THE HEUSLER ALLOYS.

Dr. A. A. Knowlton (University of Utah, U.S.A.) and **Dr. O. C. Clifford** (University of Utah, U.S.A.) also communicated a Paper on "The Heusler Alloys."

Although the relation of the magnetic properties of these alloys to the three factors, composition, thoroughness of mixing while in the molten state, and thermal treatment, has been one of the topics treated by nearly every investigator who has worked with these alloys; and in spite of the extensive and valuable results contained in the original papers by Heusler and his co-workers (1), and in subsequent researches by Take (2), Asteroth (3), and others, there are certain fundamental questions to which it does not appear

TABLE I.

No.	Cu.	Mn.	Al.	History.
1	67·8	27·8	4·4	Cast from scrap from many previous specimens. Materials have been often cast and re-melted. Chilled from 250°.
3	63·8	27·5	8·7	New mixture. Annealed to room temperature.
4	63·3	26·4	10·3	Cast from scrap. Chilled from dull red heat.
5	63·3	26·4	10·3	From same melt as No. 4, but annealed to room temperature.
6	68·0	28·0	4·0	New mixture. Annealed to room temperature.
7	63·3	29·5	7·2	Al added to No. 6, remelted and chilled from 200.
8	60·3	25·4	14·3	Al added to No. 7, remelted and chilled from 250°.
9	60·2	26·7	13·1	Remelted from scrap. Chilled from 200°.

that really satisfactory answers can yet be given. These questions may be stated as follows:—

1. What conditions of preparation and thermal treatment must be observed in order that an alloy of any given composition may be in condition to exhibit the maximum possible intensity of magnetisation when saturated?

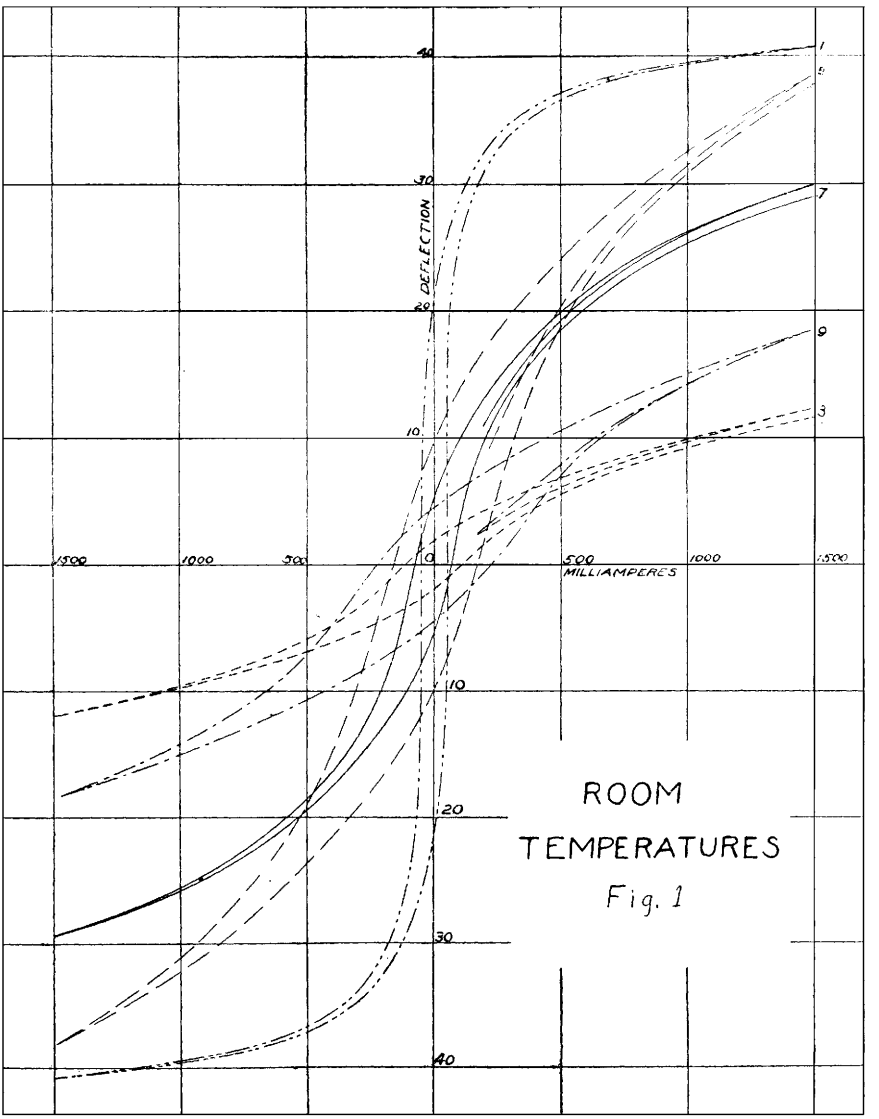
2. What are the exact relations between composition and the two factors of magnetic quality—hardness, and intensity of magnetisation at saturation?

3. Upon what factors does the transformation point of a given alloy depend, and what is the exact form of the relation?

The present paper is an account of some experiments which were undertaken as a further contribution to the study of these problems since the variables involved are so many and the relations so complex that it is only by the careful determination of the behaviour of many specimens in the hands of

different observers that we shall be likely to arrive at answers sufficiently definite to serve as criteria by which to test the various hypotheses as to the nature of the magnetic units in these alloys.

The specimens tested were in the form of rings, having the following



dimensions : Mean radius, 3·71 cm. ; radial thickness, 0·6 cm. ; width, 1·2 cm. ; and wound with a primary of 864 turns and a secondary of 100 turns of No. 22 wire. The rings were prepared by prolonged heating in a graphite crucible, and cast in a hot carbon mould, as described in a previous paper (4). It was the original intention to prepare a series of alloys with increasing

aluminium content, and to cast three rings of each composition, one of which should be chilled from a high temperature, one cooled slowly to about 250° C. before chilling, and the third cooled slowly to room temperature, but the mechanical quality of all rings chilled from high temperatures was so poor that they generally broke in the process of grinding, so that although they often appeared to be strongly magnetic, no measurements could be made. On the other hand, all rings which were allowed to cool slowly to room temperature were of good mechanical but poor magnetic quality. Thus for one reason or another all the rings cast were rejected with the exception of the seven concerning which data is given in Table I.

Besides the Cu, Mn, Al, the rings contained a trace of iron and small but varying amounts of silicon which probably did not exceed 1 per cent. in any case.

The magnetic tests were made by the step-by-step method, the resistance coils used in varying the current being wound to give equal steps at 100°. The field due to the primary was 46·5 c.g.s. units per ampere and calibration of the galvanometer by means of a wooden ring of the same dimensions and winding showed that 1 cm. deflection indicated a change of 69 lines in the flux. As we are interested in changes rather than in absolute values, currents and galvanometer throws have been used as co-ordinates in our magnetisation curves.

Fig. 1 gives the hysteresis curves for Nos. 1, 3, 7, 8, and 9 six months after casting. Data were also taken on 5 and 6, but these resemble No. 9 so closely

TABLE II.

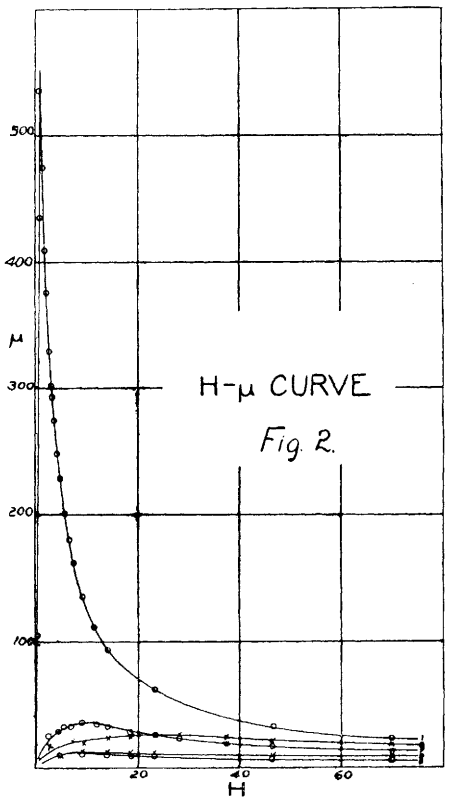
	1.	7.	9.	8.
Per cent Al.	4·4	7·2	13·1	14·3
H for max. μ	0·9	9·3	27·3	28·0

in their magnetic properties that the curves were not plotted. Perhaps the comparative softness of No. 1 is the most interesting feature of these curves. It is instructive to compare these curves with those in Fig. 3, which show the changes produced in No. 1 by heat treatment. The comparative importance of composition and thermal history is strikingly shown by these two figures.

Since it was not possible to bring the specimens to an absolutely neutral condition by the method of reversals used the curves as actually observed would have been slightly unsymmetrical with respect to the X axis. In order to make the comparison of different curves easier, this asymmetry has been overcome by using as ordinates the mean values of the summation of the throws to right and left with equal currents. In the original plot, made on 30 × 40 cm. section paper, the individual points fell, in most cases, within the width of the line drawn.

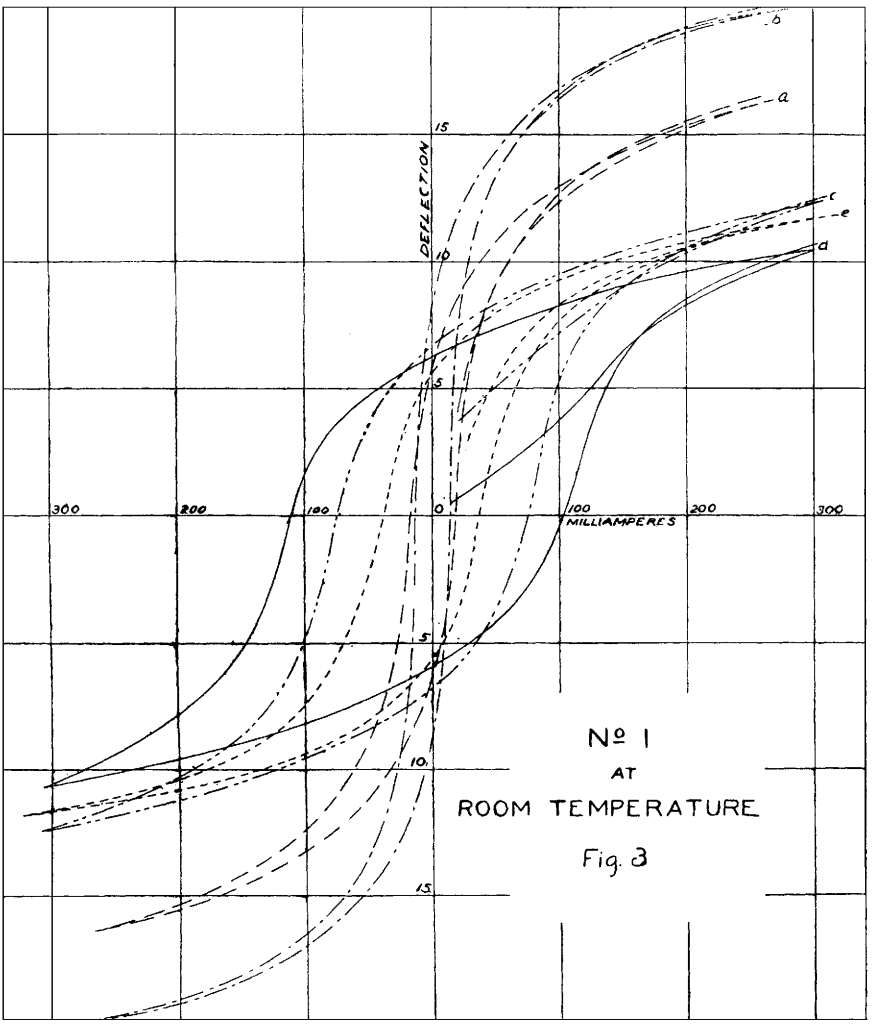
The H-μ curves (Fig. 2) were worked out from the data used in Fig. 1. If No. 3 be omitted the remaining specimens were prepared in essentially the same manner, and it would seem that the differences in the field corresponding to maximum permeability must be, for these four specimens, under the given conditions, a function of the composition. The data are insufficient to determine the precise nature of this relation further than that the maximum of the curves occurs for values of H which increase rapidly with increase in the percentage of aluminium, as is shown in the accompanying table (Table II.).

A comparison of these results with one another makes it strikingly evident that percentage composition plays a relatively unimportant part in determining the magnetic quality as compared with the effect of heat treatment. Nos. 1 and 6, for example, are of almost exactly the same composition but bear no resemblance to one another in quality. Unfortunately the history has been different in two respects—thoroughness of mixing, and method of cooling—so that it is not possible to determine from these specimens alone the part played by each. No. 1 was made from scrap, every part of which had been repeatedly remelted and cast, and probably represents as perfect a mixture as can be obtained, and was chilled from well above its transformation range.



No. 6, on the other hand, was a new mixture two or three times remelted and cast, and was chilled from a temperature slightly below its transformation point. It is, of course, impossible to separate the effects due to these two causes with certainty. We are, however, inclined to believe that the very great sensibility to heat treatment found in No. 1 was due to the perfection of mixture while the magnetic qualities as shown in Fig. 1 were due to the thermal treatment. The low induction of No. 6 is probably due to its having been cooled slowly through the lower part of its transformation range, as has been shown by Asteroth (5), and this injurious effect of annealing at the lower limit of transformation accounts also for the low maximum induction of No. 9 as compared with No. 8, which is of nearly the same composition. In both

cases the history shows treatment which must have ensured a good mixing, and the only difference is in the temperature of chilling. It may then be stated that No. 9 resembles No. 6 because it had been annealed through the lower limit of its transformation range (about 200°), and was therefore in nearly the same condition as it would have reached if cooled slowly to room temperature. No. 7, containing only one-half as high a percentage as



aluminium and with the same history as No. 9, is intermediate between No. 8 and No. 9. Here the explanation is that the lower limit of transformation for No. 7 is at 185°, hence it was not annealed through the injurious range although quenched at the same temperature as No. 9. This illustrates very strikingly the necessity of being sure that each specimen has been given the treatment required to bring it to its own best condition before exact conclusions can be drawn as to the effect of composition. The maximum

induction possible under the best conditions of mixing and chilling must depend upon the composition. It is undoubtedly true that under these conditions the maximum possible induction, for a given manganese content, increases with increasing percentage of aluminum, but there is no evidence which the writers would regard as conclusive as to precisely what composition would give the best results, although it has been assumed from the work of Heusler and Starck (*loc. cit.*) that this point was reached when atomic proportions were used.

The effects produced by thermal treatment have been extensively studied by Gumlich (4), Take (5), Hill (6), Asteroth (7), and Knowlton (8). Our results are in general in good accord with those previously obtained, but are in some particulars more detailed. The heater used was an oil bath with motor-driven stirrer. With one exception the curves given refer to ring No. 1, which showed an unusually high degree of sensitiveness to heat effects. During these experiments the specimen was wound with a secondary of only 50 turns, making the factor to be used in computing the induction from these curves 138 lines per centimetre of deflection.

A comparison with Fig. 1 shows that the induction curves of this particularly sensitive specimen taken after the various heat cycles differ more widely from one another in both saturation value and hardness than do the curves of Fig. 1, which refer to specimens of widely different composition. The curves as lettered represent the following conditions :—

(*a*) Original curve taken about six months after casting.

(*b*) After heating slowly to 120°, annealing for nine hours at that temperature and cooling slowly.

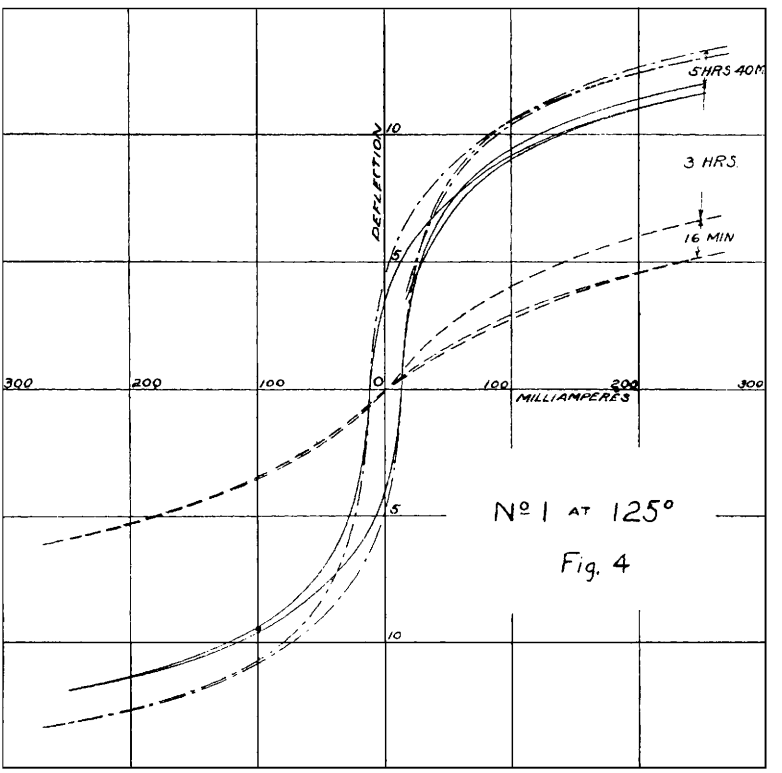
(*c*) After heating to 170°, annealing several hours and cooling slowly.

(*d*) After heating to 223°, cooling slowly.

(*e*) After heating to 250° and chilling.

It is to be regretted that the field was not pushed up in each case to the point of magnetic saturation. The procedure during these tests was to place the ring in the oil bath at room temperature and take data for a complete B and H curve, after which the temperature was raised at a fairly uniform rate of about one-half degree per minute. During this heating the magnetic quality was tested at frequent intervals, using a constant field strength of 69·8 units, and many complete induction curves were taken. Whenever the magnetic qualities showed signs of any irregular change the temperature was kept constant for so long a time as was necessary to carry that change to practical completion. During the first cycle there was a rapid loss of magnetic quality which continued at a fairly uniform rate up to about 120°, at which temperature the deflection had fallen from 20 cm. to about 5 cm. and the retentivity and coercive force were practically zero, as shown by the lower curve of Fig. 4. At this temperature the deflections began to increase with great rapidity, as is shown by the failure of the curve to close, so the temperature was kept constant and observations continued for about nine hours, during which time the change went on at a decreasing rate as shown. The increase in maximum induction is here accompanied by a slight increase in hardness. When this change was apparently complete the ring was allowed to cool slowly in the bath, and curve *b* of Fig. 3 was taken. Here we have, of course, been watching the progress of the familiar improvement produced by annealing just above 100°, which was first pointed out by Gumlich. It has also been shown that annealing at such temperatures profoundly affects the crystalline structure. Take found that in some of his specimens the transformation temperature was raised by successive heat cycles. We have never found this to be the case, and have, in fact, come to

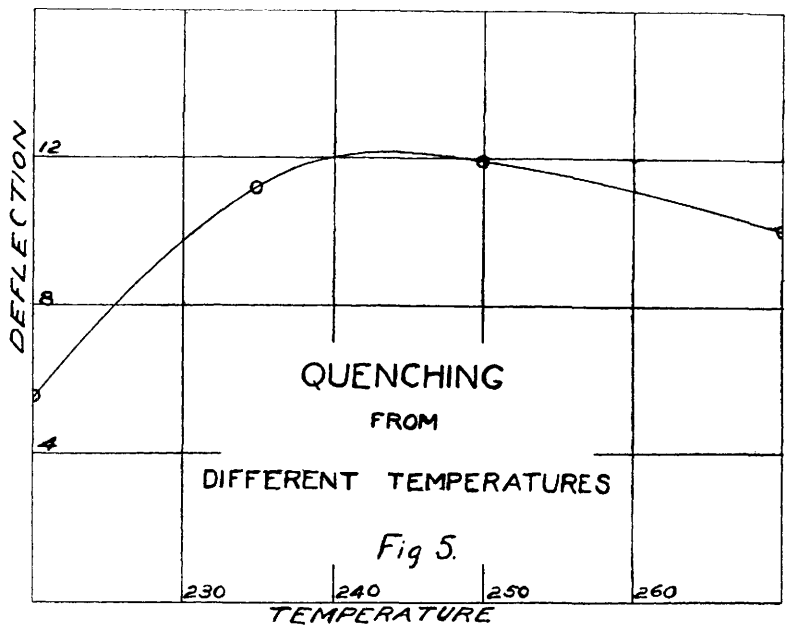
look upon the transformation temperature as being the only really constant thing connected with these alloys. The observations here recorded would appear to explain this discrepancy in a simple manner. Evidently 120° is a critical point for this specimen, but the transformation results if allowed to go to completion in the formation of a more strongly magnetic material. It appears probable that Take's specimens were cooled before the reconstruction of the elementary magnets had time to progress very far. During the second cycle the deflection decreased less rapidly with temperature, and there was no further change at 120°, although the temperature was kept constant at that



point for some time ; but at 170° a second increase began which was, however, much smaller than at 120° and was complete in a much shorter time. Slow cooling to room temperature left the ring in the magnetic condition shown in curve *c* of Fig. 3. The injurious effect of annealing at about this temperature has been previously pointed out, and it has been shown that the changes in crystalline structure at this point are in the opposite direction to those at just above 100°. A third cycle showed no change at either 120° or 170°, and resulted in complete loss of magnetic quality at 223°, with no recovery on prolonged heating at this temperature, which is then the critical temperature. The enormous increase in hardness and general deterioration in magnetic quality shown in *d*, Fig. 3, is probably due more to the slow cooling which followed than to the annealing at 220°.

Fig. 5 shows the effect produced by chilling from various temperatures. It will be noted that there is a considerable improvement in quality, which would appear to be a maximum for chilling from a temperature of slightly below 250°. After this treatment a second complete cycle was carried out, and it was found that the specimen had been so far restored to its original condition that the changes at 120° and 170° occurred as in the first cycle. The complete temperature magnetisation curve for this cycle is given in Fig. 6.

Fig. 7 shows the change in the deflection with time during the second cycle. The dotted line represents the deflection caused by the constant flux due to the applied field, and the height of the curve above this line is proportional to the intensity of magnetisation. It has been found that this curve referred



to the dotted line as an axis is very accurately represented by an equation of the form $I = I(1 - e^{-kt})$. In chemical work an equation of this form for the velocity of a reaction indicates a monomolecular change. If a like interpretation is allowable here, this curve must mean that the sudden increase in the magnetic quality was the result of some rearrangement of the molecules within previously existing groups, and that it was not brought about by the formation of new groups. Similar changes were found with other specimens, but the first change did not always occur at the same temperature in different specimens. In No. 7, for example, the first change began at 140° instead of 120°. It seems likely that this is due to the hardness of No. 7 as compared with No. 1.

Early in our experiments with the very soft No. 1 it was found that upon removing the magnetising field a sharp click was emitted, which was comparable in intensity with the sound of a weakly excited telegraph instrument, although the ring itself was wound with several layers of insulated wire and

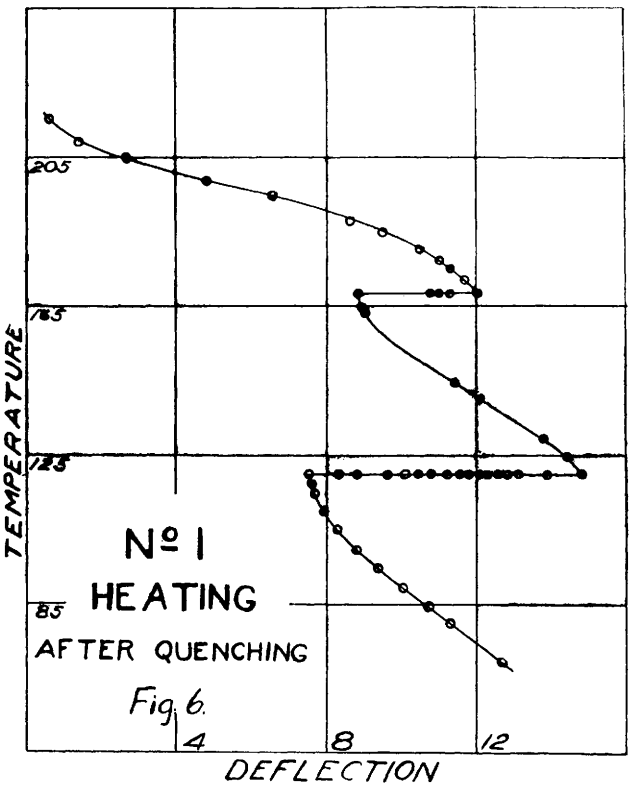


Fig. 6.

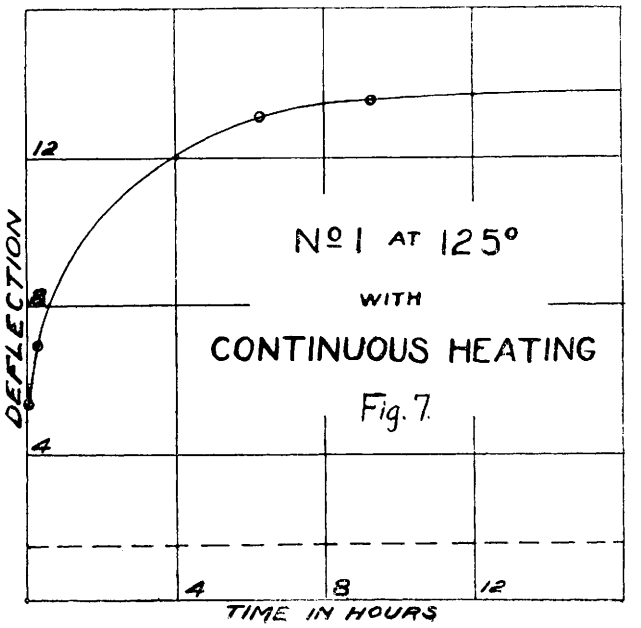


Fig. 7.

the whole thickly covered with insulating tape. This sound was always produced on demagnetisation, but its intensity was very greatly diminished by any heat treatment, which increased the magnetic hardness and restored by treatments having the opposite effect. Investigation proved that this effect was also present in all our other rings, as well as in a number of rods which had been used in previous experiments, but in no other case was it as pronounced as in No. 1. A similar but much feebler effect is, of course, well known in iron. In iron also any change in magnetisation is accompanied by the production of sound, while here no effect was ever observed at the time of making the field, a result which may point to a high magnetic viscosity.

From the evidence presented, it appears that, in spite of the work heretofore done, we do not know what proportions will give us the alloy of maximum possible magnetisation, and that it will probably be impossible to decide this definitely until the conditions of thermal treatment necessary to put particular specimens in their best condition have been worked out over a wide range of composition. A systematic study of these conditions is planned for the near future. It appears that sensitiveness to heat treatment and magnetic hardness are closely dependent upon the proportion of aluminium present, while the transformation temperatures depend largely upon the percentage of copper, but that these are not the only effective factors. Here again further work is needed with specimens carefully treated to bring out the best possible characteristics of each composition.

The fact that the audible effect is diminished by any treatment which increases the magnetic hardness appears to favour the supposition that the resistances causing hysteresis loss are in part at least mechanical and dependent upon the nature of the matrix which incloses the magnetic group. If this be true, it becomes a matter of importance to determine which changes are due to changes in the matrix (hardness) and which are due to changes in the magnetic unit itself, and for this purpose extensive determinations of the behaviour in intense fields are needed.

There seem to be three possible hypothesis as to the nature of the magnetic units in these alloys, which may be stated as follows :—

1. The magnetic units are the molecules of a chemical compound of manganese and aluminium, or groups of such molecules.

2. The magnetic units consist of manganese molecules or of groups of such molecules.

3. The magnetic units are complex groups, which form the structural elements of a certain type of mixed crystal, and contain at least two different kinds of chemical molecules.

The hypothesis of a chemical compound is perhaps the simplest, and receives strong support by analogy, since E. Wedekind (9) has shown that nearly all of the trivalent elements of the boron and nitrogen groups form strongly ferromagnetic compounds with manganese. The direct evidence, however, appears to indicate that the alloys consist of a series of solid solutions,* while it does not seem easy to account for the extreme variability of the alloys if their properties are those of a definite compound. In particular it would be expected that the transformation temperature would be the same for all specimens if the magnetic units were the same in all.

The second hypothesis which is, of course, the allotropic theory as applied to these alloys, is well stated in an abstract† of C. E. Guilhaume's article on the "Theory of the Heusler Alloys."‡ "It seems that Al and Sn possess the

* L. Guillet, Soc. d'Encouragement, *Rev. de met. Mem.*, pp. 87–111, July 1, 1906.
† *Science Abstracts*, 1905–1907.
‡ *Ind. Elect.*, **14**, pp. 533–536, December, 1905.

property of raising, in certain cases, the transformation temperatures of the metals with which they are combined, whether these transformations are characterised by the passage from the crystalline to the amorphous state (fusion) or to another crystalline state which possesses magnetic properties." The chief objection to this hypothesis upon experimental grounds seems to be that it assumes a strongly ferromagnetic state for manganese at low temperatures. P. Weiss and H. K. Onnes (10) have carried out experiments as low as 14° abs. with no indication of such a state, but find, on the contrary, that manganese freed from its oxides by prolonged heating in a stream of hydrogen is weakly ferromagnetic at ordinary temperatures, so that the effect of the aluminium would seem to be to increase the moment of the magnetic units rather than to change the temperature at which they come into existence.

The third hypothesis has much in common with the second as we understand it, but avoids the assumption of strongly ferromagnetic manganese by regarding the magnet units as complex molecular groups which form one of the structural elements of certain crystals which have been found to be present in all magnetic specimens, and to change with any heat treatment which affects the magnetic properties.* Upon this hypothesis the changes observed in No. 1 would be interpreted somewhat as follows :—

The specimen as prepared contained a certain number of elementary magnets, each consisting of a group of molecules of at least two kinds, which may be thought of as either arranged in definite positions with respect to one another (like the atomic arrangements of stereo chemistry) or as moving in well-defined orbits within the group, the magnetic moment of each group being in some way determined by this arrangement or motion. The gradual loss of magnetic quality with rising temperature would then be explained as the result of thermal agitation in which the group takes part as a whole in accordance with the kinetic hypothesis precisely as in the case of a pure ferromagnetic metal. The increase in intensity of magnetisation at 120° must, on the other hand, be due to structural changes which might conceivably be : (*a*) an increase in the magnetic moment of each group consequent upon a change to an arrangement of greater stability ; (*b*) an increase in the number of groups ; (*c*) a softening which allows the field to exert its influence more effectively. The third possibility may be rejected at once since the induction curves taken during the progress of the change show an increase in hardness rather than a decrease. On cooling to room temperature the new arrangements or new groups persist, as is shown by the fact that no change occurred at 120° on the second heating. It is in fact certain that a change similar to that which took place at 120° goes on slowly at ordinary temperatures, thus indicating that the state reached by annealing is the stable one. It will be remembered also that the change in hardness was in this case slight.

At 170° a second rearrangement results in the formation of groups of still greater stability, and at this point also the matrix undergoes a change which results in an enormous increase in hardness after cooling. At 223° the specimen has become non-magnetic because of the thermal agitation, and above this temperature the groups change back to the form stable at 250°, which is preserved on chilling, and the specimen therefore repeats the changes as found.

* *Phys. Rev.*, January, 1911.

Notes and References.

1. *Deutsch. Phys. Gesell. Verh.*, **5,** 12, pp. 219–234, June 30, 1903.
2. Ibid., **7,** 7, pp. 133–145, April 15, 1905.
3. Ibid., **10,** 2, pp. 21–32, January 30, 1908.
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5. *Loc. cit.*
6. *Phys. Rev.*, **21,** pp. 335–342, November, 1905.
7. *Loc. cit.*
8. *Phys. Rev.*, **22,** 1, pp. 54–68, January, 1911.
9. *Deutsch. Phys. Gesell. Verh.*, **8,** 20, pp. 412–416, October, 1906.
10. *Comptes Rendus*, **150,** pp. 687–689, March 14, 1910.

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March 1, 1912.