

Magnetic Interactions between Manganese Atoms in Metals

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Thermal, electrical and magnetic properties of Mn alloys in α - and γ -phases are investigated in order to understand the complicated magnetic behavior of manganese atoms in metallic systems. The resistivity shows a sharp cusp at the Néel point while the susceptibility shows only a broad anomaly and this indicates the advantage of resistivity measurements for the detection of antiferromagnetism in metals. In α -manganese, data indicate that there is a cooperative induction of the magnetic moment below the Néel point and this calls for a mechanism which is connected to the collective behavior of electrons. An explanation concerning the stability of α -phase in terms of a Jones zone and variability of the electronic state of manganese atoms is given. A tentative choice of a spin density wave vector based on this model agrees qualitatively with the result of neutron diffraction. This interpretation is consistent with the electronic specific heat of α , β and γ manganese. In γ -phase alloys, Mn atoms have a well localized moment and the paramagnetic behavior of these alloys, Cu(Mn) for example, can be explained satisfactorily from the localized picture. However the onset of antiferromagnetism at low temperatures requires again a mechanism which is different from a conventional localized picture.

Metals, alloys, and intermetallic compounds containing Mn are markedly different from one another in their physical properties, particularly in their magnetic behavior. Manganese atoms in metallic matrices exhibit magnetic moments varying from 0 to $5 \mu_B$ depending on the metallic systems studied. The interactions between manganese atoms are ferromagnetic in some materials, antiferromagnetic in others, and often the two interactions appear in direct competition. The polymorphism of Mn itself, its solubility in the noble metals, its occurrence in many intermetallic compounds, and its strong tendency to form ordered alloys add to make Mn an interesting element to study. In this paper we report and interpret some results of studies of magnetic susceptibility, electric resistance, and specific heat of some Mn alloys. In addition a possible interpretation of the polymorphism of Mn itself is given in connection with the above magnetic properties.

Pure α -Mn has a susceptibility-temperature curve with a broad maximum and the Néel point is located roughly at the positive maximum in $d\chi/dT$, (Fig. 1). On the other hand, the resistivity shows a sharp cusp at the Néel point (Fig. 2). α -Mn has a complicated structure with four different atomic sites. The atoms on these sites are considered to

be physically and chemically different from each other. In this sense, it is justifiable to view α -Mn as an alloy or an intermetallic compound.

Whereas the antiferromagnetic metal Cr has no localized moments above its Néel temperature¹⁾, α -Mn exhibits only a very small amount of localized moment. The entropy²⁾ and the neutron diffraction measure of spin disorder³⁾ are consistent with one

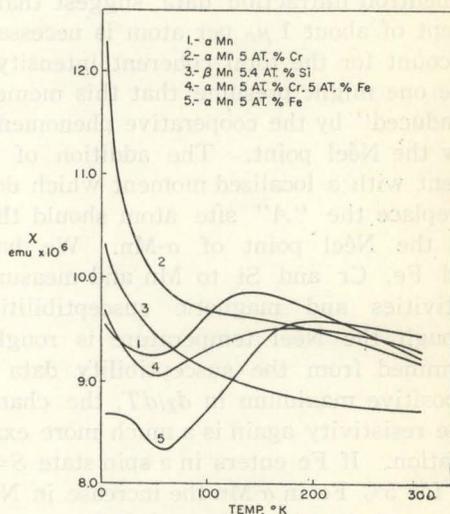


Fig. 1. Susceptibility of (1) α -Mn; (2) Mn (5% Cr), $\alpha+\sigma$ phase; (3) β -Mn (5% Si); (4) α -Mn (5% Cr+5% Fe); (5) α -Mn (5% Fe).

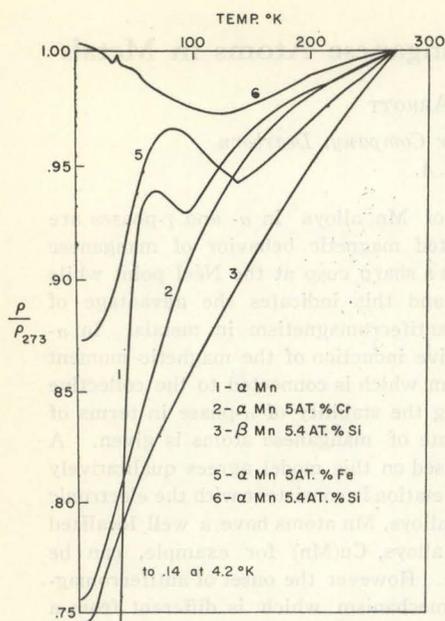


Fig. 2. Resistivity of (1) α -Mn; (2) Mn (5% Cr), $\alpha + \sigma$ phase; (3) β -Mn (5% Si); (5) α -Mn (5% Fe); (6) α -Mn (5% Si).

atom in 29 (namely all the large "A" sites) possessing a localized moment of $5 \mu_B (S=5/2)$. Magnetically α -Mn could then be compared to a magnetically dilute alloy. A direct comparison in this sense can be made with Cu(Mn) alloys for which a concentration of 100/29% Mn has a Néel temperature of almost 90°K ⁴, (compared to 95°K for α -Mn). Low temperature neutron diffraction data suggest that a moment of about $1 \mu_B$ per atom is necessary to account for the total coherent intensity⁵. Hence one might presume that this moment is "induced" by the cooperative phenomenon below the Néel point. The addition of an element with a localized moment which does not replace the "A" site atom should then raise the Néel point of α -Mn. We have added Fe, Cr and Si to Mn and measured resistivities and magnetic susceptibilities. Although the Néel temperature is roughly determined from the susceptibility data by the positive maximum in $d\chi/dT$, the change in the resistivity again is a much more exact indication. If Fe enters in a spin state $S=1$, then for 5% Fe in α -Mn the increase in Néel temperature can be estimated from

$$\frac{(T_N)_{\text{Mn(Fe)}}}{(T_N)_{\text{Mn}}} = 1 + \frac{S_{\text{Fe}}(S_{\text{Fe}}+1).1/20}{S_{\text{Mn}}(S_{\text{Mn}}+1).1/29} = 1.33,$$

while experiment gives 1.4. Si, on the other hand, should suppress the antiferromagnetism if, as expected, it enters the large A sites. This would not appear to be so (Fig. 2).

The above magnetic characteristics of α -Mn, especially the cooperative induction of the magnetic moment as well as the antiferromagnetism in what is like a magnetically dilute alloy, call for a mechanism such as the static spin density wave proposed by Overhauser⁶. Then the increase in resistivity below the Néel point, which is observed in Cr, α -Mn, the antiferromagnetic rare earth elements, and a number of alloy systems in which antiferromagnetism is suspected, is naturally understood. That is, a static spin density wave has a wave vector which spans the Fermi sea, causing energy gaps at the Fermi surface and hence lowering the conductivity. In a previous attempt to apply the spin density wave model to a solution of the neutron powder pattern of α -Mn, it was found that the number of adjustable parameters was greater than the number of peaks to be fitted. If, however, it were possible to get an independent estimate of the size and shape of the Fermi surface, a spin density wave vector could be predicted and the corresponding magnetic structure compared with experiment. This estimate we have obtained in the following manner.

The importance of the reduction of the energy of free electrons with momentum component approaching a Brillouin zone boundary to the question of stability of alloy phases with more than one atom per primitive unit cell has long been appreciated⁷. Recent success in considering the problem of the origin of long period superlattices⁸, through the use of Jones zones, has revived in us, at least, some faith in this old idea. If a system has a "spherical" Jones zone with electrons which almost fill up the zone, the condition is most favorable. In other words, the system tends to take a structure which produces a "spherical" Jones zone which just includes the electrons. Let us show how this principle works in α -Mn. We have adopted the viewpoint of including all the electrons outside the closed argon shell in the electron gas. A cubic Jones zone of higher index has the attractive feature of having a polyhedron whose sites are all equal distance

from the origin and of a number sufficient to produce an almost spherical zone boundary. Mn has seven non-core electrons per atom. In the alpha phase there are 58 atoms per cubic (non-primitive) unit cell or 406 electrons per cubic cell. In the beta phase, there are 20 atoms per cubic unit cell or 140 electrons per cell. These numbers are just about right for the volume of the inscribed spheres of the principal high index Jones zones of α and β manganese. The α -Mn high index zone has $h^2+k^2+l^2=54$ for its diameter. This is a 96-sided polyhedron formed from the {721}, {633}, and {552} reciprocal lattice points and contains 414 electrons in its inscribed sphere. There are 48 additional faces of this zone with $h^2+k^2+l^2=56$, constructed from the {642} points. The β -Mn high index zone has $h^2+k^2+l^2=26$ for its diameter. This is a 72-sided polyhedron formed from the {510} and {431} points, and contains 139 electrons in its inscribed sphere. Certainly these zone structures result in a considerable lowering of electron gas energy. The occurrence of these structures in Mn also implies that the Mn atoms are capable of forming structures generally reserved for intermetallics where a considerable difference in atomic size occurs, for it is the structure, of course, which generates the high index zone which lowers the electron energy. The hexatetrahedral packing around the A site of α -Mn, for instance, is close packing for spheres which differ in radii by 25%. In γ -Mn and δ -Mn, the concentrations of 28 and 14 electrons per cubic unit cell do not come close to zone boundaries (other than the ones they fill over).

A spin density wave can be chosen from the condition that its wave vector should span the Fermi sea other than in a direction in which the lattice has already produced gaps at the surface. For a Fermi surface bounded by the planes {721}, {633}, {552}, an ideal direction would be a vector pointed toward the middle of the triangle formed by these vectors. This is very close to a [641] direction for which $h^2+k^2+l^2=53$. (This is just right to span the Fermi surface considering that the radius is decreased in the region between the necks formed at the boundaries.) Such a choice of spin density wave vector can be seen to reproduce the qualita-

tive features of the neutron diffraction pattern without further specifying the model. This wave vector does not add (or subtract) from any of the reciprocal lattice points of strong intensity in such a way as to generate a {100} reflection (which is missing from the magnetic pattern). It will, however, generate a {111} and more strongly a {210} as well as the remainder of the magnetic reflections of odd indices as observed.

This account of the lowering of electron gas energy in α -Mn and β -Mn raises the question of the origin of the stability of the various phase at higher temperatures. One point to consider in this is the question of electronic specific heat. The electronic specific heat of α -Mn can be estimated from measurements at low temperatures⁹⁾ and also from higher temperatures²⁾ with an answer near 3×10^{-3} cal/g atom-deg² for the coefficient of the linear term. The coefficient of the linear term in β -Mn as estimated from low temperatures is very large, greater than 10×10^{-3} cal/g atom-deg². This, however, may be the result of some other mechanism operating at low temperatures, possibly magnetic. The specific heat from 100°K on up is fitted with a value very close to that of α -Mn¹⁰⁾. On the other hand, a 100°K to 300°K deduction of the coefficient of the linear term for γ -Mn gives values greater than α -Mn or β -Mn. This may well be an effect of the low temperature tail on a magnetic specific heat anomaly above room temperature for γ -Mn. Measurements of the low temperature specific heats of γ -phase Mn(Cu) alloys has been carried out¹¹⁾ and an extrapolation to pure γ -Mn yields a lower coefficient of the linear

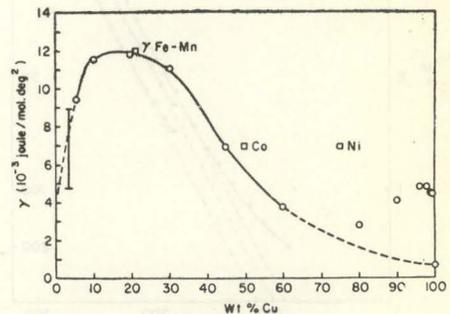


Fig. 3. Coefficient of linear term in low temperature specific heat of γ -phase alloys of Mn(Cu)¹¹⁾.

term, namely 1×10^{-3} cal/gm atom-deg² (Fig. 3). This then is consistent with lowering of electron energy through a higher density of states in the complex phase than in the simple phases. This also indicates that electron gas entropy is not a major factor in the high temperature stability of at least the γ -phase.

In many γ -phase alloy systems, Mn atoms appear to have a well localized moment, whose value depends upon environment, i.e., $S=5/2$ for Ag(Mn), $S=2$ for Cu(Mn). Analysis of a number of systems¹²⁾ shows correlation between experiment and simple models where the Mn-Mn interaction is taken as positive for second near neighbors (nearest neighbors are either taken as negative or at least less positive than second near neighbors). For instance, such an argument would account for ferromagnetism in ordered Cu_3Mn . Dilute Cu(Mn) alloys show a positive paramagnetic Curie temperature which increases 10°K per each atomic percent Mn. If Cu(Mn) alloys show a tendency for ordering and if second neighbor interactions are mainly responsible for the positive paramagnetic Curie temperature in dilute alloys, then number of nearest neighbors could be reduced below statistical expectations by slowly cooling the alloys and θ_p would be expected to rise. The results of susceptibility for 5 and 10 percent

alloys show the expected increase of θ_p for slow cooling and a decrease for very rapid quenching. The extreme variations and a furnace cooled sample are compared in Fig. 4. One could then conclude that second nearest neighbor interactions are primarily responsible for the positive θ_p in dilute Cu(Mn) alloys. The origin of the low temperature behavior should then be sought in some longer range interaction which will account for what appears to be cooperative antiferromagnetic behavior.

Overhauser has proposed that the periodicity of the spin configuration of dilute alloys of Cu(Mn) is incommensurate with the crystal lattice periodicity and that the moment is modulated sinusoidally⁶⁾. Whether Cu(Mn) alloys show a long range antiferromagnetic ordering and whether or not the periodicity is commensurate with the lattice could be determined by neutron diffraction on a single crystal of Cu(Mn) with 5% Mn. A preliminary search along three principal lines in reciprocal lattice space, carried out at 4.2°K , revealed no evidence of magnetic reflections¹³⁾. Before resorting to an apparatus for systematically scanning reciprocal lattice space to investigate this problem, we have attempted to deduce something about the magnetic structure from bulk magnetization measurements by studying the thermal magnetic remanence as a function of field cooling direction in the single crystal. These effects turn out to be quite isotropic. The same thermal magnetic remanence can be induced in any field cooling direction. This remanence can be rotated coherently by a field applied at an angle to the field cooling direction. However, several secondary effects which do reveal differences in different directions have been observed, i.e., in the high field hysteresis loop and in the sharpness of reversal of the remanence in a field applied in the reverse directions. These low temperature magnetization curves give every indication of reflecting a long range cooperative phenomenon.

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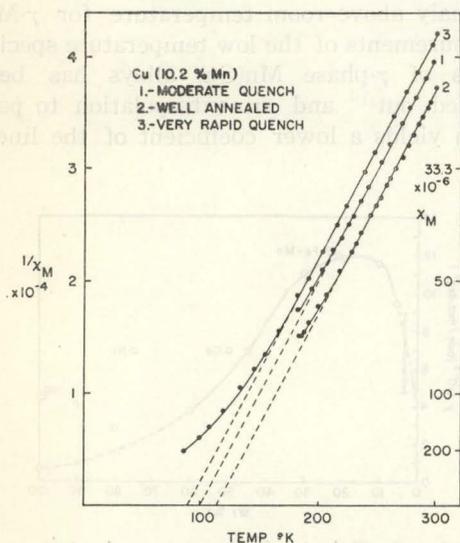


Fig. 4. Inverse susceptibility of Cu (10.2% Mn) for several heat treatments from 875°C .

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To the Problem of the Influence of the Spontaneous Magnetization on the Crystal Structure and the Phase State of Alloys

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When two processes—the magnetic transformation and the atomic order-disorder of a solid solution—are superimposed and when the leading part belongs to the first process, there are anomalies in the temperature dependence of the degree of the atomic order, the magnetization and other parameters. This problem is examined in the limits of Bragg-Williams's and Rosing-Weiss's approximations. The analysis of the experimental results of the investigation of the whole series of alloys shows that the 3*d*-exchange interaction can lead not only to the distortion of the solubility limits in one direction or another or to the change of the crystal lattice parameters but also to the formation of the superstructures of ferromagnetic nature. The corresponding supposition had been done for some systems too.

1. The elementary theory of the atomic-ferromagnetic order-disorder (a. f. o.) in Bragg-Williams's approximation

If the Curie point of a solid solution lies in the region where the atomic diffusion mobility is large enough, it makes possible to superimpose two processes—the magnetic transformation and the atomic order-disorder. To solve this problem exactly in general way

it is necessary to calculate reciprocal potentials and the exchange interaction of the components¹⁾. However, for some solid solutions the 3*d*-exchange part of order-disorder energy is apparently predominating^{2), 3)}. The spontaneous magnetization and the atomic order-disorder are examined in intercorrelation when the leading part belongs to the first process.