Ferromagnetism and antiferromagnetism in disordered Ni-Mn alloys

J.S. Kouvel, C.D. Graham, I.S. Jacobs

To cite this version:


HAL Id: jpa-00236017
https://hal.archives-ouvertes.fr/jpa-00236017
Submitted on 1 Jan 1959

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
FERROMAGNETISM AND ANTIFERROMAGNETISM IN DISORDERED Ni-Mn ALLOYS

By J. S. KOUVEL, C. D. GRAHAM, Jr. and I. S. JACOBS,
General Electric Research Laboratory, Schenectady, New-York, U. S. A.

Résumé. — Les propriétés magnétiques entre 2 et 300 °K des alliages Ni-Mn désordonnés dépendent sensiblement de leur composition au voisinage de Ni$_3$Mn. À partir des courbes d’hystérésis et des courbes d’aimantation en fonction de la température pour des champs allant jusqu’à 8 000 Oe on trouve que les alliages deviennent moins ferromagnétiques et plus antiferromagnétiques aux basses températures à mesure que la concentration en Mn augmente. Les mesures d’aimantation dans des champs « pulsés » atteignant 100 000 Oe s’accordent avec l’hypothèse de la coexistence du ferromagnétisme et de l’antiferromagnétisme dans ces alliages. Cette interprétation est également en accord avec le fait que la courbe d’hystérésis de l’alliage Ni$_3$Mn désordonné est déplacée de sa position symétrique par rapport à l’origine quand on refroidit l’échantillon à 4,2 °K dans un champ magnétique.

Abstract. — The magnetic properties of disordered Ni-Mn alloys between 2 °K and 300 °K are found to be extremely sensitive to composition (in the vicinity of Ni$_3$Mn). From hysteresis loops and magnetization vs. temperature curves for fields up to 8 000 Oe, it is deduced that with increasing Mn concentration the alloy becomes less ferromagnetic and more antiferromagnetic in its low temperature behavior. Magnetization measurements for pulsed fields up to 100,000 Oe are consistent with the coexistence of ferromagnetism and antiferromagnetism in these alloys. This interpretation is further supported by the discovery that the hysteresis loop for the 26.5 % Mn specimen cooled to 4.2 °C in a magnetic field is shifted from its symmetrical position about the origin.

Introduction. — Recent experiments have revealed some unusual magnetic properties of a disordered nickel-manganese alloy of approximate composition Ni$_3$Mn [1]. Although a ferromagnetic Curie point of about 130 °K was deduced from data of magnetization vs. field and temperature, several features of this data indicated that the material was by no means a normal ferromagnet. Most strikingly, its magnetization for any field up to 7 550 Oe had a maximum value at about 25 °K. Moreover, at temperatures as low as 2 °K, the magnetization was still increasing at the maximum field in a way that was not the normal approach to ferromagnetic saturation. This extraordinary magnetic behavior suggested that in this material there may be antiferromagnetic interactions which are strong enough at low temperatures to align some of the moments antiferromagnetically. Such a situation in disordered Ni$_3$Mn has been theoretically anticipated by both Carr [2] and Sato [3] on the basis of antiferromagnetic Mn-Mn nearest-neighbor exchange interactions and ferromagnetic Ni-Mn and Ni-Ni interactions. The concentration of Mn-Mn pairs, and hence the magnetic properties, would vary with the composition of the disordered alloy. This paper will be devoted to the results of a magnetic study of three compositions centered at about Ni$_3$Mn.

Experimental results and discussion. — Three Ni-Mn alloys were induction melted in an argon atmosphere and cold-swaged to 50 % reduction in area. Chemical analysis of the ingots gave 21.6, 26.5, and 31.1 at. % Mn with about 0.1 at. % ferromagnetic impurities. Metallographic examination of the 31.1 % ingot showed a pronounced dendritic structure, which indicates the presence of segregation. Hence, there are composition fluctuations probably centered about the quoted values. A cylinder 0.5 inch long, 0.25 inch in diameter and a cylinder 0.390 inch long, 0.147 inch in diameter were machined out of each ingot and disordered by quenching into water from 900 °C. The smaller specimens were used for measurements at high pulsed fields which will be discussed later in this paper. The larger specimens were placed in the apparatus described previously [1] and hysteresis loops for a maximum applied field of 8 000 Oe were measured between 2 °K and about 300 °K. The temperature generally increased slightly during the measurement of a complete loop; however, loops were obtained at small enough temperature intervals so that corrections could be applied to obtain true isothermal loops. Some of these loops, corrected for demagnetizing fields, are shown in Fig. 1. Using these loops, we plotted curves of magnetization vs. temperature for constant internal field; some of these are shown in Fig. 2.

It is clear from Figs. 1 and 2 that many of the features of the hysteresis loops and of the magnetization vs. temperature curves vary monotonically with composition. It can be readily observed that with increasing Mn concentration: (1) the
FIG. 1. — Hysteresis loops of magnetization vs. internal field for the alloys of (a) 21.6 at. % Mn, (b) 26.5 at. % Mn, (c) 31.1 at. % Mn.

FIG. 2. — Magnetization vs. temperature at various internal fields for the alloys of (a) 21.6 at. % Mn, (b) 26.5 at. % Mn, (c) 31.1 at. % Mn. For $H = 4000$ Oe, the solid and dashed curves represent the descending and ascending field branches of the hysteresis loops, respectively.
remanent magnetization and the magnetization at 8000 Oe have maximum values at increasing temperatures; (2) the peak values of these magnetizations decrease; (3) the relative rise of the magnetization at 8000 Oe from its value at 0 K to its peak value increases; (4) the hysteresis loop at 2 K changes from an extremely non-linear curve for the 21.6 % Mn alloy to a straight line for the 31.1 % Mn alloy.

The variation of many of the above characteristics with composition is so marked that the 21.6 and 31.1 % Mn alloys appear to be almost at the ferromagnetic and antiferromagnetic extremes in magnetic behavior. There is little doubt from its hysteresis loops and \( M \) vs. \( T \) curves that the 21.6 % Mn composition is ferromagnetic with a Curie point just above room temperature. On the other hand, the \( M \) vs. \( T \) curves (for finite \( H \)) for the 31.1 % Mn alloy closely resemble those for a typical antiferromagnet. The 26.5 % Mn alloy, whose magnetic behavior is intermediate between the two extremes, might therefore be considered to be a hybrid ferromagnetic-antiferromagnet. However, even the two end compositions are not so simple magnetically. For instance, the remanent magnetization of the 31.1 % Mn is inescapable evidence that this material has spontaneous magnetization; the 21.6 % Mn composition exhibits a small but detectable magnetization peak at low temperatures.

The fact that at 8000 Oe the magnetization of all three alloys is still increasing fairly rapidly with field even at very low temperatures was a primary reason for undertaking measurements at considerably higher fields. Magnetization measurements on the three Ni-Mn alloys were carried out at various temperatures for fields up to 100,000 Oe, using a pulsed field technique which will be described elsewhere. Since there was some irreproducibility in the zero correction to the measured magnetization, the high field curves have been drawn to connect smoothly with the results at lower fields. The results are shown in Fig. 3. Some difficulty arose due to the eddy-current heating of the solid cylindrical specimens at very low temperatures where their heat capacities and electrical resistivities were lowest; the maximum rise in temperature during a pulse was estimated to be about 3 K. For the 26.5 % Mn alloy, whose low temperature magnetization is very temperature dependent (see Fig. 2b), this temperature increase was considered excessive. Hence, in this case, we used a cylindrical samples of filings imbedded in wax for which the estimated temperature rise was less than 1 K.

It is obvious from Fig. 3 that up to the highest fields of measurement all our specimens are far from complete magnetic saturation. This is true even for the 21.6 % Mn alloy whose behavior at
fields below 8 000 Oe seems predominantly ferromagnetic. After bending over fairly sharply at these moderate fields, its $M$ vs. $H$ for curves 4.2, 20.4 and 77 °K straighten out and continue to rise almost linearly. At 300 °K, which is just below the Curie point of this alloy, there is considerable curvature in its $M$ vs. $H$ curve at very high fields. The $M$ vs. $H$ curves for the 26.5 % Mn alloy at 4.2, 20.4, and 77 °K are all curved even at the highest fields. The $M$ vs $H$ curve for 300 °K is essentially a straight line as would be expected since this temperature is presumably well above the Curie point of this alloy. For the 31.1 % Mn alloy, the $M$ vs. $H$ curve changes gradually from a straight line at 4.2 °K to a distinctly curved line at 77 °K; for 300 °K the curve is again linear presumably because the alloy is appreciably above its Curie temperature.

The continued increase of the magnetization at low temperature at fields of about 100,000 Oe could be attributed to a ferromagnetic alignment against unusually strong anisotropy forces and/or to a gradual rotation against strong antiferromagnetic forces between atomic moments. The shape of the $M$ vs. $H$ curve for the 21.6 % Mn alloy at 4.2 °K (Fig. 3a) suggests that ferromagnetic alignment is virtually complete at 10,000 Oe and that the residual increase of magnetization at higher fields can be associated with the antiferromagnetism of the material. It would appear from Figs. 3b and 3c that extremely high fields would be required for ferromagnetic saturation of the higher Mn alloys at 4.2 °K.

An additional experiment was recently performed on the 26.5 % Mn alloy. The specimen was cooled from room temperature to 4.2 °K in a field of 5 000 Oe, and a complete hysteresis loop (for a maximum field of 8 000 Oe) was measured at 4.2 °K. This hysteresis loop is shown in Fig. 4 together with the comparable loop for zero field during cooling. The field during cooling was applied in the plus direction, and we note that this has resulted in a shifted loop in which both remanent magnetizations are positive. It follows that the two coercive fields are negative; both branches of the loop cross the $H$ axis at about — 500 Oe. This hysteresis loop resembles the results obtained by Meiklejohn and Bean [4], [5] for a compact of partially oxidized fine particles of cobalt that has been cooled in a magnetic field. Hysteresis loops that are similarly shifted were recently reported by Lin and Kaufmann [6] for UMn$_2$ cooled in a magnetic field. Meiklejohn and Bean attributed their results to an exchange interaction across the interfaces between the ferromagnetic cobalt and the antiferromagnetic cobaltous oxide. Applied to the disordered Ni-Mn alloys, this explanation would be consistent with our previous evidence for the coexistence of ferromagnetism and antiferromagnetism in these alloys. If this is the origin of the shifted loop, the strength of the exchange coupling between the ferromagnetically and antiferromagnetically aligned moments is demonstrated by the following experiment. The 26.5 % Mn specimen, after being cooled to 4.2 °K in a 1 000 Oe field, was subjected to pulsed fields up to 140,000 Oe in the direction opposite to the field during cooling; the shifted loop behavior was not destroyed.

In summary, we have found that the magnetic properties of disordered Ni-Mn alloys are extremely sensitive to composition (in the vicinity of Ni$_2$Mn). From hysteresis loops and magnetization vs. temperature curves for moderately high fields, we deduce that with increasing Mn concentration the alloy becomes less ferromagnetic and more antiferromagnetic in its low temperature behavior. Magnetization measurements for very high pulsed fields are consistent with the coexistence of ferromagnetism and antiferromagnetism in these alloys. This interpretation is further supported by the discovery that the hysteresis loop for the 26.5 % Mn specimen at 4.2 °K is displaced from its symmetrical position about the origin when
the specimen is cooled in a magnetic field. A more
detailed study of this latter effect is now in
progress.

We gratefully acknowledge stimulating discus-
sions with Professor G. W. Rathenau during an
extended visit at our Laboratory, and the able
assistance of P. E. Lawrence in the pulsed field
measurements.

REFERENCES

[1] Kouvel (J. S.), Graham (C. D., Jr.) and Becker (J. J.),
and Magnetic Materials (AIEE, New-York, 1955),
p. 119.
[4] Meiklejohn (W. II.) and Bean (C. P.), Phys. Rev.,
1956, 102, 1443.
[5] Meiklejohn (W. II.) and Bean (C. P.), Phys. Rev.,
1957, 105, 904.
108, 1171.

DISCUSSION

Mr. Artman. — The mechanism proposed by
Meiklejohn and Bean for the shifted hysteresis loop
in Co-CoO presumes the existence of two separate
phases: ferromagnetic Co and antiferromag-
netic CoO. You suggest that a similar mecha-
nism may exist in the disordered ab. 5 % Mn alloy.
Do you have any evidence for the existence of such
separate phases in this Mn alloy?

Mr. Jacobs. — We may consider the possibility
of fluctuations in composition or of fluctuations in
degree of order as a source of such phases but the
existing experimental evidence casts but little light
on these alternatives. The segregation noted in
the paper was probably removed (or greatly reduced)
by subsequent long annealing and re-quench-
ing, but the shifted loop remained qualitatively
the same. It may also be possible to account for
the shifted loops without invoking the existence of
extended separate phases. Theoretical work on a
model containing the interactions noted in the
paper is being carried out by Dr. Kouvel. It
accounts for a number of features of these quenched
Ni-Mn alloys but it is too early to say if it des-
cribes a shifted loop.

M. Guillaud. — Nous avons étudié le com-
posé MnNi₃ en 1944 (C. R. Acad. Sc., 1944, 219,
614-616). Pour obtenir un état parfaitement
ordonné, il faut chauffer cet alliage pendant une
longue durée (environ 3 semaines à 470 °C dans
nos essais, car le point de transformation est à
environ 480 °C). On obtient alors des aimantations
de l'ordre de 700.

L'aimantation que vous obtenez, de l'ordre
de 400, semble indiquer un état partiellement
ordonné.

D'après nos résultats l'état désordonné n'est pas
ferromagnétique.

Mr. Jacobs. — All these alloys are disordered;
they have been quenched from 900 °C. We hope
to study the influence of ordering on these same
samples at a latter date.