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MAGNETIC STRUCTURE STUDIES OF COPPER-MANGANESE ALLOYS
BY NEUTRON DIFFRACTION

by

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MAGNETIC STRUCTURE STUDIES OF COPPER-MANGANESE ALLOYS BY NEUTRON DIFFRACTION

ABSTRACT

A series of continuous substitutional solid solutions of manganese in copper up to 85 atomic per cent manganese were studied by neutron diffraction. At compositions greater than 13 atomic per cent manganese a broad line appears in the region of a (100) reflection of the face-centered cubic lattice of copper. A correlation of this line with the magnetic attraction of the alloys indicates that it is at least in part due to short range magnetic order. The regions of ordering have dimensions of about 10 Angstroms, as determined from the width of the line. Its intensity decreases at compositions greater than about 50 atomic per cent. This broad neutron diffraction line may be caused by short range ferro-type coupling between next nearest paramagnetic manganese atoms with copper atoms as nearest neighbors to a given manganese atom, or by short range ferri-type coupling between manganese and nearest neighboring copper atoms. The latter arrangement assumes that copper becomes paramagnetic in these alloys. At compositions greater than about 69 atomic per cent manganese a neutron diffraction line appears at the position of a (110) reflection of the face-centered cubic unit cell. The intensity of this line increases with addition of manganese. The line is temperature dependent and vanishes at 380°K. It is not observed in the X-ray diffraction pattern. It is proposed that this reflection arises from a long range antiferromagnetic ordering between manganese atoms as the manganese concentration becomes predominant. A possible structure is presented. No long range crystal ordering is observed in these samples, although superlattice lines arising from such ordering should be relatively strong and readily detectable, since copper and manganese nuclei scatter neutrons with opposite phases. The incoherent diffuse scattering in the neutron patterns was analyzed at small angles to obtain the contribution of paramagnetic scattering to the diffuse background. The paramagnetic scattering is maximum at 20 atomic per cent manganese. The paramagnetic scattering in the region of 20 atomic per cent manganese is greater than the known paramagnetic scattering of the alpha phase of manganese. The neutron diffraction patterns of the furnace cooled samples did not change by heat treatment of the alloys for a period of 3 days at 750°C and followed by quenching in water.

I. INTRODUCTION

Neutron diffraction techniques should lend themselves advantageously to a study of the copper-manganese alloy system. First, the fact that the sign of the coherent neutron amplitude of manganese is opposite to that of copper would allow superlattice lines due to atomic ordering in the crystal lattice to be easily observable; whereas, with X-rays the closeness of the atomic numbers of these elements would result in relatively faint superlattice lines upon ordering. Second, copper being diamagnetic and manganese being paramagnetic, it is of interest to study by neutron diffraction any magnetic structures which might arise, and the variation of paramagnetic scattering with composition. X-ray and metallographic studies of the system have been reported by several investigators.¹⁻⁵ Magnetic susceptibility and electrical conductivity properties of the system have been studied by Valentin and Becker.⁶

II. ASPECTS OF NEUTRON DIFFRACTION BY CRYSTALS

The de Broglie wavelengths of thermal neutrons are of the order of magnitude of the atomic lattice spacings of crystals. The scattering of thermal neutrons by an individual nucleus bound in such a lattice is isotropic. The nucleus being small relative to the neutron wavelength causes the s-wave scattering. The wavelets scattered from an orderly array of nuclei, as in the crystal lattice, can interfere with each other to produce diffraction maxima in the observed scattering pattern. This phenomenon allows crystal structures to be studied in a manner analogous to the usual X-ray methods.^{7,8} The positions of neutron diffraction lines are, as with X-rays, given by the Bragg condition $n\lambda = 2d \sin \theta$, where n is a positive integer denoting the order of the reflection. The condition states that a neutron of wavelength λ , incident on lattice planes of spacing d , at a glancing angle θ , may give rise to a diffracted beam at a scattering angle of 2θ .

Although the diffraction of neutrons and of X-rays are similar, the differences in the fundamental scattering processes have enabled neutron diffraction to be a powerful supplement to X-ray methods.

The intensity of an X-ray powder diffraction line from planes having Miller indices (hkl) is given by⁹

$$P_x(hkl) \sim j_{hkl} \left| F_{hkl} \right|^2 \frac{(1 + \cos^2 2\theta)}{2 \sin^2 2\theta}, \quad (1)$$

with

$$F_{hkl} = \sum_z f_z \exp 2\pi i (hu_z + kv_z + lw_z) \quad (2)$$

¹For all numbered references, see Bibliography.

where j_{hkl} is the multiplicity factor, $1/\sin^2 2\theta$ the Lorentz factor for flat power diffraction samples in the transmission orientation, $1/2(1 + \cos^2 2\theta)$ the polarization factor for X-rays, F_{hkl} the structure factor of the crystal unit cell, and f_z the atomic scattering factor of the z 'th atom having cell coordinates u_z, v_z, w_z in the unit cell. The summation is over all atoms in the unit cell.

Correspondingly, with thermal neutrons the intensity of a diffraction line in a powder pattern is given by⁷

$$P_n(hkl) \sim j_{hkl} |F_{hkl}|^2 / \sin^2 2\theta, \quad (3)$$

with

$$F_{hkl} = \sum_z b_z \exp 2\pi i (hu_z + kv_z + lw_z) \quad (4)$$

where b_z is the coherent nuclear amplitude of the z 'th nucleus.

As the electrons are responsible for the scattering of X-rays, the scattering factors increase regularly with the atomic number of the scattering atom. The X-ray wave being scattered by the orbital electrons is always 180° out of phase with the incident wave. The space distribution of the charge about the atom is comparable in size to the wavelengths of X-ray radiation used. This produces interference effects between wavelets scattered from various parts of a given atom. An angular dependence of scattering primarily toward the forward direction results so that f_z is dependent upon scattering angle.

In contrast the scattering of neutrons by an individual nucleus bound in a lattice is isotropic. This is a result of the small nuclear diameter in comparison with the thermal neutron wavelengths used (of the order of 10^{-8} cm). The coherent nuclear scattering amplitude b_z is thus not dependent upon scattering angle. The nuclear amplitudes also do not vary in a regular manner from element to element as do the corresponding X-ray scattering factors. Although most nuclei scatter thermal neutrons with a positive phase (180° phase change), a few nuclei scatter neutrons with opposite phase (zero degree phase change).^{10,11} The result is a negative nuclear amplitude factor b_z for the latter nuclei. In addition, the various isotopes of a given element may have very different neutron scattering amplitudes.

It is these properties which make neutron diffraction applicable to such problems as the detection of the positions of hydrogen atoms in hydrogen containing substances¹² and the detection of the lattice positions of atoms of closely similar atomic numbers in alloys.¹³

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The bound coherent scattering amplitudes for neutrons of an element having only one isotope and no nuclear spin, is related to the bound scattering cross section by

$$\sigma_{\text{coh}} = 4\pi b^2 \quad (5)$$

where σ_{coh} is the total bound scattering cross section per nucleus and b is the bound nuclear scattering amplitude.

For an element containing more than one isotope, the total bound scattering cross section is

$$\sigma_s = 4\pi (p_1 b_1^2 + p_2 b_2^2 + \dots) \quad (6)$$

where the p 's are the isotopic abundances. The bound coherent scattering amplitude, which is effective in Bragg scattering by crystals, is in this case related to the bound coherent cross section

$$\sigma_{\text{coh}} = 4\pi (p_1 b_1 + p_2 b_2 + \dots)^2 \quad (7)$$

where the effective coherent amplitude is

$$b = p_1 b_1 + p_2 b_2 + \dots, \quad (8)$$

and not to the total bound cross section given by Equation 6.

In case of neutron scattering by an isotope having a nuclear spin, two scattering amplitudes exist: one for parallel and one for antiparallel orientations of the nuclear spin direction relative to the direction of the neutron spin. The total bound scattering cross section is then given by

$$\sigma_s = 4\pi \left(\frac{i+1}{2i+1} b_{i+1/2}^2 + \frac{i}{2i+1} b_{i-1/2}^2 \right) \quad (9)$$

where i is the spin of the scattering isotope, and the respective b 's are weighted by the probability of the two spin states. The coherent scattering cross section per isotope is in this case

$$\sigma_{\text{coh}} = 4\pi \left(\frac{i+1}{2i+1} b_{i+1/2} + \frac{i}{2i+1} b_{i-1/2} \right)^2, \quad (10)$$

where the coherent amplitude effective in Bragg scattering is

$$b = \frac{i+1}{2i+1} b_{i+1/2} + \frac{i}{2i+1} b_{i-1/2} \quad (11)$$

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For the case that the nuclei contain a mixture of isotopes with various nuclear spins, the total scattering cross section, coherent scattering cross section, and scattering amplitude effective in Bragg scattering by crystals are

$$\sigma_s = 4\pi \sum_j p_j \left(\frac{i_j+1}{2i_j+1} b_{i_j+1/2}^2 + \frac{i_j}{2i_j+1} b_{i_j-1/2}^2 \right) \quad (12)$$

$$\sigma_{coh} = 4\pi \left[\sum_j p_j \left(\frac{i_j+1}{2i_j+1} b_{i_j+1/2} + \frac{i_j}{2i_j+1} b_{i_j-1/2} \right) \right]^2 \quad (13)$$

$$b = \sum_j p_j \left(\frac{i_j+1}{2i_j+1} b_{i_j+1/2} + \frac{i_j}{2i_j+1} b_{i_j-1/2} \right) \quad (14)$$

where the summation is with respect to the isotopes.

The difference between the total scattering cross section and the coherent scattering cross sections is the incoherent contribution to the cross section due to nuclear spin and isotope effects

$$\sigma_{S+I} = \sigma_s - \sigma_{coh} \quad (15)$$

The nuclear spin and isotope incoherent cross section contribute isotropically to the background intensity of a neutron diffraction pattern.

It should be noted that although the coherent amplitude b effective in Bragg scattering is related to the coherent scattering cross section per nucleus by Equation 5, the σ_{coh} cannot be obtained directly by a transmission measurement corrected for neutron absorption and incoherent scattering.¹⁴ The effective coherent cross section of a nucleus in a crystalline material depends upon the number of crystalline planes effective in producing Bragg scattering. The number of such planes is in turn dependent upon the crystalline structure of the material and the wavelength of the neutron radiation employed. (It is this characteristic of σ_{coh} in crystalline media which forms the basis of another method of crystal analysis by neutrons.)^{15,16}

An ever present source of non-isotropic incoherent scattering which contributes additionally to the incoherent background is due to the thermal vibrations of the atoms in solids. According to the Debye theory as extended to the case of scattering of neutrons,¹⁷⁻¹⁹ the temperature differential diffuse scattering is

$$\frac{d\sigma_T}{d\Omega} = b_0^2 (1 - e^{-2W}) \quad (16)$$

with

||

$$W = \frac{6h^2}{mk\theta} \left(\frac{\phi(x)}{x} + 1/4 \right) \frac{\sin^2 \theta}{\lambda^2}, \quad x = \frac{\theta}{T} \quad (17)$$

where h is Planck's constant, m is the mass of the atom, k is Boltzmann's constant, θ is the Debye temperature of the crystal and ϕ is the Debye function. This thermal motion of the atoms in a crystal also results in the scattering amplitude at a temperature T to be smaller than if the atoms were at rest. The scattering amplitude at temperature T is given by

$$b(T) = b_0 e^{-W \frac{\sin^2 \theta}{\lambda^2}} \quad (18)$$

This causes a decreasing intensity of Bragg diffraction lines with increasing temperature.

Additional factors contributing to the incoherent scattering such as multiple scattering in the specimen, paramagnetic scattering and atomic disorder in crystals together with absorption effects will be discussed in a later section.

III. ASPECTS OF NEUTRON DIFFRACTION BY MAGNETIC STRUCTURES

As a consequence of the interaction of the neutron magnetic moment with the atomic magnetic moments of atoms and ions, neutrons may be magnetically scattered.²⁰⁻²³ This magnetic scattering, which has no counterpart in X-ray scattering, allows a microscopic view of the positions and orientations of the atomic magnetic moments to be studied.²⁴ The coupling of such paramagnetic atoms or ions over large distances in crystals gives rise to a magnetic structure which either adds to the intensities of the crystal diffraction lines or produces additional diffraction lines.

Halpern and Johnson²² have given the expression for the differential magnetic scattering cross section per atom per steradian as

$$\frac{d\sigma_m}{d\Omega} = \frac{2}{3} S(S+1) \left(\frac{e^2 \gamma}{\mu c^2} \right)^2 f_m^2 \quad (19)$$

where S is the spin quantum number of the atoms, e the charge on the electron, μc^2 the rest energy of the electron, γ the neutron magnetic moment in nuclear magnetons, and f_m the magnetic amplitude form factor. (Equation 19 assumes only spin angular momentum, i.e., zero or quenched orbital contributions.) For the case of randomly oriented atomic magnetic moments in a solid, the total magnetic scattering is given by the sum of the intensities

scattered by the individual atoms. Such is the case for paramagnetic substances, at temperatures where the magnetic susceptibilities obey the Curie-Weiss law²⁵

$$\chi = \frac{C_M}{T - \theta} \quad (20)$$

where χ is the magnetic susceptibility, C_M the Curie constant, T the absolute temperature, and θ the Curie-Weiss constant.

The magnetic form factor, unlike the coherent nuclear amplitude, is angularly dependent. The angular dependence is not the same as that of the X-ray atomic scattering factor, because the magnetic form factor depends only on the distribution of those electrons in the atom which contribute to the magnetic moment (for example, the 3d-shell of the iron group elements). For randomly oriented paramagnetic atoms, this scattering is incoherent and angularly dependent. It adds to the diffuse scattering in neutron diffraction patterns predominantly in the forward directions.

In some substances an ordering temperature exists below which the atomic magnetic moments couple antiferromagnetically^{24,26-31} or ferromagnetically²⁵ in the crystal lattice. The temperatures of antiparallel and parallel orderings are called the Neel and Curie temperatures, respectively. This coupling of moments in neighboring paramagnetic atoms is due to quantum mechanical exchange interactions and not to the much smaller magnetic dipole-dipole interactions. For antiferromagnetism the macroscopic magnetization is zero in the absence of an applied magnetic field, as the opposing moments compensate. (There is a form of antiparallel coupling termed ferrimagnetism in which unequal magnetic moments of neighboring atoms do not compensate to zero.)³² The onset of such ordering causes heat capacity and magnetic susceptibility to exhibit anomalous behavior.

The magnetic periodicities produced by the coupling of neighboring paramagnetic atoms in a crystal lattice result in neutron diffraction lines at scattering positions related to the interplanar spacings of the magnetic unit cell. For the case of unpolarized neutrons the magnetic scattering and the nuclear scattering are additive. (With polarized neutrons, interference terms can occur.) The magnetic structure factor of the (hkl) magnetic reflection is given by²⁴

$$F_M(hkl) = \sum_m \pm D_m \exp 2\pi i (hu_m + kv_m + lw_m) \quad (21)$$

$$D_m = \frac{e^2 \gamma}{\mu c^2} S f_m, \quad (22)$$

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where D_m is the magnetic scattering amplitude of the m 'th paramagnetic atom in the magnetic unit cell, u_m, v_m, w_m the magnetic unit cell coordinates of the m 'th atom, and the summation is taken with respect to all paramagnetic atoms in the cell. The sign to be used with a given atom depends upon the relative parallel or antiparallel orientation of the atomic magnetic moments with respect to the neutron moment. For the case of unpolarized neutrons this is equivalent to the relative atomic moments of the lattice relative to each other. The magnetic structure factor, F_m , does not involve the orientation of the moments with respect to the crystallographic axes. Halpern and Johnson²² have shown that the differential magnetic scattering cross section of an oriented paramagnetic atom for unpolarized neutrons

$$\frac{d\sigma_m}{d\Omega} = q^2 D_m^2 \quad (23)$$

with

$$q^2 = 1 - (\bar{e} \cdot \bar{\kappa})^2 \quad (24)$$

and

$$\bar{e} = \frac{(\bar{k} - \bar{k}')}{|\bar{k} - \bar{k}'|} \quad (25)$$

where $\bar{e}$ is the scattering vector, $\bar{k}$ and $\bar{k}'$ are the incident and scattered wave vectors, respectively, and $\bar{\kappa}$ is the unit vector along the direction of the magnetic moment.

For the case of coherent magnetic scattering from a crystalline plane, $\bar{e}$ is then the unit normal to that plane. This orientation of the magnetic moments relative to the crystal axes is not due to the exchange interaction responsible for the relative orientations of atomic moments relative to each other. It is due to the magnetic anisotropy of the crystal. The factor q^2 can take on values between zero and unity. For the case of randomly directed moments with respect to the crystal axes (not random with respect to each other), $q^2 = 2/3$.

The intensity of a magnetic neutron diffraction line from planes having Miller indices (hkl) in the magnetic unit cell is then

$$P_M(hkl) \sim j_{hkl} q^2_{hkl} \left| F_M(hkl) \right|^2, \quad (26)$$

where j_{hkl} is now the multiplicity factor of the (hkl) planes in the magnetic unit cell. The magnetic unit cell need not have the same symmetry as the crystal unit cell and it often does not.

The coherent intensities of magnetic diffraction lines are decreased by the effect of thermal agitation producing a decreased alignment of the neighboring moments. (This is in addition to the usual Debye-Waller factor

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 produced by vibration of the scattering centers about a mean position.) As the temperature is increased to the magnetic disordering temperature, this effect results in the vanishing of the magnetic diffraction lines and thus of the magnetic structure. The temperature dependence of both types of magnetic lines (antiferromagnetic and ferromagnetic) is a function of the Brillouin function, relating saturation intensity of magnetization to the ratio of temperature divided by Curie temperature. For ferromagnetics, the temperature factor can be obtained by magnetic susceptibility measurements.³³ Van Vleck²⁸ has theoretically extended the Heisenberg model of ferromagnetism to the case of rather restricted types of antiferromagnetic structure, which describes the observed temperature dependence of the antiferromagnetic orderings of such lattices.

IV. APPARATUS AND PROCEDURE

The neutron crystal diffraction spectrometer arrangement at the heavy-water moderated reactor at the Argonne National Laboratory was used to obtain the diffraction patterns. The diffraction spectrometer is shown schematically in Figure 1. A heteroenergetic beam of thermal neutrons emerges through a 1 in. by 2 in. slit in the pile shielding. The beam is monochromatized by diffraction from the (111) plane of a bank of 4 lithium fluoride single crystals. In this study a neutron wavelength of 1.19 Angstrom units was diffracted from the crystals. These crystals are enclosed in a shielding of boron carbide and paraffin to reduce the neutron background. The monochromatic neutron beam emerges from this shielding through a 1 in. by 2 in. slit in a cadmium-lined, boron carbide shielded collimator.

The specimen to be studied is placed in position on the spectrometer table. The scattered intensity from the specimen is observed through a 1 in. by 2 in. cadmium-lined, boron carbide shielded collimator placed in front of the neutron detector. The collimator used in the present study was such as to give a 1° angular resolution with a 1 in. wide collimation. The diffracted neutrons are detected by an enriched-BF₃ proportional counter. The counter is shielded from background neutrons by cadmium surrounded with boron carbide. The diffraction pattern is observed by counting the neutron intensities at various angular positions of the counter arm which can move about the specimen table as a center. For flat specimens in the transmission orientation the specimen table is geared to rotate at one-half the angular rotation of the spectrometer arm.

The apparatus has been equipped with a motor drive and for automatic recording of the data. The spectrometer arm automatically stops at angular intervals of one-sixth of a degree, and a neutron count is taken for a preset interval of time, usually about 3 min. On alternate sixths of a degree a cadmium sheet is inserted into the beam by a solenoid, thereby correcting the previous or following no-cadmium count for background

FIG.1. Arrangement of Neutron Diffraction Spectrometer.

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effects. At the end of each counting interval, the counts are recorded by a tape recorder and the drive motor moves the detector arm to the next angular position.

A thin, flat, fission counter containing a foil of uranium-235 and located in the pre-specimen collimator is used to monitor the neutron intensity striking the sample. The counts recorded by the monitor are also printed on a tape recorder, thereby allowing corrections for reactor power changes to be accounted for in the diffraction pattern. A record of the neutron background in the room is also recorded by a BF_3 neutron counter located near the equipment.

A photograph of the spectrometer, shielding and electronic apparatus is reproduced in Figure 2. The cryostat-heater to be described is shown in position upon the specimen table.

The ordering of atoms in order-disorder studies and the ordering of magnetic moments in magnetic structures are both dependent upon temperature. To carry out such studies for the copper-manganese alloys a simple apparatus was designed and constructed to operate in the temperature range of 100° to 800°K .

The schematic arrangement of the cryostat-heater is shown in Figure 3. The specimen to be cooled or heated is inserted into the conducting copper frame which is permanently attached to the cover of the vacuum chamber. If a powder, the specimen is first placed into a suitable sized thin aluminum container. The cylindrical wall of the cryostat-heater is of such a diameter that neutron diffraction from the forward or rear $1/16$ in. aluminum windows of the chamber will not be detected with the collimation described. The relations of the various heat radiation shields are shown in the schematic of Figure 3. To cool the specimen, liquid nitrogen or other coolant is placed into the coolant reservoirs after removal of the copper heating inserts and the heater elements. To heat the specimen, the copper inserts which make contact with the copper specimen holder frame are inserted and the heating elements placed into position. Variac control allows the heating temperature to be varied. A mechanical vacuum pump and a cold trap reduced the pressure to less than one micron. At equilibrium, temperature gradients in the sample were at most 2° , as determined by iron-constantan thermocouples placed at various positions in the sample. This was found to be sufficient for the present study. Provisions have been made for the addition of a vacuum diffusion pump for future experiments.

FIG. 2 NEUTRON CRYSTAL DIFFRACTION SPECTROMETER

FIG. 3 SCHEMATIC ARRANGEMENT OF THE CRYOSTAT-HEATER

V. DISCUSSION OF THE PROBLEM

The crystal structure of copper is face-centered cubic with a lattice parameter of 3.608 Angstroms. Addition of manganese results in the formation of a substitutional solid solution.¹⁻⁵ Manganese atoms replace copper atoms in the face-centered cubic lattice accompanied by an increase in the lattice parameter. At elevated temperatures^{2, 4, 34} the gamma phase solid solution has a face-centered cubic structure up to 82 per cent manganese and a face-centered tetragonal structure from 82 per cent to compositions approaching 100 per cent manganese. The axial ratio changes gradually from unity at 82 per cent manganese to 0.938 at compositions approaching 100 per cent manganese.

Manganese is known to have 3 or 4 allotropes. As reported by Dean et al.,⁴ the first, or alpha phase, is stable up to 705°C, the second, beta phase, is stable from 705°C to 1092°C, the third, gamma phase, is stable from 1092°C to 1133°C, and the fourth, delta phase, is said to be stable from 1133°C to melting point, 1246°C.

The alpha and beta phases have been established as complex cubic structures with 58 atoms and 20 atoms, respectively, in the unit cells. Gamma manganese has a face-centered tetragonal structure. Its lattice parameters are equal to those of the face-centered tetragonal cell of the copper-manganese solid solution, if the lattice parameters of the solution are extrapolated to one hundred per cent manganese.

According to the equilibrium diagram for the alloys, at room temperature, the gamma solid solution exists as a single phase up to 22 weight per cent manganese. At compositions exceeding 22 weight per cent manganese the gamma solid solution exists together with alpha manganese as a second phase. There is no general agreement as to the composition where the alpha manganese phase is first detected, and the phase boundary is believed to be dependent upon the rate of cooling of the alloys. Thus Dean et al.^{4, 5} found that the X-ray diffraction patterns of furnace-cooled alloys had a single phase instead of 2 phases up to 89 per cent manganese and 2 phases at higher manganese content. They attribute the discrepancy to the alloys not attaining equilibrium.

Ellsworth and Blake³ found single phase structures at compositions as high as 90 per cent manganese. The second phase, occurring above 90 per cent manganese is again the alpha manganese phase. It is not the purpose of the present investigation to clarify this phase boundary. It is mentioned in order to indicate the necessity of correlating the neutron diffraction results with the X-ray diffraction analysis of the samples used in the present investigation.

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The formation of substitutional solid solutions, such as the gamma solid solution of copper and manganese, where atoms of type B replace those of type A in the matrix A-lattice, can take place at random lattice positions or in ordered lattice positions.³⁵ The ordered substitutional solid solution requires a simple stoichiometric ratio of the constituent atoms in order to bring about a large degree of ordering. In a face-centered cubic structure ordering might, for example, occur at compositions such as A_3B , AB , and AB_3 . At compositions deviating from the simple ratios a lesser degree of ordering may be expected.

In some systems the transitions from disorder to order can be brought about by suitable heat treatment. If the degree of order is observed with increasing temperatures it is found that the order may decrease rather abruptly at a given ordering temperature above which the alloy is disordered. The alloy Cu_3Au , for example, exhibits such a change in ordering at $380^\circ C$. In the alloy $CuZn$ the order decreases less abruptly with temperature and resembles the decrease of saturation magnetization of ferromagnetic materials with temperature. Beta-brass is disordered above $480^\circ C$.

Ordering in substitutional alloys can be studied by diffraction, specific heat, resistivity, and chemical methods. The methods of X-ray and more recently of neutron diffraction, however, allow a direct measurement of the degree of ordering and the localization of each type of atom at a definite site in the unit cell.

The X-ray diffraction pattern of a random solid solution will exhibit the same diffraction lines as that of the solvent, with only an increase or decrease in the intensities of these fundamental lines by an equal factor and a shift in the positions of the lines. Ordering of the sample produces all these fundamental lines and, in addition, superlattice lines. The superlattice lines allow, in many cases, the location of each type of atom to be localized. The relative intensities of the superlattice lines relative to the fundamental lines can be related to the degree of ordering. Detection of superlattice lines by X-rays in the copper-manganese system is difficult due to the closeness of the X-ray scattering factors of copper and manganese.

In addition to the long range crystal order which measures the extent to which the positions of atoms in different unit cells of the crystal lattice are correlated, there is a second type of crystal ordering, short range order, which measures the extent to which the positions of neighboring atoms in the lattice are correlated.³⁵⁻³⁸ Short range ordering exhibits liquid-like, or diffuse, superlattice diffraction lines in addition to the sharp fundamental lines.

The intensities of diffraction lines from planes having Miller indices (hkl) for both X-rays and neutrons are directly proportional to the square of the absolute values of the structure factors $F(hkl)$. Frequently such factors

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involve sums of X-ray atomic scattering factors in the case of fundamental diffraction lines in ordered alloys and differences of X-ray atomic scattering factors in the case of superlattice lines. Thus superlattice lines can, in the case of ordered alloys of close atomic number, be difficult to detect with X-rays. Such is not necessarily the case if neutrons are used, for the neutron scattering amplitudes of elements do not bear any correlation with the atomic number. Indeed, in some cases the superlattice lines may be intensified and the fundamental lines depressed if the signs of the neutron scattering amplitudes of the elements are opposite. Such is the case in the ordered Ni_3Mn alloy.¹³ The copper-manganese system should also exhibit the depression of the fundamental lines, and, clearly indicate the presence of superlattice lines if any ordered structures occur.

Ellsworth and Blake³ have studied the copper-manganese alloy system by X-ray diffraction. They utilized the known³⁹ depression of the atomic scattering factor of manganese with iron $\text{K}\alpha$ radiation to improve the difference in atomic scattering factors between copper and iron by 3 units. They found no evidence of crystal ordering in the system, as exhibited by the absence of superlattice lines.

The intensities of the diffraction lines which should be observed for Cu, disordered Cu_3Mn , and an ordered Cu_3Mn alloy (assuming that Mn atoms localize in the corners of the face-centered cubic unit cell of Cu) have been calculated for X-rays and neutrons. X-ray intensities based on both the Thomas f-factor curves⁴⁰ and $\text{FeK}\alpha$ radiation were calculated. The comparison is given in Table I. The intensities in the case of X-rays are calculated for a cylindrical powder specimen and in the case of neutrons for a flat powder sample in the transmission orientation. The intensities are relative to the copper (111) line in all cases.

It is seen that although the "anomalous" scattering of $\text{FeK}\alpha$ radiation by manganese improves the superlattice intensities by about a factor of 4 over that of a "normal" scattering, neutrons give an improvement of a factor of 16 over the iron radiation. These calculated intensities also illustrate the absence of the superlattice lines in disordered alloys and the much greater decrease in the fundamental lines due to the negative neutron scattering amplitude of manganese relative to copper. Thus the (111) reflection in Cu_3Mn by neutron diffraction is about 59 per cent lower in intensity than the (111) reflection of copper, whereas for X-rays the corresponding decrease is only about 13 per cent.

In addition to the desirability of a neutron diffraction study of the system to further substantiate the X-ray findings of Ellsworth and Blake³ as to the absence of crystal ordering, such a study would also indicate the randomness or ordering of atomic magnetic moments of the constituent atoms. The measurements of Valentiner and Becker⁶ show a rather broad

TABLE I

Calculated Intensities of Diffraction Lines of Cu, Disordered Cu₃Mn, and An
Assumed* Ordering of Cu₃Mn, for X-rays and Neutrons

(hkl)	X-rays (Thomas f-values)			X-rays (FeK α -rad.)			Neutrons ($\lambda = 1.19\text{\AA}$)		
	Cu	Cu ₃ Mn* Ordered	Cu ₃ Mn Disordered	Cu	Cu ₃ Mn* Ordered	Cu ₃ Mn Disordered	Cu	Cu ₃ Mn* Ordered	Cu ₃ Mn Disordered
(100)		0.5			1.8			27.6	
(110)		0.4			1.5			28.2	
(111)	**100.0	88.2	88.2	**100.0	86.0	86.0	**100.0	41.1	41.1
(200)	46.5	43.9	43.9	46.5	40.3	40.3	58.4	24.1	24.1
(210)		0.2			0.8			24.8	
(211)		0.1			0.6			21.2	
(220)	36.0	33.6	33.6	36.0	30.2	30.2	66.1	27.2	27.2

*Calculated assuming Mn atoms ordered at corner positions in the F.C.C. unit cell.

**Intensities normalized relative to a value of 100.0 for the Cu (111) reflection in all cases.

peaking of the magnetic susceptibility of these alloys in the region of 22 atomic per cent manganese. At liquid nitrogen temperatures this region increases by a factor of nearly 7 in susceptibility, while the susceptibility below and above this composition increases very little.

It is to be noted that, generally, the presence of lines in neutron diffraction patterns which are not present in a corresponding X-ray diffraction pattern indicates magnetic structure reflections. In the present case, where the X-ray scattering properties of copper and manganese are similar, such an absence may be caused by weak superlattice lines due to crystal ordering and not magnetic ordering.

VI. PREPARATION OF THE ALLOYS

The copper-manganese alloys studied, together with their chemical analysis, are listed in Table II.

Table II.

Chemical Analysis of the Copper-Manganese Alloys

Alloy Designation	Atomic % Manganese	Atomic % Copper
11Mn-89Cu	10.5	89.4
13Mn-87Cu (c)	12.7	87.2
18Mn-82Cu	17.5	82.5
33Mn-67Cu (c)	33.2	66.9
48Mn-52Cu	47.7	52.3
48Mn-52Cu (q)	48.4	51.7
69Mn-31Cu	69.0	31.0
75Mn-25Cu	74.6	25.4
85Mn-15Cu	85.1	14.9

(c) Designates commercial samples.

(q) Designates alloy quenched.

The alloys designated 13Mn-87Cu (c) and 33 Mn-67Cu (c) were commercial cupromanganese alloys which had been prepared by melting together copper and manganese and allowing them to cool to room temperature in a cast.

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The remaining alloys were prepared by weighing about 350 g total weight of reagent grade chemicals for each composition desired. They were placed into an alundum crucible of 2 in. inside diameter. The alloys were fused in a vacuum induction furnace at a temperature of 1300°C for 20 min. The samples were allowed to cool to room temperature by turning off the furnace. In the case of high manganese content alloys, an argon pressure of 5 in. of mercury was introduced into the furnace to prevent loss of manganese from the melt. After cooling to room temperature the crucibles were broken and the alloys machined into disks 3/8 in. thick and 2 in. in diameter. The 2 commercial samples were machined to similar size.

Spectrochemical analysis showed about 0.7 per cent iron contaminant in the commercial alloy 13Mn-87Cu (c) and 0.1 per cent iron contaminant in the commercial alloy 33 Mn-67Cu (c). The laboratory-prepared alloys showed about 0.05 per cent iron contaminant. The X-ray examinations of the materials showed no lines due to impurities. Any impurities present were therefore considered negligible in a neutron diffraction study. An accurate susceptibility measurement, however, would not be too reliable in the case of the commercial samples.

Although a similar size disk of pure copper was also cast, subsequent neutron diffraction work showed that not sufficient randomness of grains existed to give powder-type diffraction lines. This was evident both from the relative intensities of the lines in the neutron pattern and by the change in intensity of a reflection upon rotation of the sample in the beam. It was necessary to use powdered copper held in a container 3/8 in. thick having 10 mil aluminum walls.

A copper disk, however, was employed to determine the level of incoherent scattering which a powdered sample of equal linear density to that of the disk would exhibit. This was done in order to correct later for multiple scattering in the sample.

The sample 48Mn-52Cu (q) was remelted in an air furnace before machining, quickly removed from the furnace, quenched in water, and then also machined into a disk.

Later, each alloy disk was enclosed in a snug-fitting copper holder and annealed for 3 days at 750°C. This was followed by quenching the copper-enclosed alloy in water. The copper holder was sufficiently air-tight to prevent oxidation of the sample, except for a thin surface layer which was readily removed. No difference was observed in the neutron diffraction patterns before and after this treatment.

VII. X-RAY DIFFRACTION ANALYSIS OF THE ALLOYS

The X-ray diffraction studies of the copper-manganese alloys have been reported by several investigators.²⁻⁵ The results of the X-ray diffraction analysis of the alloys used in this study are included, for, as suggested,^{4,5} the presence of the alpha phase of manganese, as well as the change from face-centered cubic to face-centered tetragonal, may depend upon the rate of cooling of the alloys. The X-ray patterns will also be helpful in understanding the subsequent neutron diffraction patterns.

Fine filings of each alloy were held with mucilage on a quartz fiber of 5 mil diameter. Debye-Scherrer X-ray patterns were taken using iron radiation with a camera of 57.3 mm diameter. The tube was operated at 30 kv and 11 ma. A pre-sample manganese filter and a contact manganese filter adjacent to the photographic film were employed.

The X-ray patterns are reproduced in Figure 4. The expansion of the copper lattice is evident by the contraction of the lines toward smaller scattering angles. The patterns exhibit the face-centered cubic lines, except for the highest manganese composition alloy, 85Mn-15Cu, where the splitting of the (200) and (220) is sufficient to be noticeable as the face-centered tetragonal lattice is forming. These samples have the gamma solid solution phase. No lines due to alpha manganese are present. The tabulation of the results of the X-ray analysis is given in Table III.

Table III

X-ray Diffraction Analysis of the Copper-Manganese Alloys

Alloy Designation	Phase	Lattice Parameters	
		a	c
Copper	F.C.C.*	3.61 $\text{\AA}$	
11Mn-89Cu		3.64	
13Mn-87Cu (c)		3.65	
18Mn-82Cu		3.66	
33Mn-67Cu (c)		3.72	
48Mn-52Cu		3.75	
48Mn-52Cu (q)		3.74	
69Mn-31Cu		3.75	
75Mn-25Cu	F.C.T.**	3.75	
85Mn-15Cu		3.76	3.64 $\text{\AA}$

*F.C.C.: face-centered cubic

**F.C.T.: face-centered tetragonal

Fig. 4. X-ray diffraction patterns of the Cu-Mn alloys.
(Fe, $K\alpha$ -radiation, 57.3-mm. diameter camera.)

VIII. NEUTRON DIFFRACTION STUDY OF THE ALLOYS

The neutron diffraction patterns of the copper-manganese alloys exhibited some unusual and unexpected characteristics. The main features are exemplified by the following 3 patterns:

The neutron diffraction pattern of copper, Figure 5a, presents the usual face-centered cubic lines having all even and all odd Miller indices, i.e., (111), (200), (220), etc. The pattern for the 33Mn-67Cu alloy, Figure 5b, shows, in addition to the fundamental diffraction lines, a broad liquid-like maximum in the region of a (100) reflection. This broad maximum is not present in the corresponding X-ray pattern. At high concentrations of manganese, illustrated by the neutron pattern of the 85Mn-15Cu alloy, Figure 5c, the fundamental lines of the X-ray pattern are again present in the neutron pattern. (The resolution of the neutron diffraction pattern does not allow the small line splitting to the tetragonal structure to be resolved.) In addition the previous broad peak in the region of the (100) reflection has been much depressed and a sharp diffraction line is present at the position of the (110) reflection. This line is not observed in the X-ray pattern.

The details of the low-angle portion of the neutron diffraction patterns for the alloys corrected to the same number of atoms per unit area of sample are plotted to scale in Figure 6. Four points are to be noted. With substitution of manganese atoms for copper atoms the intensity of the (111) fundamental line decreases rapidly. Addition of manganese first causes an increase in diffuse background, followed by the formation of the broad peak. In the 69 atomic per cent manganese alloy the intensities of the diffuse background as well as the broad peak have decreased and the line at the (110) position appears. At 75 atomic per cent and at 85 atomic per cent manganese the broad peak continues to decrease and the line at (110) position continues to increase.

The absence of numerous sharp superlattice lines at positions of mixed Miller indices shows that no long range crystal orderings occur in the alloys.

The decreasing intensity exhibited by the (111) fundamental reflection with substitution of manganese for copper atoms in the lattice also occurs similarly for the other fundamental lines. The calculated change of intensity with composition for the (111) fundamental line relative to the (111) of copper follows:

For the copper (111) line

$$P(111)_{Cu} \sim |F(111)_{Cu}|^2 \quad (27)$$

$$F(111)_{Cu} = 4b_{Cu} \quad (28)$$

$$P(111)_{Cu} \sim |F(111)_{Cu}|^2 = 16 |b_{Cu}|^2 \quad (29)$$

FIG.5. Neutron diffraction patterns of (a.) Cu, (b.) ³³Mn - ⁶⁷Cu, and (c.) ⁸⁵Mn - ¹⁵Cu.

FIG.6. Low angle portions of neutron diffraction patterns of copper-manganese alloys.

where $P(111)_{Cu}$ is the intensity of the (111) line of copper, $F(111)_{Cu}$ the structure factor, and b_{Cu} the neutron coherent scattering amplitude of copper.

For an alloy of x manganese atoms and $(1 - x)$ copper atoms the weighted coherent scattering amplitude

$$\bar{b} = (1 - x)b_{Cu} + xb_{Mn} \quad , \quad (30)$$

so that

$$F(111)_x = 4(\bar{b}) \quad , \quad (31)$$

and

$$P(111)_x \sim |16 \bar{b}|^2 \quad . \quad (32)$$

Therefore,

$$\frac{P(111)_x}{P(111)_{Cu}} = \frac{|\bar{b}|^2}{|b_{Cu}|^2} = \frac{|(1 - x)b_{Cu} + xb_{Mn}|^2}{|b_{Cu}|^2} \quad (33)$$

Substituting the values⁸ of the neutron amplitudes

$$b_{Cu} = +0.76 \times 10^{-12} \text{ cm}$$

and

$$b_{Mn} = -0.33 \times 10^{-12} \text{ cm}$$

into Equation 33, one obtains

$$\frac{P(111)_x}{P(111)_{Cu}} = \frac{|F(111)_x|^2}{|F(111)_{Cu}|^2} = \frac{(0.76 - 1.09x)^2}{(0.76)^2} \quad (34)$$

The calculated and observed neutron structure factors for the (111) reflection of the copper-manganese system are plotted in Figure 7. The finite value of observed intensity in the region of 70 atomic per cent manganese is considered to be due to lack of perfect randomness of manganese and copper atoms on the matrix lattice, such as a tendency of manganese atoms to congregate on adjacent sites. That orientation in the latter samples did not cause these greater observed intensities was verified by repeating the neutron patterns utilizing alloy filings.

The position of the broad maximum in the low-angle neutron diffraction patterns for the copper-manganese alloys is within the limits set by the formula for the diffraction by 2 diffracting centers⁴¹

$$\lambda = 2(0.8d) \sin\theta \quad (35)$$

FIG.7. Calculated and observed neutron structure factors for the (111) reflection of the copper-manganese alloys.

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and the Bragg formula valid for long-range periodicity

$$\lambda = 2d \sin\theta \quad (36)$$

if for the d-spacing the lattice parameter of the unit cell, a , is used. The observed value of the d-spacing from the position of the maximum is such that

$$0.8a(100) < d(\text{obs}) < a(100) \quad \text{i.e.,} \quad (37)$$

$$2.98\text{\AA} < 3.27\text{\AA} < 3.73\text{\AA}$$

The domain size of the region having the periodicity responsible for this broad maximum can be estimated by applying the Scherrer equation for line broadening⁴²

$$L = \frac{\lambda(0.9)}{(B - b) \cos\theta} \quad (38)$$

where B is the observed width expressed in radians of scattering angle, b the natural width determined by the experimental resolution, λ the wavelength of the radiation, L the effective size of the domain, and 2θ the scattering angle at which the broadened line occurs. The observed line width in the alloy 48Mn - 52Cu at half maximum is 6.5° . The inherent width due to the diffraction equipment is 1° . The broadening due to domain size thus is 5.5° . With a wavelength of 1.19 Angstroms and a Bragg angle of 10.5° , this gives an effective domain size of 10 Angstroms. This is of the order of 3 times the dimension of the unit cell.

The effect of temperature of sample on the form of the broad line is illustrated in Figure 8 for the alloy 33Mn - 67Cu at temperatures of 300°K and 748°K . The intensity of the line decreases, whereas the width at half-maximum remains substantially the same. The integrated intensity of the broad maximum compared with that of the (111) reflection at various temperatures in the range 100°K to 748°K is plotted in Figure 9. Below room temperature no change was observed in the intensity or shape of the broad line. Above room temperature the broad line decreased more rapidly in intensity than did the fundamental (111) reflection.

As the decrease in intensity due to thermal Debye-Waller vibration of the atoms affects both lines by the same factor (the lines are not greatly separated in angle), and as the decrease of intensity of the (111) reflection is due to thermal vibrations, the additional decrease of the broad line can be attributed to a decrease of short-range crystal or magnetic ordering.

For atoms whose atomic numbers are not too close in value, the non-existence of such a broad maximum in the X-ray diffraction pattern would clearly indicate that the broad maximum is due to a short-range

FIG.8. Neutron diffraction patterns of the diffuse (100) reflection at (a.) 300°K and (b.) 748°K for the alloy 33 Mn-67 Cu.

FIG.9. Relative integrated intensities of the (100) diffuse reflection and the (111) reflection for the temperature range 100°K to 750°K of the alloy 33 Mn-67 Cu.

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magnetic coupling and not a short-range atomic ordering. In the present case, however, the correlation of the broad line with magnetic coupling cannot be readily deduced from a comparison of the X-ray and neutron diffraction patterns. That the broad maximum is associated with magnetic coupling was determined by the existence of a correlation of the integrated intensities of the broad peaks with the magnetic attraction of the alloys.

The integrated intensity of the broad line relative to the integrated intensity of the (111) reflection of copper is shown in Figure 10 as a function of atomic per cent manganese. It does not maximize sharply in any region of composition. The dependence with composition is broad and attains a maximum in the region of 50 atomic per cent manganese. The sample 48Mn - 52Cu (q), which had been remelted and water quenched, gave a smaller (100) diffraction intensity than the 48Mn - 52Cu which was furnace-cooled.

The relative magnetic attraction of these alloys was determined by measuring the maximum horizontal displacement produced by a permanent magnet of 2000 gauss upon each alloy disk when the disk was suspended vertically between the magnetic poles by a string. The purpose of the magnetic measurements was not to determine susceptibilities, but only to show semi-quantitatively the relative magnetic attraction of these alloys. The relative magnetic attraction of the alloys is plotted in Figure 11 as a function of atomic per cent manganese. The attraction of a similar sized disk of alpha manganese is indicated by the broken horizontal line. The correlation of the integrated intensities with the magnetic attraction shows that the broad line of the neutron patterns is due, at least in part, to a short range magnetic coupling between atoms.

The magnetic susceptibility measurements of Valentiner and Becker⁶ show a maximum in the region of 22 per cent manganese. Their samples followed the Curie law temperature dependence at room temperatures. They observed deviations from the Curie law near liquid nitrogen temperatures. These differences may be due to variations in alloy preparation and heat treatment. Further clarification would require susceptibility measurements at various temperatures and applied magnetic fields.

Attempts were made to detect the broad line obtained with neutron diffraction by very long X-ray exposures. Exposures of 400 hr using highly filtered FeK α radiation were made. No broad maximum was observed. An upper limit to the percentage of the broad maximum, appearing in the neutron diffraction pattern due to crystal short range ordering, was estimated as follows:

The smallest structure factor possible for an ordering which can be associated as having as its nucleus a region of short range crystal ordering the least detectable by X-rays would involve differences of X-ray atomic

FIG. 10. Observed integrated neutron intensities of the diffuse (100) reflections of the copper-manganese alloys relative to the observed integrated intensity of the (111) reflection of copper.

FIG. 11. Observed relative magnetic attraction of the copper-manganese alloys.

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scattering factors of copper and manganese. This same structure factor applied to neutron diffraction would make for the largest possible intensity because of the opposite signs of copper and manganese for scattering. The intensity for neutrons and X-rays in such case for the (100) diffuse line for a 50-50 composition would be

$$P_n(100)_{\text{calc.}} = \beta |b_{\text{Cu}} - b_{\text{Mn}}|^2 \quad (39)$$

and

$$P_x(100)_{\text{calc.}} = \beta |f_{\text{Cu}} - f_{\text{Mn}}|^2 \quad (40)$$

where β is a constant involving unknown factors of about equal magnitude for neutrons and X-rays. Similarly for the (111) reflections

$$P_n(111)_{\text{calc.}} = 16 \left| \frac{b_{\text{Cu}} + b_{\text{Mn}}}{2} \right|^2 \quad (41)$$

and

$$P_x(111)_{\text{calc.}} = 16 \left| \frac{f_{\text{Cu}} + f_{\text{Mn}}}{2} \right|^2 \quad (42)$$

Now, if t_x is the minimum exposure to X-rays necessary to observe the (111) reflection of a 50Cu - 50Mn alloy above the incoherent film blackening of a much longer exposure of time t , then, in time t one can observe an X-ray diffraction line of calculated intensity $\frac{t_x}{t}$ of the (111) calculated intensity.

Hence, if the diffuse (100) reflection is not observed after such an exposure of time t , one has

$$P_n(100)_{\text{calc.}} < \frac{t_x}{t} P_x(100)_{\text{calc.}} \quad (43)$$

and

$$\beta |f_{\text{Cu}} - f_{\text{Mn}}|^2 < \frac{t_x}{t} 16 \left| \frac{f_{\text{Cu}} + f_{\text{Mn}}}{2} \right|^2 \quad (44)$$

Solving Equation 44 for β , and substituting the expression for β into Equation 39 gives

$$P_n(100)_{\text{calc.}} < \frac{t_x}{t} \frac{4 |f_{\text{Cu}} + f_{\text{Mn}}|^2 |b_{\text{Cu}} - b_{\text{Mn}}|^2}{|f_{\text{Cu}} - f_{\text{Mn}}|^2} \quad (45)$$

By dividing Equation 45 by Equation 42 one obtains

$$\frac{P_n(100)_{\text{calc.}}}{P_n(111)_{\text{calc.}}} < \frac{t_x}{t} \frac{|f_{\text{Cu}} + f_{\text{Mn}}|^2 |b_{\text{Cu}} - b_{\text{Mn}}|^2}{|f_{\text{Cu}} - f_{\text{Mn}}|^2 |b_{\text{Cu}} + b_{\text{Mn}}|^2} \quad (46)$$

Thus, inserting the appropriate scattering factors of copper and of manganese for neutrons and for iron $K\alpha$ -radiation,

$$\frac{P_n(100)_{\text{calc.}}}{P_n(111)_{\text{calc.}}} < \frac{344t_x}{t} \quad (47)$$

which, for $t_x = 0.3$ hr and $t = 400$ hr, gives

$$\frac{P_n(100)_{\text{calc.}}}{P_n(111)_{\text{calc.}}} < \frac{1}{3} \quad (48)$$

The observed ratio of the peak levels from the neutron pattern of the $48\text{Mn} - 52\text{Cu}$ is

$$\frac{P_n(100)_{\text{obs. total}}}{P_n(111)_{\text{obs.}}} \sim 1 \quad (49)$$

Therefore, the contribution to the intensity of the broad (100) neutron reflection from short range crystal ordering cannot be more than $\frac{1}{3}$. With a longer exposure and additional filtering of the fluorescence, it may be possible to lower this limit considerably.

The (100) position of the broad maximum, together with its intensity correlation with magnetic attraction, suggests the following short range structural possibilities that may account for the experimental observations:

1. Manganese atoms may tend to have copper atoms as nearest neighbors on the face-centered cubic lattice and manganese atoms as next-nearest neighbors. Such a structural tendency would space manganese atoms one unit cell distance apart over short distances. This would result in a contribution to the observed (100) neutron diffraction maximum by short range crystal ordering. The magnetic contribution would arise from partial ferromagnetic coupling of the manganese atoms separated by distances comparable to the size of the unit cell parameter a .
2. The second possibility is similar to the first except that the magnetic contribution arising from ferro-type coupling between next-nearest neighbors or the manganese atoms does not occur by itself. The magnetic attraction of the alloys, instead, is caused by an unbalanced antiferromagnetic coupling between nearest-neighbors, i.e., between copper and manganese; and ferromagnetic coupling between the next-nearest neighbors, i.e., the manganese atoms. This structure assumes that the copper atoms become paramagnetic by the addition of manganese atoms. The observed magnetic attraction would, in this case, be due to a ferrimagnetic short range coupling.

For the alloys 69Mn - 31Cu, 75Mn - 25Cu and 85Mn - 15Cu the neutron diffraction patterns in Figures 5c and 6 show a decrease in the intensity of the (100) diffuse peak and the appearance of a line at the (110) position. This line does not maximize at the composition corresponding to the chemical formula CuMn_3 , and it is not accompanied by other diffraction lines at superlattice positions as would be expected if it were caused by a crystal ordering at the stoichiometric composition CuMn_3 .

The neutron patterns for the alloy 85Mn - 15Cu at 300°K and 558°K are shown in Figures 12a and 12b. The effect of increased temperature results in the disappearance of the (110) line accompanied by perceptible increase in the diffuse background at small angles. The fundamental lines, i.e., (111), (200), etc., are slightly decreased by the Debye-Waller temperature factor. The absence of a (110) reflection in the X-ray pattern and the absence of a number of additional lines in the neutron pattern, together with the increased paramagnetic diffuse scattering at small angles accompanying its disappearance with temperature, show it to be an antiferromagnetic reflection. It is not ferromagnetic for otherwise the magnetic attraction of the alloys would increase with intensity of the (110) reflection.

The antiferromagnetic reflection of the alloy 85Mn - 15Cu observed at various temperatures is illustrated in Figure 13. The integrated neutron intensities of the antiferromagnetic line are plotted for various temperatures in Figure 14. The intensity curve shows the usual Brillouin type of decrease with temperature exhibited by antiferromagnetic reflections. Extrapolation of the curve to zero intensity gives a Neel temperature of $380^\circ\text{K} \pm 10^\circ\text{K}$ for the alloy 85Mn - 15Cu.

An antiferromagnetic diffraction line corresponding to the position of a (110) interplanar spacing of the face-centered cubic (or slightly tetragonal) unit cell would arise from a periodicity of relative magnetic moment orientations of period equal to this interplanar spacing. The increased intensity of the antiferromagnetic line with increasing manganese composition, together with the absence of crystal superlattice lines, suggests an antiferromagnetic structure based on the following considerations:

Consider at these high concentrations of manganese, for example in the alloy 85Mn - 15Cu, that the crystal lattice is equivalent to the high temperature (gamma) form of manganese with 15 per cent of the lattice sites occupied by copper atoms. If gamma manganese has an antiferromagnetic structure, we can suppose this magnetic structure to still partially exist as long as only a small percentage of manganese atoms have been replaced by copper atoms.

The gamma phase of manganese, which is face-centered tetragonal, is not stable at room temperature. By addition of manganese atoms to the copper lattice it is possible to approach a face-centered tetragonal unit cell

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FIG.12. Low angle portions of the neutron diffraction patterns for the alloy 85 Mn-15 Cu at (a.) 300° K and (b.) 558° K.

FIG.13. The antiferromagnetic reflection of the alloy 85 Mn-15 Cu observed at various temperatures.

FIG.14. Temperature dependence of the antiferromagnetic reflection of the alloy 85 Mn-15 Cu.

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having closely similar dimensions to that of the gamma phase of manganese.³ Thus, a crystal structure similar to that of gamma manganese, would be formed at room temperature with the copper atoms in the lattice functioning to prevent the manganese atoms from forming the alpha phase of manganese. X-ray studies by previous investigators²⁻⁵ have shown that at high manganese compositions the alpha phase of manganese does appear in the alloys. The compositions at which the alpha phase of manganese is first detected varies. Ellsworth and Blake³ have reported as high a value as 90 per cent manganese. In the present study the alloy of highest manganese composition, 85Mn - 15Cu, did not exhibit X-ray diffraction lines due to the alpha phase of manganese.

The presence of the (110) antiferromagnetic reflection together with the absence of antiferromagnetic lines at positions corresponding to lines having Miller indices (100), (001), (111), (200), etc., suggests the antiferromagnetic structure in Figure 15 as that to which the gamma solid solution phase of the copper-manganese alloys may tend at high manganese compositions. The moments are parallel to the face-centered tetragonal c axis with the direction of moments alternately pointed upward and downward at distances of $\frac{c}{2}$ along the c axis. There are 4 manganese atoms per unit magnetic cell as there are in the crystal unit cell. The symmetry of the magnetic unit cell is tetragonal. The directions and positions of the 4 manganese atoms in such a magnetic cell are:

$$+. \ 000, \frac{11}{22}0 \quad ;$$

$$-. \ \frac{1}{2}0\frac{1}{2}, \ 0\frac{11}{22} \quad .$$

The magnetic structure factor $F_m(hkl)$ of such an antiferromagnetic structure for lines which have Miller indices (hkl) is

$$F_m(hkl) = f_m(1 + e^{i\pi(h+k)} - e^{i\pi(h+l)} - e^{i\pi(k+l)}) \quad (50)$$

where f_m is the atomic magnetic form factor which depends upon the distribution within the atom of only those electrons which contribute to the magnetic moment of the atom.

The intensity P_m of the antiferromagnetic line (hkl) is

$$P_m(hkl) \sim \frac{q^2(hkl) j_m(hkl) |F_m(hkl)|^2}{\sin^2 2\theta} \quad , \quad (51)$$

with

$$q^2 = 1 - (\vec{e} \cdot \vec{\kappa})^2 \quad (52)$$

FIG.15. Possible antiferromagnetic structure approached by the gamma solid solution phase of copper-manganese alloys at large manganese compositions.

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where $j_m(hkl)$ is the magnetic multiplicity factor, $\vec{e}$ is the scattering vector, i.e., a unit vector in the direction perpendicular to the scattering Bragg plane (hkl) , and $\vec{k}$ is a vector along the direction of alignment of the atomic magnetic moments in the cell. To estimate the angular dependence of the magnetic form factor f_m , the curve given by Shull et al.²⁴ for Mn^{++} ions as found from the paramagnetic diffuse scattering of MnO was used.

The relative calculated intensities for the suggested antiferromagnetic structure are compared in the last 2 columns of Table IV. The factors entering into the calculated magnetic intensities are also tabulated. The observed and calculated presence and absence of lines are in agreement except for the absence of the weak (201) reflection in Figure 5c. Such a (201) line having 14 per cent the integrated intensity of the observed (110) reflection may not be observable in the diffraction pattern because of the added effects of line broadening with angle and the Debye-Waller thermal factor dependence with scattering angle would depress it within the incoherent background variations. The absence of the (201) reflection in the observed neutron diffraction pattern is not sufficient reason to discard the suggested antiferromagnetic structure as a possibility. A study by neutron diffraction of the high temperature gamma phase of manganese may help to clarify this structure.

An attempt has been made to analyze the incoherent diffuse background at small angles for the copper-manganese alloys. In a neutron diffraction pattern it generally consists of contributions from nuclear spin, isotope incoherent scattering, thermal diffuse scattering, and multiple scattering.^{7,8} If the sample is paramagnetic, there is present also a paramagnetic incoherent scattering.²⁴ In the case of a random substitutional solid solution there should be an additional contribution to the incoherent scattering due to the randomness of atoms on the lattice sites. The differential neutron scattering cross section per atom per unit solid angle due to this atomic disorder can be given, by analogy with the corresponding quantity for X-rays,³⁸ as

$$\frac{d\sigma_R}{d\Omega} = x(1-x)(b_{Cu} - b_{Mn})^2 \quad (53)$$

$$x = \frac{\text{Mn atoms}}{\text{Cu atoms} + \text{Mn atoms}}$$

As the atomic scattering factors of X-rays are always of the same sign, the difference of X-ray scattering factors of copper and manganese occurs in Equation 53. With neutrons, the opposite signs of b_{Cu} and b_{Mn} result in a considerable contribution to the background from this source. In the case of neutrons this random crystal scattering is isotropic because the neutron coherent amplitudes are isotropic.

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TABLE IV

Miller Indices, Multiplicities, Magnetic Structure Factors,
Interplanar Spacings, Magnetic Form Factors, Scattering
Angles, q^2 -Factors, Relative Calculated and Observed
Antiferromagnetic Neutron Intensities for the
Suggested Antiferromagnetic Structure

hkl	J	F _m	d*	f _m **	2θ	q ²	Calc*** P/P ₁₁₀	Obs. P/P ₁₁₀
100	4	0						
001	2	4f _m	3.65Å	0.76	18.8°	0.00	0.00	0.0 ± 0.1
110	4	4f _m	2.66	0.62	25.8	1.00	1.00	1.0
101	8	0					0.00	0.0
111	8	0					0.00	0.0
200	4	0					0.00	0.0
002	2	0					0.00	0.0
210	8	0					0.00	0.0
201	8	4f _m	1.67	0.28	41.8	0.80	0.14	0.0
102	8	0					0.00	0.0

*d-spacings calculated from X-ray data of alloy 85Mn - 15Cu having a = 3.76Å and c = 3.65Å.

**f_m taken from magnetic form factor curve in Reference 24.

***Debye-Waller temperature dependence not included.

The observed incoherent neutron intensity level (at scattering angle of ten degrees on the diffraction patterns) was converted to observed differential scattering cross section per atom per steradian for each of the alloys. By analogy with the expression for the intensity of a X-ray diffraction line for flat samples,⁹ in the neutron case,^{7,8}

$$P_{hkl} = P_0 \frac{\lambda^3 l h \rho' e^{-\mu h} \sec \theta}{4\pi r \rho \sin^2 2\theta} j_{hkl} N^2 F_{hkl}^2 \quad (54)$$

where P_{hkl} is the total power in a (hkl) reflection as measured by a counter slit of height l at a distance r from the specimen, P_0 the primary beam power, ρ' the apparent density of the powder, ρ the density of the solid crystal, $e^{-\mu h}$ the transmission of the specimen of thickness h , N the number of unit cells per cubic centimeter of crystal, and other symbols as previously defined. The observed integrated area A_{Obs} under a powder diffraction line (in units of radians/time) is

$$A_{Obs} = \frac{W}{r} P_{hkl} \quad (55)$$

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Thus

$$A_{\text{obs}} = \frac{w}{r} \frac{P_0 \lambda^3 l h}{4\pi r} \frac{\rho'}{\rho} \frac{jF^2 N^2 e^{-\mu h} \sec \theta}{\sin^2 2\theta}$$

$$= K \frac{\rho'}{\rho} \frac{jF^2 N^2 e^{-\mu h} \sec \theta}{\sin^2 2\theta} \quad (56)$$

where w is the width of the counter slit, and

$$K = \frac{P_0 \lambda^3 l h w}{4\pi r^2} \quad (57)$$

From the known neutron coherent scattering amplitude of copper and the observed (111) diffraction intensity of the powdered copper sample, the constant K for the experimental arrangement was determined.^{8,24} The observed differential scattering cross section per atom per steradian can then be found by substitution of Equation 57 into the relation between the detected neutron counts per unit time, I , and the differential cross section $\frac{d\sigma}{d\Omega}$:

$$I = \frac{d\sigma}{d\Omega} \frac{P_0 \eta h}{\cos \theta} \frac{l w}{r^2} \quad (58)$$

where η is the density of atoms in the sample.

Solving Equation 58 for the cross section gives

$$\frac{d\sigma}{d\Omega_{\text{obs}}} = \frac{\lambda^3 I}{4\pi \eta K \cos \theta} \quad (59)$$

For the experimental arrangement used

$$\frac{d\sigma}{d\Omega_{\text{obs}}} = 0.0083I \quad (60)$$

where the observed differential cross section is expressed in barns per atom per steradian and the observed intensity in counts per minute. The observed differential cross section is plotted in Figure 16a.

The contribution to the observed diffuse scattering due to multiple scattering in the samples was calculated from tables* prepared by Brockhouse et al.,^{43,44} and are based on an assumption of isotropic scattering. The multiple scattering for a given specimen is then found by knowledge of two parameters:

$$\tau = \ln T = \text{total cross section of the specimen per unit area} \quad (61)$$

(normal incidence)

*The authors are indebted to Dr. B. N. Brockhouse for use of the tables in advance of publication. (Private communication).

FIG.16. Analysis of the observed diffuse neutron scattering at low angles (10°) for the copper-manganese alloys. (The paramagnetic contribution (f.) is estimated from the residue scattering after contributions from other effects are removed.)

and

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$$\omega = 1 - \frac{n\sigma_a}{\ln T} = \frac{\text{scattering cross section of specimen}}{\text{total cross section of specimen}} \quad (62)$$

As the copper-manganese neutron patterns can be calculated to have a considerable isotropic incoherent background due to crystal disorder, γ and ω were redefined so that the total observed cross sections of the specimens are first corrected for the isotropic scattering cross section contribution. The isotropic scattering cross sections in these cases are σ_R , the total cross section due to randomness, and $\sigma_S + I$, the contribution of nuclear spin and isotope effects to the incoherent scattering. $\ln T$ in Equations 61 and 62 was replaced by

$$\ln T - n\sigma_R - n\sigma_S + I \quad (63)$$

where n is the number of atoms per unit area of sample. The effective differential cross section per atom for multiple processes is given in Figure 16b as a function of atomic per cent manganese. The decrease of multiple scattering with increased manganese is due primarily to the greater absorption cross section of manganese. The known thermal absorption cross sections⁴⁵ of copper and manganese were corrected to a neutron velocity corresponding to a wavelength of 1.19 Angstroms by the $1/v$ dependence of absorption upon neutron velocity.

The thermal vibration contribution to the diffuse scattering

$$\frac{d\sigma_T}{d\Omega} = \bar{b}_0^2(1 - e^{-2W}) \quad , \quad (64)$$

where $\bar{b}_0$ is the mean neutron scattering amplitude per atom, and e^{-2W} is the Debye-Waller factor, was neglected. At these small scattering angles (10°) the exponential factor is nearly unity.

The contribution due to nuclear spin and isotopic diffuse scattering was estimated from the difference between the total bound scattering cross sections, as would be observed in transmission measurements corrected for absorption in the sample and magnetic effects, and the coherent scattering cross section:

$$\sigma_S + I = \sigma_s - \sigma_{coh} \quad (65)$$

where $\sigma_S + I$ = total incoherent cross section due to nuclear spin and isotope effects.

σ_s = total bound scattering cross section.

As the total coherent scattering cross section is

$$\sigma_{\text{coh}} = 4\pi b^2 \quad , \quad (66)$$

where a is the coherent neutron amplitude, the differential cross section for this process is

$$\frac{d\sigma_{S+I}}{d\Omega} = \frac{1}{4\pi} (\sigma_S - \sigma_{\text{coh}}) \quad (67)$$

since the scattering is isotropic. For copper⁸

$$\begin{aligned} \sigma_S(\text{Cu}) &= 7.8 \text{ barns} \\ \sigma_{\text{coh}}(\text{Cu}) &= 7.3 \text{ barns} \\ \sigma_{S+I}(\text{Cu}) &= 0.5 \text{ barn} \\ \frac{d\sigma_{S+I}(\text{Cu})}{d\Omega} &= 0.04 \text{ barn/steradian} \end{aligned} \quad (68)$$

Similarly for manganese⁸

$$\begin{aligned} \sigma_S(\text{Mn}) &= 2.2 \text{ barns} \\ \sigma_{\text{coh}}(\text{Mn}) &= 1.35 \text{ barns} \\ \sigma_{S+I}(\text{Mn}) &= 0.85 \text{ barn} \\ \frac{d\sigma_{S+I}}{d\Omega}(\text{Mn}) &= 0.07 \text{ barn/steradian} \end{aligned} \quad (69)$$

The differential cross section per atom for isotope and nuclear spin contribution for a copper-manganese alloy of composition x manganese and $(1 - x)$ copper atoms per total atoms is then

$$\frac{d\sigma_{S+I}}{d\Omega} = x \frac{d\sigma_{S+I}(\text{Cu})}{d\Omega} + (1 - x) \frac{d\sigma_{S+I}(\text{Mn})}{d\Omega} \quad (70)$$

$= 0.07x + (1 - x)0.04$ barns per atom per steradian,
which is plotted in Figure 16d.

Before the subtraction of the spin, isotope and random crystal contributions from the observed diffuse scattering, Figure 16a, the multiple scattering, Figure 16b, was subtracted, and the resulting curve corrected for neutron absorption in the sample. The absorption attenuation factor is

$$e^{-\bar{\sigma}_a \eta h \sec \theta} \quad (71)$$

where

$$\bar{\sigma}_a = (1 - x) \sigma_a(\text{Cu}) + x \sigma_a(\text{Mn}),$$

the average absorption cross section per atom.

Figure 16c is the observed total differential scattering cross section corrected for multiple scattering and absorption in the samples.

The differential scattering cross section Equation 53 due to crystal disorder assumes that no long range crystal order is present. Any short range crystal ordering, by analogy with X-rays, should be an alternating variation above and below this random scattering. The calculated crystal disorder contribution to the differential diffuse scattering cross section for the copper-manganese system is, from Equation 53,

$$\frac{d\sigma_R}{d\Omega} = 1.19x(1 - x) \text{ barns per steradian per atom} \quad (72)$$

The cross section as given by Equations 53 and 72 will overcorrect for the effect of crystal disorder by an amount depending upon the contribution of short range crystal order to the observed (100) maximum. Less than one-third the broad line is caused by crystal short range order. The decrease in the observed diffuse scattering level because of this short range crystal ordering is less than one-half of one-third the peak intensity of the observed (100) line. For the alloy 48Mn - 52Cu the calculated contribution given by Equation 72 will at most overcorrect the observed diffuse scattering by 0.05 barn per atoms per steradian. The vertical lines in Figure 16e indicate the estimated lower limit of this contribution to the observed scattering. At compositions having smaller (100) intensities a correspondingly smaller error can be expected.

After subtracting the spin, isotope, and random crystal contributions, Figure 16d and 16e, from the observed scattering corrected for absorption and multiple scattering in the sample, Figure 16c, the residue, Figure 16f, is an estimate of the paramagnetic contribution to the diffuse background at low angles. The negative values indicate cumulative errors in overcorrecting for the various contributions. The scattering first increases gradually to about 0.18 barn at 20 atomic per cent manganese, after which it gradually decreases to a value less than 0.06 barn at 50 atomic per cent manganese. Further addition of manganese up to 85 atomic per cent does not appreciably change the paramagnetic scattering.

The diffuse paramagnetic scattering is due to neutron scattering from disordered, randomly oriented paramagnetic atoms. This diffuse scattering first increases gradually by the addition of paramagnetic manganese atoms to the copper lattice. After 20 atomic per cent manganese

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the gradual decrease in paramagnetic scattering is due to the increase of the short range magnetic order reflection, Figure 10. At about 50 atomic per cent, when the broad (100) line is a maximum, the paramagnetic diffuse scattering is at most about 0.06 barn. Further addition of manganese atoms, while decreasing the short range magnetic order (100) reflection, Figure 10, does not result in a corresponding increase in the diffuse paramagnetic scattering. This indicates that the formation of a long range antiferromagnetism, such as the structure suggested in Figure 15, may be responsible at least in part for the continued small paramagnetic diffuse level. The gradual transition from short range magnetic order to the long range antiferromagnetic order is not accompanied by an appreciable intermediate diffuse paramagnetic scattering. The transition appears predominantly direct i.e., short range magnetic order to long range antiferromagnetic order, and not short range magnetic order to random magnetic moments to long range antiferromagnetic order.

The maximum observed paramagnetic scattering of 0.18 ± 0.06 barn at 20 atomic per cent manganese is larger than the 0.06 barn found by Shull and Wilkinson⁴⁶ for alpha manganese at room temperature. The larger value at 20 atomic per cent manganese shows that the average magnetic moment per atom in this alloy is greater than the average moment per atom in alpha manganese. The gradual decrease of paramagnetism following the 20 per cent composition does not necessarily mean that the average moment per atom is here decreasing. In this region the effect of short range magnetic ordering is effective. This prevents further interpretation of the observed paramagnetic scattering in terms of average atomic moments as a function of composition. There is some evidence in the region following 50 atomic per cent manganese that the average magnetic moment per paramagnetic atom may be decreasing with increasing manganese concentration. The integrated intensity of the (100) reflection, Figure 10, decreases substantially without an increase in the paramagnetic diffuse level. The formation of the antiferromagnetic (110) line in the alloys 69Mn - 31Cu and 75Mn - 25Cu does not appear sufficiently intense to account fully for the large depression of the (100) reflection.

IX. SUMMARY AND CONCLUSIONS

A neutron diffraction study of the gamma substitutional solid solution phase of a series of copper-manganese alloys up to 85 atomic per cent manganese has been made. The diffraction patterns of the alloys were examined for the presence of superlattice lines.

A broad neutron diffraction line was observed in the region of the face-centered cubic (100) reflection. Its dependence upon composition and temperature was found. The reflection was shown to be predominantly due to short range magnetic ordering. The domains of ordering were found from the observed width of the line. An estimate was made of the upper limit of the contribution of short range crystal ordering to the (100) line. Possible structural models were presented to account for the observed magnetic correlation of the broad line and of its observed interplanar spacing.

At concentrations greater than 69 atomic per cent manganese a neutron diffraction line was observed at the (110) face-centered cubic position. Its temperature and composition dependence was found. The line was shown to be due to long range antiferromagnetism. The Neel temperature for the alloy 85Mn-15Cu was determined by the temperature at which the line vanished. A structure was proposed to account for the observed antiferromagnetism.

An analysis was made of the observed incoherent diffuse scattering at small scattering angles (10° angle). Corrections for the known contributions to the incoherent scattering were made. The residue scattering gave an estimate of the amount and composition dependence of the paramagnetic scattering. The interrelation of the paramagnetic scattering with both the short range magnetic ordering and the antiferromagnetic ordering was discussed. Evidence was given that the average magnetic moment per paramagnetic atom in at least some of the alloys is larger than that of random alpha manganese.

In conclusion for the series of copper-manganese alloys studied:

1. No long range atomic ordering was found, substantiating the less sensitive X-ray findings of Ellsworth and Blake.³
2. Short range magnetic coupling in domains of about 10 Angstroms occurs over a broad region of compositions.
3. The short range magnetic ordering maximizes in the region of 50 atomic per cent manganese.

4. The short range magnetic ordering gives rise to a broad neutron diffraction line at a position corresponding to a magnetic periodicity of about one unit cell dimension.
5. Short range crystal ordering contributes at most one-third of the observed intensity of the broad line.
6. The short range magnetic coupling is not greatly temperature dependent.
7. The broad neutron line may be caused by (a) short range ferro-type coupling between next-nearest paramagnetic manganese atoms, copper atoms being the nearest-neighbors to a given manganese atom or, (b) short range ferri-type coupling between manganese and nearest-neighbor copper atoms, assuming copper becomes paramagnetic in these alloys.
8. Long range antiferromagnetism gradually forms at manganese concentrations above 69 per cent, whereas the short range coupling gradually decreases.
9. The amount of antiferromagnetism increases as the manganese composition is increased from 69 atomic per cent to 85 atomic per cent.
10. The Neel temperature is $380^{\circ}\text{K} \pm 10^{\circ}\text{K}$ for the alloy 85Mn-15Cu.
11. The antiferromagnetism may be due to an antiferromagnetic coupling between manganese atoms as in Figure 15.
12. Paramagnetism contributing to the diffuse incoherent neutron background at small scattering angles is a maximum at 20 atomic per cent manganese.
13. The average magnetic moment per atom in at least some of the alloys is larger than that of alpha manganese.

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