MAGNETIC PROPERTIES OF MnPt

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Magnetic properties of MnPt

by

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ABSTRACT*

The magnetic properties of quenched and annealed powder specimens of MnPt were investigated using x-ray diffraction, magnetization measurements and neutron diffraction techniques. Thin films of MnPt were prepared by rf sputtering techniques and the films were investigated by x-ray diffraction and magnetization measurements. The powder specimens of MnPt were found to be typically antiferromagnetic in an $L1_0$ structure with Mn atoms occupying the (001) planes. The Mn moments were antiparallel to their nearest neighbors in the (001) planes. The atomic moment of Mn is $(4.1 \pm .2)\mu_B$ for the annealed specimens and $(3.9 \pm .2)\mu_B$ for the quenched specimens. Neutron data failed to determine whether or not Pt carries a moment. Assuming a moment associated with the Pt atoms, the maximum value is $0.2\mu_B$ per atom. The quenched specimens contained small ferromagnetic regions probably with a composition of 18-32 at.% Mn. The sputtered films of MnPt were highly disordered in all but one specimen, which was amorphous. The films were ferromagnetic with the deduced Mn moment of $(3.0 \pm .3)\mu_B$ per atom, which may not represent the true value because the films were not entirely ferromagnetic.

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INTRODUCTION

Literature Review

The magnetic study of alloys of 3d transition metals with platinum (5d) was initiated by Friederich and Kussmann (1935) on the Cr-Pt system. The exceptionally high coercive force and $(BH)_{\max}$ displayed by CoPt (Jellinghaus, 1936) further stimulated interest not only in this particular alloy as a potential hard magnet, but also in the study of the environmental effect of Pt when it is alloyed with the iron group of transition metals.

Pt is paramagnetic in the pure form, but may be capable of ferromagnetic interaction when alloyed with elements of the ferromagnetic transition metals. For instance, Besnus and Meyer (1973) reported that ordered CrPt_3 is ferrimagnetic and that Pt carried a moment of $0.27 \mu_B$ per atom. MnPt_3 is also ferromagnetic (Pickart and Nathans, 1962) and the atomic moment of Pt is $0.17 \mu_B$. However, Bacon and Crangle (1963) reported that in the Fe-Pt they could not detect any aligned moment on the Pt atoms. They concluded that the Pt moment is very small, although there is a very strong environmental effect on the spins of the Fe atoms as a result of the Pt atoms.

This environmental effect is also observed in Ni-Pt. Chen et al. (1974) found that the magnetic behavior of the equiatomic alloy NiPt is complex and resembles that of FePt_3 .

NiPt shows antiferromagnetism in the ordered state and ferromagnetism in the disordered state. For CoPt, van Laar (1964) reported that Co has a moment of less than $1.6 \mu_B$ per atom and Pt carries an atomic moment greater than $0.3 \mu_B$.

The onset of ferromagnetism in Cr-Pt and Mn-Pt alloys is a very interesting phenomenon because both Cr and Mn are antiferromagnetic at low temperatures. Friederich and Kussmann (1935) reported that ferromagnetism existed in Pt-rich Cr-Pt alloys such that when the Cr content increased from 22 to 47 at.%, the Curie temperatures increased from 50 to 750°C and the maximum spontaneous magnetization was found in CrPt_3 . Subsequent neutron diffraction studies by Pickart and Nathans (1963) showed that the magnetic structure of ordered CrPt_3 is ferrimagnetic with two sublattices. The superlattice is of the $\text{Cu}_3\text{Au}(\text{Ll}_2)$ type and the Cr atoms are located at the corner positions.

MnPt_3 also has a superlattice of the Cu_3Au type. However the alloy is ferromagnetic with a total moment of $4.12 \mu_B$ per molecule (Pickart and Nathans, 1962). The atomic moments of Mn and Pt were 3.6 and $0.17 \mu_B$ respectively. Auwarter and Kussmann (1950) had previously indicated that ferromagnetism exists in Mn-Pt from 18 to 32 at.% Mn, with the maximum spontaneous magnetization occurring at the stoichiometric composition MnPt_3 . The Curie temperatures increase from -100 to 425°C over this range of compositions.

The Mn-Pt system was investigated by Krén et al. (1968) in the composition range of 18 to 29 at.% Pt. They reported that the alloys with 25 at.% or more Pt have a Cu_3Au superlattice with a triangular antiferromagnetic arrangement of the spins on the Mn atoms. Pt is assumed to carry no moment and the maximum atomic moment of Mn ($3.4 \mu_B$ per atom) occurs in $\text{Mn}_{73}\text{Pt}_{27}$. For the alloys with a Pt concentration less than 25 at.%, this triangular antiferromagnetic arrangement is maintained, but there may be an antiferromagnetic alignment of the magnetic moments of the excess Mn atoms on the Pt sublattice (the corner positions). This alignment is collinear, similar to that of γ -Mn-type antiferromagnetic order. The Néel temperatures for the alloys increase with increasing Mn concentration, with the T_n for the stoichiometric Mn_3Pt being 475°K .

Near the equiatomic composition Pt forms a series of isomorphous solid solutions, designated as MPt, with M being the iron group transition metals. These MPt alloys order chemically into the L1_0 (CuAuI) superlattice. The disordered states of all the MPt alloys except MnPt, is face-centered cubic. MnPt is thought to crystallize into a B2 CsCl-type cubic structure.

Because of the striking similarities in crystal structure and the tendency of these alloys to order, it is thought that they constitute a system within which the dependence of

magnetic properties on certain factors could be studied. For example, by varying the M component and the degree of order, it might be possible to obtain information on the magnetic moment as a function of the number of nearest neighbors and the spatial distribution of the magnetic moments. The onset of antiferromagnetism in these alloys could be a means of correlating experimental results with the Slater-Bethe criterion for the sign of the exchange integral, J , in the Heisenberg theory of magnetism. Table 1 shows the known magnetic behavior to date of the ordered and disordered phases of the MPt alloys.

Table 1. Summary of the type of magnetism displayed by the disordered and ordered phases of MPt

MPt	Disordered	Ordered
CrPt	Antiferromagnetic	Antiferromagnetic
MnPt	?	Antiferromagnetic
FePt	Ferromagnetic	Ferromagnetic
CoPt	Ferromagnetic	Ferromagnetic
NiPt	Ferromagnetic	Antiferromagnetic

Within this group, CrPt and MnPt are remarkably similar. Ordered CrPt ($c/a = 1.0$) has a lattice constant $a = 3.816 \text{ \AA}$ (Raub and Mahler, 1955), and it is an antiferromagnet. All the Cr atoms are located in alternate (001) planes and the moments of Cr atoms in the next nearest neighbors are antiparallel. Pickart and Nathans (1963) reported an atomic

moment of $2.24 \mu_B$ for Cr, but they could not determine whether or not the Pt atoms carry any moment.

Ordered MnPt has lattice constants of $a = 4.004 \text{ \AA}$ and $c = 3.664 \text{ \AA}$ (Brun et al., 1964) and is also an antiferromagnet, but with moments of the Mn atoms aligned perpendicular to the (001) planes (Andresen et al., 1965). No determination of the Pt moment was made, but in the neutron diffraction studies of the latter authors, good agreement between observed and calculated data was obtained when the Mn moment was assumed to be $4.0 \mu_B$ per atom. Krén et al. (1968) investigated Mn-Pt alloys in a composition range of 41 to 66 at.% Mn. They found that the largest moment ($4.3 \mu_B$ per Mn atom) and the highest Néel temperature (975°K) is in the stoichiometric alloy MnPt. This alloy also has the smallest c/a ratio (.918). When the Pt concentration exceeds 50 at.%, the Mn moments are parallel to the (001) plane, as in CrPt, but the atomic moment of Mn is still about $4.2 \mu_B$. However, in the Mn-rich alloys, the Mn moments are aligned normal to the (001) plane until the Mn concentration exceeds 57 at.%. The Mn moment decreases to $3.5 \mu_B$ per atom in $\text{Mn}_{62}\text{Pt}_{38}$ ($c/a = .95$) and the T_N of this alloy is 500°K . Magnetic ordering of the excess Mn atoms on the Pt sublattice is a possibility, but this was not determined within the experimental accuracy.

Statement of Problem

In all cases Pt is assumed to have no moment or a very small moment. The difficulty in detecting the Pt moment by neutron diffraction techniques arises because its contribution enters the intensity as a square and because there is uncertainty in the magnetic form factors of Pt used in the calculations. One of the purposes of the present study was to determine whether Pt carries a moment. The use of the form factors of Pt as deduced from CoPt_3 (Menzinger and Paoletti, 1966) in this study represents an improvement over previous studies in which the form factors of Pt were approximated by using form factors for 3d or 4d transition metals.

Another purpose of this study was to determine the form of magnetism displayed by the disordered MnPt and the spin alignment of the magnetic moments of Mn, and possibly Pt, atoms by neutron diffraction experiments. Andresen et al. (1965) and Krén et al. (1968) reported that ordered MnPt had an antiferromagnetic structure, but no determination was made on the disordered phase.

The study was also aimed at the structural and magnetic behavior of thin films of MnPt prepared by rf sputtering at liquid nitrogen temperature. The presumably highly disordered or amorphous alloys would allow the magnetic properties of MnPt to be examined as a function of the degree of order by magnetization measurements,

EXPERIMENTAL PROCEDURE

Sample Preparation

Three Mn-Pt alloys were prepared from 99.99% pure Pt and at least 99.9% pure Mn by arc melting in an argon atmosphere. The nominal compositions of the alloys were: I-50.0, II-50.9 and III-50.0 at.% Mn. To attain compositional homogeneity, the ingots were remelted several times on alternate sides.

Alloys I and II were finally melted into the shape of a finger and were further homogenized for 20 hours at 1370°C in a high purity helium atmosphere. Alloy III was made into a flat disk 5 cm in diameter. No further homogenization treatment was performed on it. Subsequent chemical analysis revealed that the compositions were: I-49.9, II-50.9 and III-50.0 at.% Mn.

Alloys I and II were crushed to powders with maximum particle size of 50 microns. The powders were sealed in quartz tubes under a vacuum with a residual pressure around 10^{-6} torr. From alloy I, two quenched specimens, #1 and #2, were obtained by holding the specimen at 1150°C and 1050°C respectively for twelve hours and then quenching into ice-brine. An annealed specimen, #3, was obtained by annealing the specimen in a sealed quartz tube for eight hours at 970°C and then cooling at a rate of 20°C per hour until 920°C, after which time, the specimen was furnace-cooled. One quenched specimen, #4, and one annealed specimen, #5, were

obtained from alloy II by similar methods. However, quenching was done from 1130°C for specimen #4. Another annealed specimen, #6, was obtained by annealing for 24 hours at 970°C in a sealed quartz tube and then quenching into ice-brine.

Sputtering experiments were performed in order to obtain amorphous or highly disordered films. The thin films of MnPt were prepared by rf sputtering in a dynamic argon atmosphere on various substrates (Scotch-brand tape, Mylar and surgical glass slides) cooled to liquid nitrogen temperature. The sputtering area of the target was kept about 4 cm in diameter so as to concentrate the power of the sputtered atoms. Back sputtering was also performed to reduce the concentration of Pt atoms on the substrate because the sputtering rate for the Pt atoms is higher than that of the Mn atoms. Microprobe analysis of one deposition on Scotch-brand tape at room temperature revealed that it contained 47.8 at.% Mn.

X-ray Diffraction Experiments

X-ray diffraction patterns were obtained for the six powder specimens using a Philips diffractometer equipped with a chart recorder. The x-ray tube was operated with a power of 40 kV at 25 mA. Fe-K α radiation with a wavelength of 1.9372 Å was used. A quantitative x-ray diffraction analysis was also performed on specimen #5 on a Picker diffractometer interfaced with a Digital Equipment Corporation computer, model PDP-15. Reflective intensities were obtained at steps

of 0.033 degree with 30 seconds per step. Mo-K_{α_1} radiation with a wavelength of 0.70926 Å was used. For the thin films, x-ray diffraction patterns were obtained with both Cu-K_{α} and Fe-K_{α} radiation.

Neutron Diffraction Experiments

Neutron diffraction experiments were conducted on the six powder specimens at room temperature at the Ames Laboratory Research Reactor. The specimens were each packed in a cylindrical holder made of vanadium, and mounted on a double-axis spectrometer. Data collection and equipment control were made with a PDP-15 computer interfaced with the equipment. The beam collimator was 30° between the sample and the reactor, and 20° between the sample and the detector. The neutron beam was monochromated with a single crystal of beryllium using the (311) plane, resulting in a wavelength of 1.05 Å.

A preset of 120 seconds per tenth of a degree was used for specimens #1 and #2. A preset of 75 seconds per tenth of a degree was used for the other four powder specimens. Only reflections in the angular range up to $2\theta = 50^\circ$ were recorded, because resolution above 50° was unsatisfactory. A separate measurement of the instrumental background for the (002) reflection was made with the sample holder located at the position of the specimen. All measurements were made in the absence of a magnetic field.

Magnetometer Measurements

Bulk magnetization measurements were performed on all seven specimens using the modified Faraday's method on a Foner Vibrating Sample Magnetometer with a maximum reliable field of 19 KOe (1.5×10^6 A/m). A cryostat attachment was used to perform experiments from 4.2° to 290°K. Temperature was measured by means of a digital PAR-156 cryothermometer with a diode located less than a mm from the specimen. The temperature was maintained with a PAR-152 cryogenic temperature controller in a bath of liquid helium or liquid nitrogen. Accuracy of measuring and maintaining the temperature was within two degrees.

Measurements at elevated temperatures up to 950°C involved a furnace, PAR-151, which is equipped with a power supply having a maximum out put of 400 mA. The chromel-alumel thermocouple located in the sample chamber was within five degrees of the actual temperature. Stability of temperature could be maintained within five degrees.

Magnetization measurements were performed under a magnetic field up to 19 KOe. The field was maintained by a power supply with a digital current readout and the instability observed was insignificant. The relationship between the current and the field was obtained with a gauss meter.

RESULTS

The Bragg reflection peaks obtained from the x-ray diffraction data for each of the six powder specimens can be indexed on the basis of a simple body-centered tetragonal structure. However, because of the subsequent magnetic structure obtained from the neutron diffraction studies, it is advantageous to index the diffraction patterns on the basis of a face-centered tetragonal structure, similar to that of a CuAu I ($L1_0$) structure as shown in Figure 1.

The Fe- K_α radiation was advantageous for exhibiting superlattice reflections because it depresses the scattering factor of Mn more than it does that of Pt. These superlattice reflections established that the ordered structure consists of (001) planes which contain alternately all Mn or all Pt atoms. The superlattice reflection peaks occur for mixed (hkl) with $h+k = \text{even number}$ (Figure 2).

The deduced values of the lattice parameters and c/a ratios for various specimens are shown in Table 2. The c/a ratio of 0.9166 for specimen #1 was obtained from a precise lattice parameter analysis. The c/a ratio of 0.918 for specimen #5 was obtained from a diffraction pattern using Fe-K radiation and also from a pattern using Mo- K_{α_1} radiation (Figure 3).

Figure 3 is a pattern derived from the intensity data of the Bragg reflections. The data established that there is a

Figure 1. L1₀ crystal structure of ordered MnPt

Figure 2. X-ray diffraction pattern of quenched MnPt (Fe- K_{α} radiation)

Figure 3. X-ray diffraction pattern of ordered MnPt ($\text{Mo-K}\alpha_1$ radiation)

Table 2. Values of the lattice parameters and c/a ratios of MnPt specimens

Specimen #1	Specimen #5	Thin film
a = 4.013	a = 4.01	a = 4.00
c = 3.678	c = 3.68	c = 4.00
c/a = .9166	c/a = .918	c/a = 1.00

high degree of preferred orientation in specimen #5. For instance, the observed integrated intensity of the (200) reflection is about twice the calculated value for a sample with no preferred orientation. Because of the problem caused by preferred orientation, the x-ray results could not be used to obtain reliable information about the degree of long range order in the powder specimens. Nevertheless, the deduced value of the long range order parameter from the x-ray patterns indicated that the quenched samples are still appreciably chemically ordered.

Figure 4 shows a profile of the x-ray diffraction pattern for a thin film of MnPt. A broad peak was observed between 2θ -values of 18 and 30°. Two sharp peaks, the (111) and (200) were also observed. No superlattice peaks were detected in the diffraction patterns for any of the thin films. The films have a highly disordered f.c.c. structure with a lattice parameter of 4.00Å, indicating the absence of the superlattice $L1_0$ structure ($a = 4.01$ Å and $c = 3.68$ Å) of the powder specimens. For another film which was deposited on Scotch-brand

Figure 4. Profile of x-ray diffraction pattern of MnPt film (Fe- K_{α} radiation)

tape at liquid nitrogen temperature, no discernible peaks were obtained in the diffraction pattern, implying that the film was amorphous (Figure 5).

The magnetization curve at 291°K for specimen #1 is shown in Figure 6. When the applied field is above 4 KOe, the dependence of magnetization on the applied field appears to be linear, but below 4 KOe, a non-linear relationship prevails. The M versus H curves for the other quenched specimens have similar shapes. This is taken to be evidence of the coexistence of antiferromagnetic and ferromagnetic regions, the nature of which will be discussed later. Also consistent with the coexistence is the observation of resolvable hysteresis loops in the quenched specimens of Alloy I. A typical hysteresis loop obtained at 77°K is shown in Figure 7. This loop features a remanence of about 0.5×10^{-2} emu/gm and a coercive force of 1 KOe. An important feature of the loop is that it is symmetrical and not displaced from the origin. The physical significance of the symmetrical shape of the hysteresis loop will be discussed in the next section.

The effect of chemical order on magnetization was observed in specimen #2. When the specimen was air-cooled from 1150°C, the magnetization at 294°K for $H = 16$ KOe was 5×10^{-2} emu/gm. When this specimen was subsequently deformed the magnetization at the same temperature and field was 5.7×10^{-2} emu/gm. The magnetization for the specimen after being

Figure 5. X-ray diffraction of amorphous MnPt film (Fe-K radiation)

Figure 6. Field dependence of magnetization in quenched MnPt at 294°K

Figure 7. Hysteresis loop displayed by quenched MnPt at 77°K

reheated to 1150°C and then quenched into ice-brine became 7.7×10^{-2} emu/gm.

The M versus H curve for a thin film of MnPt is shown in Figure 8. The film seemed to be ferromagnetic with a saturation value, $M_s(T)$, of 63.6 emu/gm at 4.2°K. The saturation of the films occurred at 5 KOe. Figure 8 also shows the effect of temperature on the saturation value of the magnetization. $M_s(T)$ was seen to decrease from 63.6 emu/gm at 4.2°K to 51.2 emu/gm at 290°K. By extrapolation the value of saturation magnetization at 0°K, $M_2(0)$ was found to be 63.6 emu/gm.

The effect of temperature on magnetization, $M_{H=200 \text{ Oe}}$, of a thin film of MnPt at a constant small field of 200 Oe is shown in Figure 9. The value of $M_{H=200 \text{ Oe}}$ was 12 emu/gm at 290°K and underwent progressive decrease with rising temperature and eventually vanished at 990°K. Figure 10 shows a comparison of the M versus H curves measured at 294°K before and after the high temperature measurements. The value of the magnetization at a field of 16 KOe was 41 emu/gm and 12 emu/gm for the pre- and post-high temperature measurements, respectively. Hence the magnetization at 16 KOe suffered a reduction of 71 percent as a result of the heat treatment.

The neutron diffraction results for the six quenched specimens are shown in Figures 11-16. In addition to the nuclear reflections that were in accord with x-rays (for $h+k = \text{even number}$), there were separate magnetic reflections

Figure 8. Field dependence of magnetization in MnPt film at various temperatures

Figure 9. Temperature dependence of magnetization in MnPt film at constant field of 200 Oe

Figure 10. Field dependence of magnetization in MnPt film before and after heat treatment

Figure 11. Neutron diffraction pattern of $\text{Mn}_{49.9}\text{Pt}_{50.1}$ quenched into ice-brine from 1150°C

Figure 12. Neutron diffraction pattern of $\text{Mn}_{49.9}\text{Pt}_{50.1}$ quenched into ice-brine from 1050°C

Figure 13. Neutron diffraction pattern of annealed $\text{Mn}_{49.4}\text{Pt}_{50.1}$

Figure 14. Neutron diffraction pattern of $\text{Mn}_{50.9}\text{Pt}_{49.1}$ quenched into ice-brine from 1130°C

Figure 15. Neutron diffraction pattern of annealed $\text{Mn}_{50.9}\text{Pt}_{49.1}$

Figure 16. Neutron diffraction pattern of annealed $\text{Mn}_{50.9}\text{Pt}_{49.1}$

corresponding to $h+k = \text{odd number}$. The ratio of the integrated intensities of the first two magnetic reflections, (100) and (101), was approximately unity in all cases, a significant result which will be discussed later.

The (210) magnetic reflection occurred very close to the (201) nuclear reflection, and in some cases (Figures 11 and 12) it was difficult to separate them. Similar difficulties existed with the (221) nuclear reflection and the (300) magnetic reflection, and also with the (310) nuclear and the (212) and (301) magnetic reflections.

The intensities of the nuclear superlattice reflections were much greater than those of the fundamental reflections because of the differing signs of the nuclear scattering amplitudes of Mn and Pt. This factor made the intensities very sensitive to the composition of the alloy. The intensity of the (200) reflection was unusually high, especially in the pattern for specimen #3 (Figure 13). Results from a separate neutron diffraction experiment on the sample holder revealed that the sample holder had a high scattering at that particular value of the scattering angle. The source of this scattering was traced to an aluminum ring at the base of the vanadium sample holder. The Bragg diffraction angle for the (200) planes of Al is almost coincident with that for MnPt. When the contribution of sample holder was subtracted from the total intensity, the resulting intensity agreed with

the calculated intensity for the (200) reflection of MnPt.

The neutron diffraction results allowed the possible magnetic structures of the alloys to be examined. Also, based on the most likely magnetic structure, the neutron data yield values for the magnetic moments of the constituent atoms in the alloys.

DISCUSSION

X-ray Studies

The x-ray diffraction patterns clearly established that the quenched specimens contained a high degree of long range order. The specimens attained the $L1_0$ superstructure despite being quenched into ice-brine from 1150°C . Barrett and Massalski (1966) have observed that for structures in which a consistent antiferromagnetic arrangement of unpaired spins of d electrons is possible, as in MnPt, the energy associated with antiferromagnetism may be a factor influencing superlattice formation, i.e., preserving the chemical order.

The c/a ratios for the annealed samples are very close to those obtained by Brun et al. (1964) for ordered MnPt (.915). The c/a ratio of the quenched specimens (.9166) did not deviate very much from the value for the annealed specimens. Borelius (1947) has stated that if the structure of a superlattice is tetragonal, the axial ratio can be used as an index of order. The tetragonality of CuAu has been studied in this manner (Roberts, 1954). Therefore, it may be concluded that the degree of long range (S) in the quenched specimens is close to 1. From the neutron diffraction data, the deduced value of S is .86 for specimen #1 and .91 for specimen #4.

Preferred orientation in the specimens prevented a precise determination of the degree of order from the x-ray diffraction data. However, the effect of preferred orientation

on the neutron diffraction intensities is less than its effect on x-ray diffraction intensities. Therefore, information about the degree of long range order was determined from neutron diffraction data.

Some of the thin film specimens appear to have a mixture of amorphous and f.c.c. MnPt. In Figure 4, for example, the broadened peak observed could be an indication that the material is partly amorphous. The sharp peaks of the (111) and (200) indicate that the material is also partly crystalline. The appearance of these two reflections is consistent with the fact that disordered MnPt has an f.c.c. structure. From the x-ray pattern shown in Figure 5, the specimen seems to be completely amorphous. The occurrence of amorphous structure in films whose constituents are metallic and have comparable atomic radii is rare. Lukens (1971) speculated that he might have prepared such films for Ag-Cu and Cu-Mg alloys, but his speculation was not subsequently substantiated. The attempts to duplicate the production of another amorphous MnPt were not successful, however. Despite the failure, it is believed that preparation of amorphous films of MnPt is possible.

Magnetic Behavior

The typical M versus H curve shown in Figure 6 indicates that the quenched specimens are not entirely antiferromagnetic, as is the case of ordered MnPt (Andresen et al., 1965). The

linear relationship observed above 4 KOe may be related to antiferromagnetism, whereas the nonlinear relationship observed below 4 KOe is similar to the low field behavior of ferromagnets. The observed curve could be the result of the existence of ferromagnetic regions in the otherwise antiferromagnetic matrix. Although the resolvable hysteresis loop (Figure 7) obtained from the same specimen provides inadequate evidence, by itself, for the existence of ferromagnetism (Kouvel and Graham, 1959 and Meiklejohn and Bean, 1957), it is consistent with the interpretation that the quenched specimens contained some ferromagnetic regions.

Above 4 KOe, the linearity of the M versus H curve implies that the contribution to the total magnetization, other than that from antiferromagnetism, is constant. If this contribution is due to ferromagnetism, then its constant value would be an indication that saturation has been achieved. With this assumption it is possible to separate the ferromagnetic contribution from the dominant antiferromagnetic contribution.

A computer code was written to perform linear regressions on the M versus H curves in order to separate out the ferromagnetic contribution. It is necessary to determine the saturation field, H_s , which is equivalent to the lowest value of the field where the M versus H curve begins to depart from linearity. In a linear regression analysis, a departure from

linearity can be detected from the root mean square error (RMS error). The RMS error is given by the expression:

$$\text{RMS error} = \left[\sum_{i=0}^N (M_i - M_j)^2 / N \right]^{1/2}$$

where M_i is the magnetization value obtained experimentally at field H_i , M_j is the value of the magnetization at H_i obtained from the straight line fitted to the experimental data, and N is the number of data points. Because of the error and therefore, the uncertainty in the measurement of the experimental value of the magnetization, M_i , the RMS error is expected to be greater than zero. The estimated error in the M_i values is about 0.2×10^{-2} emu/gm. If the RMS error is $> 0.2 \times 10^{-2}$ emu/gm, this is an indication that the deviation of the curve from linearity is due to factors other than the intrinsic error in the value of M_i . A series of linear regressions was performed on the data from 19 KOe to H_s to determine the lowest value of H_s where the RMS error $< 0.2 \times 10^{-2}$ emu/gm. This H_s value was interpreted as the point above which the ferromagnetic contribution was constant and the regions were saturated.

A typical resolution of the total magnetization curve into the antiferromagnetic and ferromagnetic components is shown in Figure 6. The deduced $M_s(T)$ values associated with ferromagnetism are essentially constant in the 4.2-300°K range. A slight consistent decrease was observed over 100°K, however.

Again, this result is consistent with an interpretation of ferromagnetism in the quenched specimens.

The slope of the linear component associated with antiferromagnetism (slope = dM/dH) may be approximated to the field independent mass susceptibility, $\chi_m (= M/H)$, of the specimen. χ_m was found to be essentially constant over the 4.2-300°K range. The slow increase to a broad maximum between 70 and 120°K and the slight monotonic decrease from 120°K to room temperature are not taken as indications of a transition at the Néel temperature. The high value of the susceptibility, 6×10^{-5} for Pauli paramagnetism is theoretically consistent with an antiferromagnetic state having a Néel temperature substantially above room temperature. Calculations made in Appendix B, using the S_{Mn} value from the neutron diffraction study, result in a Néel temperature of about 960°K. The value of T_N for ordered MnPt from Krén et al. (1968) and Andresen et al. (1965) is about 970°K. This would tend to indicate that the antiferromagnetic matrix of the specimens behaves very much like the fully ordered MnPt.

The possibility that the observed phenomenon is the result of mictomagnetism was investigated. One of the criteria for mictomagnetism is that there is a time dependence of the magnetization at constant temperature and constant field. A quenched specimen of Alloy I was investigated for mictomagnetism at a field of 12 KOe. No time dependence of magnetism

was observed at 4.2, 13.9 or 31.9°K.

Another criterion for mictomagnetism is the thermomagnetic history effect. The theory (Beck, 1972) suggests that magnetization at low temperatures and constant field would be much higher for a specimen cooled in the applied field than for the same specimen cooled in zero field. No such effect was observed for the MnPt specimens. There was no significant difference in the magnetization values for the specimens that were given the two types of treatment.

A third criterion for mictomagnetism is the displaced hysteresis loop effect. As can be seen in Figure 7, the observed hysteresis loop is not displaced. A companion mictomagnetic criterion is the remanence effect. For a zero-field cooled mictomagnet the isothermal magnetization vs. field behavior at low temperatures is linear and reversible with no history effect. However, for a field cooled specimen, a large remanence would be observed. This remanence would increase with the magnitude of the cooling field. No such remanence effect was observed for the powder specimens of MnPt. Therefore, it is concluded that the composite phenomenon observed is not the result of mictomagnetism.

On the other hand, there is evidence for a mixed ferromagnetic-antiferromagnetic state. However, the symmetry of the hysteresis loop (Figure 7) would rule out the existence of exchange anisotropy of the type found by Meiklejohn and Bean

(1956,1957) in intimate mixtures of antiferromagnetic CoO and ferromagnetic Co. The mixed ferromagnetic-antiferromagnetic state is thought to be the presence of small ferromagnetic regions in an antiferromagnetic matrix. Such a system would produce a symmetrical hysteresis loop. Moreover, the ferromagnetism observed in the thin films of MnPt is in accord with such an interpretation because the larger magnetization value obtained in the films could be the result of a greater number of ferromagnetic regions.

The $M_s(0)$ for the films is 63.6 emu/gm and assuming that only Mn atoms carry the moment, the atomic moment of Mn in the films is about $(3.0 \pm .3)\mu_B$. This value is much lower than the deduced values $(4.1 \pm .2)\mu_B$ in the present study and $4.3\mu_B$ by Krén et al., (1968) for Mn in MnPt. However, Auwarter and Kussmann (1950) reported that ferromagnetism occurs only in the 18-32 at.% Mn range in the Mn-Pt system. Pickart and Nathans (1963) also reported that the atomic moment of Mn in MnPt_3 is $3.6\mu_B$. It is possible that the films are not 100% ferromagnetic since it is impossible to obtain 100% of the regions with 18-32 at.% Mn for the obvious reason that the initial composition of the alloy was close to 50 at.% Mn. The slight dependence of M on the field at high fields (Figures 8 and 10) could be an indication of a mixture of ferromagnetic regions and antiferromagnetic regions. This type of high-field dependence of the magnetization (non-zero slope) in

the sputtered films has also been observed in Fe-Al alloys by other researchers. Wakiyama (1972) and Chang et al. (1964) have discussed this phenomenon in terms of a localized electron model, which assumes the existence of small antiferromagnetic regions in a long-range ferromagnetic structure. This model could be applied to the thin films of MnPt which display predominantly ferromagnetic behavior.

The occurrence of ferromagnetism in the thin films of MnPt is not entirely surprising because the sputtered films are highly compositionally inhomogeneous, thus producing a mixture of Mn- and Pt-rich regions. In this connection we recall that ordered MnPt_3 has been shown to be ferromagnetic (Pickart and Nathans, 1962). Also, there is the possibility of small crystalline regions dispersed in the amorphous film on a fine spatial scale. In either case, the ferromagnetic effects observed in the powder specimens should be enhanced in the films.

The observed low coercive force, H_c , and the low remanence, M_r , are likely due to the almost amorphous nature of the films, rather than to the intrinsic properties of MnPt. Pan and Turnbull (1974) have stated that an outstanding characteristic of amorphous ferromagnets is the absence of macroscopic magnetocrystalline anisotropy which would result in high permeabilities and low coercivity.

The ratio of M_r/M_s as an indication of the degree of

amorphousness of the film was not investigated. Egami, Flanders and Graham (1975) have stated that this ratio should be unity for an ideal amorphous ferromagnet. However, Schneider et al. (1976) found that this ratio is critically dependent on the strain induced in sputtering, and that the ratio can be used as a measure of the anisotropy constant K_u . Therefore, according to the latter authors, the ratio would not furnish reliable information about the structure of the film.

Magnetic Structure

The neutron diffraction patterns of quenched and ordered specimens of MnPt at room temperature consisted of reflections which can be indexed on the basis of a C-centered Bravais cell of the CuAu I structure. The reflections can be separated into two groups. Those reflections with $h+k = \text{even number}$ can be interpreted as nuclear, with good agreement between observed and calculated intensities (Tables 3,4). The other reflections with $h+k = \text{odd number}$ are interpreted as magnetic and in support of this, the structure factors used in obtaining the deduced values of μ_{Mn} (Table 5) indicated a dependence with scattering angle as expected for magnetic reflections (Kasper and Kouvel, 1959).

In this type of CuAuI structure, the separation of nuclear and magnetic reflections suggests an antiparallelism of moments for atoms related by C-centering, i.e. atomic moments

Table 3. Comparison of the calculated and the observed nuclear structure factors for Alloy I

(hkl)	F_{calc}^2	F_{obs}^2	
		Specimen #1	Specimen #3
(001)	6.69 $\pm$.03	6.71 $\pm$.10	6.77 $\pm$.15
(110)	6.55 $\pm$.03	6.54 $\pm$.10	6.47 $\pm$.15
(111)	1.12 $\pm$.01	1.12 $\pm$.05	1.12 $\pm$.05
(200)	1.10 $\pm$.01	---	1.16 $\pm$.05
(201)	6.19 $\pm$.03	6.63 $\pm$.20	---
(112)	6.06 $\pm$.02	6.09 $\pm$.10	---
(202)	1.03 $\pm$.01	.88 $\pm$.05	---

Table 4. Comparison of the calculated and observed nuclear structure factors for Alloy II

(hkl)	F_{calc}^2	F_{obs}^2	
		Specimen #4	Specimen #6
(001)	6.58 $\pm$.03	7.09 $\pm$.51	6.59 $\pm$.20
(110)	6.44 $\pm$.03	5.93 $\pm$.43	6.45 $\pm$.20
(111)	1.01 $\pm$.01	1.01 $\pm$.05	1.01 $\pm$.05
(002)	.98 $\pm$.01	.94 $\pm$.07	.98 $\pm$.05
(201)	6.09 $\pm$.03	6.13 $\pm$.44	6.23 $\pm$.20
(112)	5.96 $\pm$.02	6.24 $\pm$.45	7.23 $\pm$.30
(220)	.94 $\pm$.01	.93 $\pm$.07	1.15 $\pm$.05
(202)	.93 $\pm$.01	.75 $\pm$.05	.95 $\pm$.04

Table 5. Atomic moment in units of Bohr magneton for Mn using experimental form factors and theoretical form factors

Type of form factor used	Specimen #			
	1	3	4	6
f_{exp}^a	$3.8 \pm .2$	$4.1 \pm .2$	$3.9 \pm .2$	$4.0 \pm .2$
f_{calc}^b	$3.7 \pm .2$	$3.9 \pm .2$	$3.8 \pm .2$	$3.9 \pm .2$

^aForm factors are from the work of Corliss et al. (1956).

^bForm factors are those calculated from Hartree-Fock wave equations by Freeman and Watson (1961).

in the (001) planes are antiparallel to their nearest neighbors in the same plane (Kasper and Kouvel, 1959).

Three possible antiferromagnetic structures are shown in Figure 17. For the sake of clarity the models are drawn for the fully ordered equiatomic alloy. The effect of disorder caused by quenching will be considered later and in Appendix A.

Model A represents an antiferromagnetic structure with the moments confined to Mn atoms aligned in the [001] direction. The atomic moments in the (001) planes are antiparallel to their nearest neighbors in the same plane. The magnetic structure has tetragonal symmetry. A variation of this model would be one with moments on the Pt atoms, but the symmetry would be reduced to that of orthorhombic symmetry unless the Pt moments are also aligned in the [001] direction.

Figure 17. Models showing the possible magnetic structure of MnPt

Model B also represents an antiparallel arrangement of the Mn moments, but the moments are aligned normal to the [001] direction and the magnetic symmetry is therefore orthorhombic. The Mn moments are assumed to be in the $\pm$ [100] direction, but neutron diffraction patterns of polycrystalline MnPt would be the same for this antiparallel arrangement regardless of the direction of the moment within the (001) plane. As it is shown in Appendix A, the magnetic intensity of an (hkl) reflection depends on the average of the magnetic interaction vector which in turn depends only on the angle ψ_c between the [001] direction and the direction of the moment. For moments aligned within the (001) planes, ψ_c would be 90° regardless of the direction of the moments within those planes, $\pm$ [010], $\pm$ [110], etc.

Model C is similar to model B except that the Pt atoms are assumed to carry an induced moment, possibly by spin polarization. The spin arrangement shown for the Pt atoms is only one of several possibilities consistent with the observed intensities.

Model A was rejected for all six specimens on the basis of the observed integrated intensities for the (100) and (101) reflections. Applying the expression for the average of the magnetic interaction vector for tetragonal symmetry developed by Shirane (1959), the $\langle q_{hkl}^2 \rangle$ values for the (100) and (101) reflections from polycrystalline specimens are 1.00 and 0.46

respectively (Appendix A). Using values of .125 and .185 for $(\sin\theta)/\lambda$, .82 and .66 for the magnetic form factors of Mn and the 1.00 and 0.46 for the $\langle q_{hkl}^2 \rangle$ values ($\psi_c = 0$) for the (100) and (101) reflections respectively in the expression for the integrated intensity ($I = k j \langle q_{hkl}^2 \rangle F_{\text{magn}}^2 / \sin\theta \sin 2\theta$, see Appendix A), the ratio of the integrated intensities of (100) and (101) magnetic reflections should be 4. The ratio of the observed reflections is close to unity for all six specimens. Moreover, for the annealed specimen, #6, this interpretation is contradictory to that of Andresen et al. (1965) and Krén et al. (1968), who concluded that model A would be the magnetic structure for an ordered Mn-Pt alloy with a Mn concentration in the range of 50-55 at.%. However, they found that Model B would be the magnetic structure for ordered $\text{Mn}_{45}\text{Pt}_{55}$. They concluded that whenever some Pt atoms reside on the Mn sublattice, the Mn spins would be within the (001) planes and normal to the [001] direction, as in model B. It is possible that because of the thermal history of specimen #6 (the specimen was first quenched and then annealed), there is still substitution with Pt on the Mn sublattice, a condition which could result in spins being normal to the [001] direction, as is the case for $\text{Mn}_{45}\text{Pt}_{55}$ (Andresen et al., 1965).

For models B and C the $\langle q_{hkl}^2 \rangle$ values for the same reflections are 0.50 and 0.77, respectively, resulting in an integrated intensity ratio of about 1. Therefore, these two

models can possibly be used to interpret the observed reflections of all six powder specimens.

The observed intensities were compared to the calculated intensities for models B and C. The calculated intensity for an hkl reflection is given by the formula $I = KjF^2/\sin\theta\sin2\theta$, where K is the normalizing factor, j is the multiplicity factor, F^2 is the structure factor and $\sin\theta\sin2\theta$ is the angular correction factor. All these parameters are fully defined in Appendix A.

Included in the structure factor is the Debye-Waller temperature correction factor, e^{-w_n} , for Mn and Pt. This factor was calculated using room temperature values of the Debye temperature. θ_D is 461°K for Mn and 229°K for Pt (Gschneidner, 1964). These values result in $w_{Mn} = .25(\sin\theta/\lambda)^2$ and $w_{Pt} = .27(\sin\theta/\lambda)^2$.

When calculating the intensities for models B and C, attention must be paid to the degree of long range order. In the fully ordered system, the Mn sublattice is considered to be the (000) and (1/2 1/2 0), and the Pt atoms occupy the (1/2 0 1/2) and (0 1/2 1/2) position. Even in the equiatomic alloy that has been annealed below the transition temperature extensively, there is the possibility of some atomic disorder because the ordering process is uncomplete. Brun et al. (1964) have observed such atomic disorder in some annealed samples. In the quenched specimens partial disorder certainly

prevails. Therefore, the deduced value of the fraction of A atoms on α sites γ_A^α (calculated from the large order parameter, S), was used in each case to calculate the magnetic moments.

When Pt is considered to have a moment (model C) an antiferromagnetic arrangement of the Pt spins in nearest neighbors is assumed because of the Pt-Pt atom separation. For models B and C there would be difficulty in detecting from the neutron diffraction patterns a ferromagnetic arrangement of the Pt moments on the Pt sublattice. The contributions from the Pt moments to the intensities of the $h+k = \text{odd}$ number reflections would be zero, and their contributions to the intensities of the $h+k = \text{even}$ number would be very small. These magnetic contributions would be masked by the nuclear contribution since the scattering experiments are not sensitive enough to detect the magnetic contributions in the observed intensities of different reflections.

The nuclear scattering amplitudes ($b_{\text{Mn}} = -.39 \times 10^{-12}$ cm and $b_{\text{Pt}} = .95 \times 10^{-12}$ cm) were obtained from data compiled by Bacon (1972). In calculating the magnetic scattering amplitude (p) the expression of Halpern and Johnson (1939) for an ion where the magnetic moment is determined solely by its total spin quantum number, i.e., for a quenched orbital moment, is used. It is also permissible to use S instead of $\sqrt{S(S+1)}$ because of the rigid alignment of the magnetic spins in the

antiferromagnetic substance. The magnetic form factors deduced for Mn^{++} from the work of Corliss et al. (1956) were used. These values were compared favorably with the form factors from the work of Jacobson et al. (1973).

The use of the magnetic form factors of Mn^{++} for Mn in MnPt is justified when the form factors for different ionic states of the iron group of transition metals are compared (Bacon, 1975). There is little variation among the experimental values for these states. Moreover, in the case of Mn, Shull and Wollan (1956) made a comparison of the experimental values of the different states and the calculated value for Mn^{++} using the method of Pauling and Sherman (1932), and very little deviation was observed, especially at low values of $(\sin\theta)/\lambda$.

A separate calculation was made using the magnetic form factors of Mn computed from nonrelativistic Hartree-Fock wave functions by Freeman and Watson (1961). Freeman and Weiss (1959) have previously shown that form factors computed by the same method can be used to determine from neutron diffraction data the symmetry of the outer electron distribution in magnetic materials.

For Pt the magnetic form factors used are from the work of Menzinger and Paoletti (1966) on CoPt_3 . These values can be used for Pt in MnPt since the values compared very well with the form factors for Pt computed by Cromer and Waber (1964).

Comparisons of the observed and calculated nuclear structure factors are given in Tables 3 and 4. In Table 3, the results are for a quenched and an annealed specimen of alloy I, respectively. The results for a quenched and an annealed specimen of alloy II (Mn-rich) are shown in Table 4. The very good agreement especially at the low scattering angles, indicates that the structure shown in models B and C are consistent with the experimental results.

Table 5 shows the deduced values of the atomic moment of Mn calculated by using the experimental form factors of Mn^{++} and also by using the theoretical values of the form factors of Mn. Pt is assumed to have no moment in each case.

The deduced values of the atomic moment calculated from the experimental form factors of Mn^{++} are consistently greater than those obtained using the calculated values of the form factors. This is because the f_{calc} values are greater than the f_{exp} values. Although the difference between the two sets of values is negligibly small for $(\sin\theta)/\lambda < .30$, significant discrepancies arise for $(\sin\theta)/\lambda > .30$. For instance, at $(\sin\theta)/\lambda = .31$, $f_{\text{exp}} = .34$ and $f_{\text{calc}} = .40$. Such a difference would cause a 15 percent difference in the deduced value of the atomic moment. Because it is difficult to ascertain which set of f values are appropriate and also because the accuracy of the magnetic intensities decrease for $(\sin\theta)/\lambda > .30$,

the deduced values of the atomic moment reported in Table 5 are from reflections for $(\sin\theta)/\lambda < .30$.

By assuming complete magnetic and atomic ordering and using the $\text{Mn}^{++} f_{\text{exp}}$ values, Krén et al. (1968) arrived at a value of $(4.3 \pm .2) \mu_B$ per Mn atom in the ordered MnPt. The average moment deduced from data for specimens #3 and #6 is $(4.1 \pm .2) \mu_B$, which compares very well with their value. The slightly lower value of μ_{Mn} obtained here may be due to the difference in the nuclear scattering amplitude of Mn used. The nuclear scattering amplitude affects the deduced value of the magnetic moment because it is involved in the evaluation of the normalizing factor K in the expression for the integrated intensity. Krén et al. used $b_{\text{Mn}} = -.36 \times 10^{-12}$ cm. Subsequent refinements in the method of determining nuclear scattering amplitudes have established $b_{\text{Mn}} = -.39 \times 10^{-12}$ cm (Bacon, 1975). Such a change in b_{Mn} will depress the deduced value of μ_{Mn} .

The question of whether Pt carries a moment also cannot be resolved from the present neutron diffraction studies. Because the small contribution of a Pt moment would enter the intensity expression as a square and because the magnetic form factors of Pt fall off about three times as fast as those of Mn (Menzinger and Paoletti, 1966), it is difficult to determine the moment of the Pt atoms with any certainty. The degree of the uncertainty in the μ_{Mn} values could be as large

as the Pt moment. However, it may be stated that the maximum value of the atomic moment allowed on Pt in MnPt is $0.2 \mu_B$.

Andresen et al. (1965) have observed weak ferromagnetism in powder samples of ordered MnPt at low temperatures. Using a concept of Moriya (1964), they have attributed this phenomenon to a slight canting of the antiferromagnetically aligned spins resulting in a net moment. Krén et al. (1968) have discounted this interpretation and stated that the ferromagnetism was probably due to $\text{Mn}_2\text{Pt}_2\text{O}$. Chen and Buttry (1975) also observed ferromagnetism, but only in the quenched samples of MnPt, a result which is consistent with the present study. They attributed this ferromagnetism to a nonuniform distribution of the constituent atoms, an explanation which is also consistent with the model described here. Moreover, the likelihood of the thin films having inhomogeneous regions and the ferromagnetism observed in them seem to further support this interpretation.

CONCLUSION

While the fully ordered phase of MnPt is typically antiferromagnetic, the quenched specimens of MnPt show evidence for the existence of small ferromagnetic regions. These ferromagnetic regions are attributed to a nonuniform distribution of the constituent atoms. The regions are assumed to have a composition of 18-32 at.% Mn, a range within which Mn-Pt is known to be ferromagnetic.

The magnetic unit cell for the annealed MnPt specimens coincides with the unit cell of the $L1_0$ structure. The Mn atoms occupy alternate (001) planes and the Pt atoms occupy the remaining lattice sites. The spins on the Mn atoms are aligned antiparallel to their nearest neighbors in the (001) planes and are normal to the [001] direction. The atomic moment of the Mn is $(4.1 \pm .2) \mu_B$.

The quenched specimens of MnPt have a similar $L1_0$ structure with a c/a ratio of 0.917, as compared with $c/a = 0.918$ for the annealed and thus more pronouncedly ordered MnPt. The Mn atoms occupy alternate (001) planes, but there is some interlayer mixing because of quenching. The Mn spins are also aligned normal to the [001] direction. The atomic moment of Mn in the quenched specimens is $(3.9 \pm .2) \mu_B$.

The question of whether Pt carries a moment in the annealed or quenched specimens could not be resolved. If Pt does carry a moment, its maximum value would be $0.2 \mu_B$ per

atom.

Amorphous and highly disordered films of MnPt can be prepared by rf sputtering. In the sputtered films of MnPt, the ferromagnetic regions seem to be more extensive than those observed in the quenched specimens. The deduced Mn moment for the sputtered film is $(3.0 \pm .3) \mu_B$ per atom, which may not represent the true moment of Mn because the films were not entirely ferromagnetic.

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APPENDIX A. CALCULATION OF INTEGRATED INTENSITY

The integrated intensity for a polycrystalline specimen in a cylindrical configuration is given by the formula (Bacon, 1975):

$$I = K_j F_{hkl}^2 (\sin\theta \sin 2\theta)^{-1} A_{hkl}, \quad (1)$$

where K = scaling factor,

j = multiplicity (for Model B and C, the tetragonal values can be used for the nuclear reflections, but the orthorhombic values must be used for the magnetic reflections, since, for example, the (100) reflection is not equivalent to the (010) reflection),

F_{hkl}^2 = structure factor = $F_{nuc1_{hkl}}^2 + \sin^2 \alpha F_{magn_{hkl}}^2$ for coherent scattering.

$(\sin\theta \sin 2\theta)^{-1}$ = angular correction factor for the cylindrical configuration of the sample,

and

A_{hkl} = the absorption factor.

The absorption factor depends on μR_s and the scattering angle θ . R_s is the radius of the cylindrical sample (0.5cm) and μ is the absorption coefficient of the alloy (0.5 cm^{-1}). Because $R_s < 0.3$, A_{hkl} is essentially constant for all reflections for θ values up to 45° , and it can therefore be included in the scaling factor.

The nuclear component of the structure factor is given by

$$F_{\text{nuc1}} = \sum_n b_n e^{-w_n} e^{\pi i (hx_n + ky_n + \ell z_n)}, \quad (2)$$

and the magnetic component is given by

$$\sin \alpha F_{\text{magn}} = \sin \alpha \sum_n p_n e^{-w_n} e^{2\pi i (hx_n + ky_n + \ell z_n)}, \quad (3)$$

where the summation is made over the constituent atoms of the alloy. In the above expressions, b_n and p_n are the nuclear and magnetic scattering amplitudes, respectively, of the n th atom. The b_n values can be obtained from tables (Bacon, 1972). The p_n values for quenched orbital moments can be evaluated from the expression (Halpern and Johnson, 1939):

$$p = \left(\frac{e^2 \gamma}{mc^2} \right) S f, \quad (4)$$

where m = mass of the electron

e = charge of the electron

γ = magnetic moment of the neutron

S = total spin quantum number

f = magnetic form factor.

Therefore,

$$p = 0.539 \times 10^{-12} \text{ Sf cm.} \quad (5)$$

In the expression for the structure factor, $\sin^2 \alpha = \langle q_{hkl}^2 \rangle$, the average value of the magnetic interaction vector, which, for tetragonal symmetry, is given by the expression (Shirane, 1959):

$$\langle q_{hkl}^2 \rangle = 1 - \frac{\ell^2 + \left[\frac{1}{2} (c/a)^2 (h^2 + k^2) - \ell^2 \right] \sin^2 \psi_c}{(c/a)^2 (h^2 + k^2) + \ell^2} \quad (6)$$

where ψ_c = angle between the [001] and the direction of the magnetic moment. For model A, $\psi_c = 0^\circ$ and for models B and C, $\psi_c = 90^\circ$.

The factor e^{-W_n} is the Debye-Waller temperature correction factor to the structure factor of the n th atom. In the Debye approximation (Weinstock, 1944),

$$W = \frac{6h^2}{m_A k \theta_D} \left[\frac{\phi(x)}{x} + \frac{1}{4} \right] \frac{\sin^2 \theta}{\lambda^2}, \quad (7)$$

where h = Planck's constant

m_A = nuclear mass

k = Boltzmann's constant

θ_D = Debye temperature of the alloy

θ = scattering angle

λ = wavelength of the incident neutrons

$x = \theta_D/T$, T being the absolute temperature of the measurement.

The function $\phi(x) = 1/x \int_0^x (\xi d\xi)/(e^\xi - 1)$ can be evaluated from tables once the value of the Debye temperature is known.

For the ordered structure of Model C, the structure factor for an hkl reflection is:

$$\begin{aligned} F_{hkl} = & b_{Mn} e^{-W_{Mn}} e^{2\pi i(h \cdot 0 + k \cdot 0 + l \cdot 0)} \\ & + b_{Mn} e^{-W_{Mn}} e^{2\pi i(h/2 + k/2 + l \cdot 0)} \\ & + b_{Pt} e^{-W_{Pt}} e^{2\pi i(h/2 + k \cdot 0 + l/2)} \\ & + b_{Mn} e^{-W_{Pt}} e^{2\pi i(h \cdot 0 + k/2 + l/2)} \end{aligned}$$

$$\begin{aligned}
& + \sqrt{\langle q_{hk} \rangle^2} [p_{Mn} e^{-w_{Mn}} e^{2\pi i(h \cdot 0 + k \cdot 0 + l \cdot 0)} \\
& \quad - p_{Mn} e^{-w_{Mn}} e^{2\pi i(h/2 + k/2 + l \cdot 0)} \\
& \quad + p_{Pt} e^{-w_{Pt}} e^{2\pi i(h/2 + k \cdot 0 + l/2)} \\
& \quad - p_{Pt} e^{-w_{Pt}} e^{2\pi i(h \cdot 0 + k/2 + l/2)}]. \quad (8)
\end{aligned}$$

For $h+k = \text{even number}$

$$F_{hkl}^2 = 4 [b_{Mn} e^{-w_{Mn}} + b_{Pt} e^{-w_{Pt}} e^{\pi i(h+l)}]^2, \quad (9)$$

and for $h+k = \text{odd number}$

$$F_{hkl}^2 = \langle q_{hkl} \rangle^2 > 4 [p_{Mn} e^{-w_{Mn}} + p_{Pt} e^{-w_{Pt}} e^{(h+l)}]^2. \quad (10)$$

Therefore the nuclear and magnetic reflections are separable. Fundamental nuclear reflections occur for hkl unmixed, and superlattice nuclear reflections occur for hkl mixed with $h+k = \text{even number}$. Nuclear reflections are forbidden for $h+k = \text{odd number}$. Magnetic reflections are only allowed for $h+k = \text{odd number}$.

The long range order parameter S is obtained from:

$$S^2 = I_{\text{obs}} / I_{\text{calc}}(\text{superlattice}) \cdot I_{\text{calc}} / I_{\text{obs}}(\text{fundamental}) \quad (11)$$

where the intensities are all for the nuclear reflections. An order parameter γ_A is now defined as the fraction of α sites occupied by A atoms. From the long range order parameter, and from F_A , the fraction of A atoms in the binary alloy,

$$\gamma_A = S(1-F_A) + F_A. \quad (12)$$

Therefore, in a partially disordered specimen, the structure factors for model C are, for the nuclear reflections,

$$F_{\text{nuc1}} = 2(b_{\text{Mn}}e^{-w_{\text{Mn}}} + b_{\text{Pt}}e^{-w_{\text{Pt}}}) \quad (13)$$

for hkl unmixed, and

$$F_{\text{nuc1}} = 2S(b_{\text{Mn}}e^{-w_{\text{Mn}}} - b_{\text{Pt}}e^{-w_{\text{Pt}}}) \quad (14)$$

for hkl mixed with $h+k = \text{even number}$. For the magnetic reflections with anti-parallel magnetic ordering of the Mn moment on the Pt sublattice:

$$\begin{aligned} F_{\text{magn}} = & 2\gamma[p_{\text{Mn}}e^{-w_{\text{Mn}}} + p_{\text{Pt}}e^{-w_{\text{Pt}}}e^{\pi i(h+l)}] \\ & + (1-\gamma)(p_{\text{Mn}}e^{-w_{\text{Mn}}} + p_{\text{Pt}}e^{-w_{\text{Pt}}})[1 + e^{\pi i(h+l)}], \end{aligned} \quad (15)$$

and therefore,

$$F_{\text{magn}}^2 = 4[(p_{\text{Mn}}e^{-w_{\text{Mn}}} + p_{\text{Pt}}e^{-w_{\text{Pt}}})^2 + \gamma^2(p_{\text{Mn}}e^{-w_{\text{Mn}}} - p_{\text{Pt}}e^{-w_{\text{Pt}}})^2]; \quad (16)$$

if Pt carries no moment, as in model A and B,

$$F_{\text{magn}}^2 = 4(1+\gamma^2)p_{\text{Mn}}^2 e^{-2w_{\text{Mn}}}. \quad (17)$$

The calculated nuclear and magnetic structure factors obtained from the above formulations are compared to the observed structure factors to determine which of the models A, B or C, can correctly be used to interpret the neutron diffraction data.

APPENDIX B. NÉEL TEMPERATURE

The Néel temperature is defined as:

$$T_N = 2(z_O - z_S)JS(S+1)/3k, \quad (18)$$

and the volume susceptibility is defined as

$$\chi_V = Ng^2 \mu_B^2 / 6z_O J \quad (19)$$

$$T_N = \frac{Ng^2 \mu_B^2 S(S+1)}{9k\chi_V} \frac{z_O - z_S}{z_O}, \quad (20)$$

where N = number of magnetic atoms per unit volume,

g = Landé splitting factor (=2 for quenched orbital moments),

μ_B = Bohr magneton,

k = Boltzmann's constant,

J = exchange interaction parameter,

S = magnetic spin value for Mn,

z_O = number of nearest neighbors of the opposite sublattice, and

z_S = number of nearest neighbors of the same sublattice.

Assuming that only nearest neighbor interactions are significant, i.e., the magnetic state is governed primarily by a strong antiferromagnetic exchange coupling between the moments of nearest neighbor Mn atoms, then

$$T_N = \frac{Ng^2 \mu_B^2 S(S+1)}{9k\chi_V}. \quad (21)$$

From the experimental magnetic work on $\text{Mn}_{49.1}\text{Pt}_{50.9}$,

$$a = 4.013 \text{ \AA}$$

$$c = 3.678 \text{ \AA}$$

$$\chi_m = 4.25 \times 10^{-6} \text{ emu/gm/Oe}$$

$$T_N = 147 \text{ S(S+1)^\circ K.}$$

(22)

From the neutron diffraction studies, $S_{\text{Mn}} = 2.1$

$$T_N = 957^\circ \text{K.}$$