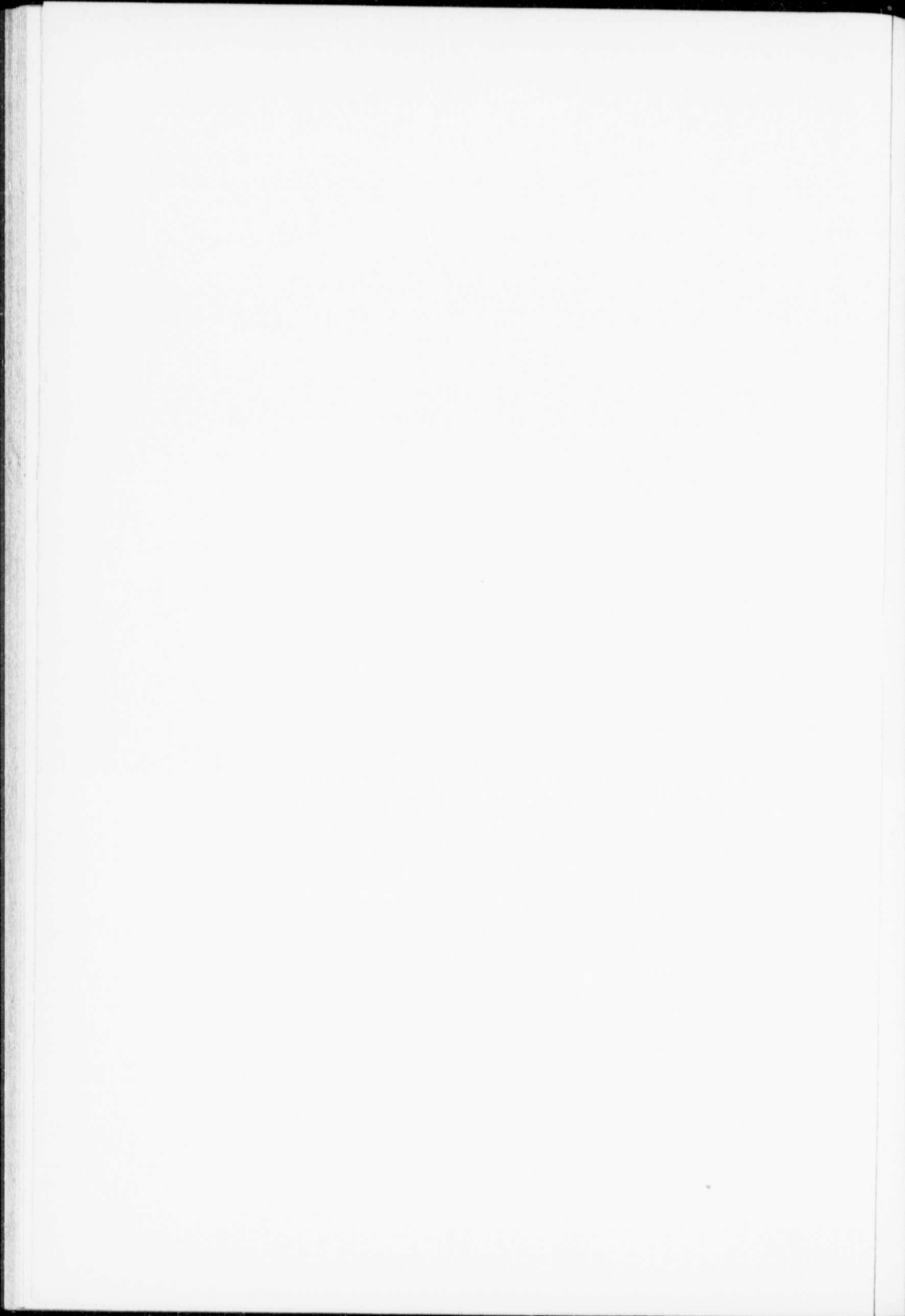


DIAGRAM 6.

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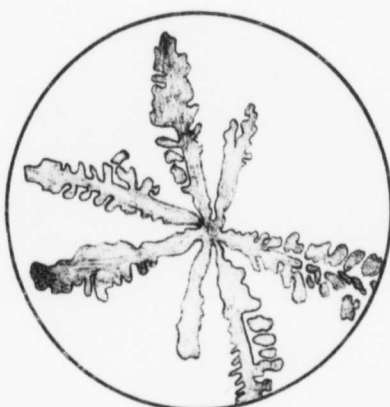
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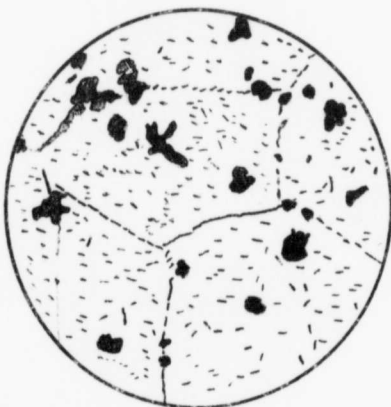
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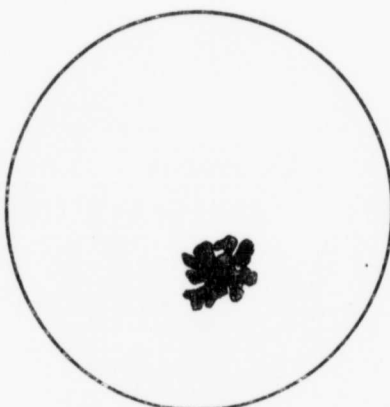
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