NOTE ON THE IRREVERSIBILITY OF THE HEUSLER ALLOYS.

By Bruce V. Hill.

BEING attracted by the accounts of Heusler's magnetic alloys of copper, manganese and aluminium, the author cast several of these alloys which showed some properties so interesting that it seemed worth while to give a brief preliminary description of them.

It may not be out of place to say something of the history of the discovery of these alloys and of the theory which applies to such cases. It is common to think of iron, cobalt, nickel and bismuth as the only substances having a measurable magnetic susceptibility. As a matter of fact, however, a large number of the elements show either para- or dia-magnetic properties. Stephen Meyer[1] found that some of the rare metals are strongly para-magnetic. The metals themselves were very difficult to obtain in a pure state and in quantities sufficient for the purposes of testing. When the salts of some of them were examined they exhibited even a greater susceptibility than those of iron. Defining the *atomic susceptibility* as the mean susceptibility of a space containing one gram atom of the substance in 1,000 cubic centimeters, Meyer gives the atomic susceptibilities of a number of the elements in the following order : Ho, Er, Gd, Mn, Fe, Sa, Co, Yt, Nd, Ni, Pr.[2] He says that if then, the susceptibility of metallic erbium were as much greater than that of iron as the susceptibility of the oxide is greater than that of the oxide of iron, dynamo-machinery and other apparatus could be built having only one sixth the weight of those of iron for the same output, since the density of erbium is only two thirds that of iron. This premise is not necessarily true, however, for manganese also stands before iron in the above list and it is not magnetic in the ordinary metallic form, though electrolytic manga-

[1] Stephen Meyer, Ann. d. Phys , 68, p. 325, 1899.
[2] Stephen Meyer, Ann. d. Phys., 69, p. 236, 1899.

nese was found to be slightly magnetic. It may be possible to account for the different magnetic properties of these metals in their salts and in the metallic condition in a simple manner however.

So far as iron and nickel, at least, are concerned there seems to be abundant reason to believe that they can exist in several allotropic forms. This is the "allotropic theory" of Osmond. The facts supporting it can not be enumerated here; a number are given with references in my paper mentioned under 8. In iron there are supposed to be three such modifications: the alpha form, soft, magnetic and stable below 700° to 750° C.; the beta form, hard, unmagnetic and stable between 750° and 860° C.; and the gamma form, soft, unmagnetic and stable above 860°C. In passing one of these transformation points heat is evolved as is seen in the recalescence of steel. In nickel there have been found but two allotropic forms: the alpha form, magnetic and stable below 340° to 360° C., and the beta form, unmagnetic and stable above that temperature.

This temperature of transformation may be depressed by alloying a second metal with the iron or nickel. This depression is proportional to the amount of the alloy as is seen in the case of the alloys of aluminium and iron[1] or of copper and nickel.[2] In this the alloys behave as other solid solutions.[3] This depression of the transformation point is analogous to the depression of the freezing point of a solvent by the dissolved substance.

The allotropic theory explains the phenomena of the tempering of steel as the older theory that the hardening was due to strains set up in the metal by the sudden cooling never did. The compound steels furnish much of interest in this connection, especially the self-hardening and irreversible nickel-steels.[4] The irreversible steels[5] (so-called from the fact that if, starting in the magnetic condition, they be heated to dull redness they become unmagnetic, but on cooling do not regain their magnetic properties until a tempera-

[1] Lownds and Richardson, Phil. Mag. (6), 1, p. 601, 1901.

[2] B. V. Hill, Verh. d. Deut. Phys. Gesell. Jahrgang, IV., Nr. 9, 1902.

[3] Bruni, Feste Loesungen, German edition, Stuttgart, 1901.

[4] For a full account of these steels see L. Dumas, Recherches sur les aciers au nickel a haute teneures, Paris, 1902.

[5] Ewing, Magnetization in Iron and Other Metals, p. 185, 1900.

ture is reached much lower than that at which they originally became unmagnetic ; if the temperature be again raised the material remains magnetic till the original point of transformation is attained) make it possible to compare the properties of these alloys in the magnetic and the unmagnetic conditions at the same temperature. This has been done by a number of experimenters.[1] It appears also that while one allotropic form, the magnetic, is that ordinarily existing at room temperature, it is possible to render the other, the unmagnetic, stable at that temperature.

It has been seen that the salts of manganese and chromium are in the same class, so far as the magnetic properties are concerned, with those of iron, cobalt and nickel. Might it not then be conjectured that manganese and chromium also have several allotropic forms or phases, of which it is the unmagnetic with which we are acquainted, but that, if the right alloy could be found, the magnetic form might be had.

Heusler's[2] discovery of such an alloy in the case of manganese seems to have been accidental, however. When working with an alloy prepared for another purpose and with a tool of whose magnetization he was not aware, he found that the alloy was attracted by the tool. He then sought in a systematic way to produce magnetic alloys of manganese. He found that certain of the trivalent elements have a particularly strong effect upon manganese even at comparatively low temperatures. If one part of powdered antimony and four parts of powdered manganese be heated together to 500° or 600° C., which is still far below the melting point of manganese, the mixture becomes noticeably magnetic. I tried a similar experiment with chromium, but without success.

Starting with the commercial alloy of 70 per cent. copper and 30 per cent. manganese, Heusler made several series of alloys using as a third metal tin, antimony, arsenic, aluminium, etc., of all of

[1] Ch. Ed. Guillaume, Comt. Rend., 124, p. 176 ; 1515, 1897 ; 125, p. 235, 1897. E. Dumont, C. R., 126, p. 741, 1898   L. Dumas, C. R., 130, p. 1311, 1900. F. Osmond, C. R., 118, p. 532, 1894 ; 128, p. 304, 1899. H. Tomlinson, Proc. Roy. Soc., 56, p. 103, 1894. J. Hopkinson, Proc. Roy. Soc., 47, p. 23 ; 38, 189 ; 48, p. 1 ; 442, 1890, 50, p. 121, 1891. B. V. Hill, Verh. d. Deut. Phys. Gesell., III., Nr. 10, 1901.

[2] Schriften d. Gesell. z. Befoerderung d. gessammt. Naturwiss. zu Marburg, Bd. 13. 5te. Abtheilung, Marburg, 1904. (Verh. d. Deut. Phys. Gesell., 5, 12, p. 220, 1903.)

these the last gave the best results.   In the alloys of copper, man-
ganese and aluminium the susceptibility increased until the masses
of the manganese and aluminium were in the ratios of their atomic
weights, and then grew less again as the amount of aluminium was
increased.   The magnetic properties of these alloys were investigated
by W. Starck and E. Haupt,[1] the magnetic expansion by L. Austin[2]
and the effects of prolonged heating and cooling by E. Gumlich.[3]
Continued heating at a temperature of 110° C. increased the
susceptibility, while annealing at 500° C. left the material practically
unmagnetic.   Cooling in liquid air had no effect.   None of these
authors mention a temperature over 580° C.

Of the alloys made by the author one contained about 60 per
cent. copper, 25 per cent. manganese and 15 per cent. aluminium,
the other a higher per cent. of aluminium.   They were made by
melting the aluminium with the 30 per cent. manganese-copper
alloy, and were cast in the form of rods 0.45 cm. in diameter and
12 cm. long.   The metal was very hard and brittle.   The magnetic
testing was done by the ballistic method.   About a porcelain tube
70 cm. long and 2.5 cm. in diameter was wound a nickel heating
coil.   This was put into a glass tube 5 cm. in diameter and packed
about with kaolin.   The glass tube fitted closely into a brass water
jacket having a space 0.5 cm. between the walls.   The magnetizing
coil was wound upon this jacket and could thus be kept at a con-
stant temperature even when the interior of the apparatus was very
hot.   The secondary coil was would upon a smaller porcelain tube
which was placed within the heating tube.   The specimen, together
with one junction of a thermo-element, was within this second
porcelain tube and packed with asbestos to prevent heat losses.
Corrections were of course made for the demagnetizing effect of the
ends of the rod and for the area between the rod and the secondary
coil.   It may be remarked here that an apparatus of this kind is
intended to measure changes of induction with temperature and does
not profess to give absolutely accurate values of the induction itself
though the error in this respect is not large.   M. L. Dumas[4] deter-

[1] Verh. d. Deut. Phys. Gesell., 5, 12, p. 224, 1903.
[2] Verh. d. Deut. Phys. Gesell., 6, 14, p. 211, 1904.
[3] Ann. d. Phys., 16, p. 535, 1905.
[4] See 6.

mined the transformation points of his nickel-iron alloys by merely observing the temperature at which a compass needle near the specimen ceased to be affected by it.

The first rod tested was that of higher percentage of aluminium. It showed an induction of $B = 5750$ c.g.s. in a field on $H = 87$ c.g.s. with a comparatively large area of the hysteresis curve. On being heated it behaved as those of the other observers had done (up to $500°$ C.), yet it may be of interest to give the curves showing the relation of the intensity of magnetization, I, to the temperature as the metal is heated and cooled, since no such have been published. The field was kept constant and equal to 85 c.g.s. A relatively strong field was used to avoid the occurrence of maxiam
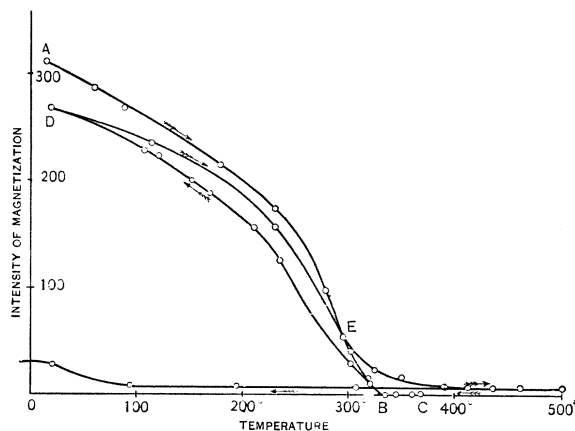
as in the curves for iron and nickel in weak fields.[1] The general form of the curves here is similar to that for the other magnetic metals and their alloys. Beginning at A with an intensity of $I = 311$ c.g.s. the curve falls till it reaches the axis at B. The temperature was carried $33°$ higher bringing the curve to C. On cooling the line leaves the axis again at B but does not return to A but to a lower value at D, $I = 267$. With the second heating the curve lies above that for the first cooling and does not come to the axis at B but crosses the former heating curve at E and when

[1] Ewing, Mag. in Iron, Figs. 79, 85, 8 , 1900.

heated to 500° C. retains a slight susceptibility, I being equal to
7. After falling the second time to 17° C. the intensity was only
27, that is the susceptibility was only 0.32. A reading was taken
with the specimen in liquid air, giving $I = 36$. This remained un-
changed when room temperature was again reached.

It now occurred to me that, from the general behavior of the
alloy, it might be expected that the magnetic qualities of the metal
would be restored if it were taken to a temperature considerably
higher than those previously attained. The specimen was, there-
fore, heated, in the flame, to dull redness (650° to 700° C.) and
allowed to cool slowly. When tested in the same way as before
the intensity was $I = 90$ in the field of $H = 85$. Reheating to the
same temperature and cooling rapidly did not alter this value of I.
The rod was then heated to a bright red (850° C.?) and when tested
at room temperature the intensity was $I = 155$. After cooling in
liquid air $I = 162$.

We have here then a new type of irreversible alloy, but in a
sense opposite to the irreversible nickel-steels. Compare this with
one of the specimens used in the study of the specific heats of some
of these nickel-steels.[1] The alloy contained twenty-four per cent.
of nickel. Let B_H represent the induction B for the field H at the
temperature of the room. The temperatures given are those to which
the metal was cooled, or heated, immediately before the induction
was determined. For the sake of the comparison $B = H + 4\pi I$ is
used instead of the values of I given in the preceding paragraphs.
Tabulating the results for the two alloys :

Nickel-steel,				
When received,	0°	− 20°	− 79°	− 190°
Unmagnetic,	$1,200_{136}$	$3,700_{135}$	$9,200_{135}$	$10,200_{136}$
Heusler alloy,				
When cast,	368°	500°	650° ?	850° ?
	$4,020_{85}$	$3,440_{85}$	427_{85}	$1,220_{85}$	$2,030_{85}$

In the first case the alloy, after cooling from the temperature of
forging, was unmagnetic, but its permeability was found to be

[1] Verh. d. Deut. Phys. Gesell., III., Nr. 10, 1901.

greater the lower the temperature to which it had been cooled. Heating to dull redness left it again unmagnetic. In the other alloy the metal was magnetic when first cast. Cooling to very low temperatures had only a very inconsiderable effect. If heated and allowed to cool to room temperature, the permeability varied with the temperature to which it had been carried, showing a minimum in the neighborhood of 500° C. One might venture a further comparison, as the merest conjecture. In the nickel-steel here spoken of, the magnetic state, when cooled from the temperature of the furnace, is that of iron at high temperatures. Dr. D. K. Morris[1] found also that iron regains its susceptibility to a slight degree between 800° and 1000° C. It is then possible that manganese would be found to be magnetic at a sufficiently high temperature.

Returning to the description of the alloys in hand, the second rod tested was that of lower per cent. of aluminium. It had an induction of $B = 11,800$ in a field of $H = 75$, with very little hysteresis. Its behavior was in general like that of the first one, but, when heated to 950° C. and cooled to room temperature, it remained unmagnetic. There was a great difference in the density of this alloy in the magnetic and in the unmagnetic conditions. When first cast the density was 6.61. After annealing at 950° C. it was but 5.80. Here again the nickel-steels show an opposite change. One of the alloys of nickel and iron referred to above had a density of 7.91 in the magnetic state, 8.09 in the unmagnetic, a change of about 2 per cent. This agrees with the results of H. Tomlinson[2] and J. Hopkinson.[3]

Stephan Meyer found that, when a diminution of volume occurs in a compound, the para-magnetic character of the substance is increased and *vice versa*. In the case of alloys we are, in general, dealing with solid solutions and not with compounds of the constituents, so that the applicability of this statement to alloys would have to be tested by experiment. There is possibly more reason to suspect chemical combination between the manganese and the aluminium in the Heusler alloy than between the iron and the

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[1] Phil. Mag., 44, p. 213, 1897.
[2] See footnote No. 8.
[3] See footnote No. 8.

nickel in the nickel-steel, since the permeability of the former is greatest when the percentages of the two metals are proportional to their atomic weights. These alloys are also those which are most dense in the magnetic condition.