

Magnetic Remanence in Cu(Mn) Alloys*

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An experimental investigation of the saturated magnetic remanence in dilute Cu(Mn) alloys ranging from 0.47 to 10.0 at. % Mn has been carried out in the temperature range 0.6° to 40°K. At low temperatures the remanence has a temperature dependence resembling that of a paramagnetic material in a constant magnetic field H_0 . Domain sizes derived from the estimated remanence at 0°K are larger than expected from the assumption that domain boundaries coincide with nearest neighbor Mn pairs. At higher temperatures the effective magnetic field H_T is defined on the basis of the deviation of the remanence from the constant-field curve. For the smaller concentrations the temperature dependence of H_T/H_0 appears intermediate between $[1 - (T/T_c)^2]^{\frac{1}{2}}$ and $[1 - (T/T_c)^2]$. The ratio H_0/T_c is approximately the same for all concentrations.

INTRODUCTION

THE phenomena encountered in alloys of manganese in copper represent a cooperative transition in a dilute magnetic system. Previous experimental investigations have revealed the major features of this transition. These are a susceptibility maximum and a small remanent magnetization which occurs at temperatures below that of the maximum after application of a field.¹ Some of the qualitative properties of this remanence are its saturation in sufficiently high fields,^{2,3} its decay with time,⁴ and its marked increase at lower temperatures.³ The unusual temperature dependence, indicated by the early results,³ and the regular variation with concentration have now been investigated in greater detail with respect to both temperature and concentration. One of the original objects of this further work was to ascertain the limiting saturated remanence at lower temperatures. For this reason and also for the purpose of making meaningful measurements on more dilute alloys, a He³ refrigerator was incorporated in our apparatus. Following a brief description of the alloy preparation and of the magnetic measurements, a discussion is given of the method of measurement of the quantity of principal interest, the saturated remanence. The main results concerning the temperature dependence are then given. Finally, an analysis of the results is presented leading to an estimate of the limiting remanence and to the derivation of an effective internal magnetic field together with its temperature dependence.

EXPERIMENTAL PROCEDURE

Alloy Preparation

The alloys were prepared from American Smelting and Refining 99.999% copper and Johnson-Matthey

manganese. The manganese was further refined by melting in a hydrogen atmosphere to minimize the presence of oxides. The manganese and copper were placed in an evacuated, sealed quartz tube. The charge was then heated to 1200°C and the melt agitated. After homogenization for several hours at about 900°C, the alloy was quenched in water. Subsequent chemical analysis showed the manganese concentration to be close to the nominal value and to vary only slightly along the length of the ingot. Spherical samples were machined from the ingot to a diameter of 0.32 in. After machining, the spheres were etched in dilute HNO₃ to about 0.31-in. diam. The samples were polycrystals with average grain size about 2-3 mm.⁵ The weight of each sphere was subsequently used in determining the absolute magnitude of the magnetization.

Magnetic Measurements

The measurement of magnetic moment is performed by means of a sample motion technique similar in principle to that used elsewhere.⁶ The essential features are shown in Fig. 1. The sample, a $\frac{5}{16}$ -in. diam sphere, is held in a copper sample holder and is translated a regulated distance between opposing pickup coils. Sample and coils are situated between the tapered pole pieces of a 12-in. Varian magnet (not shown). Thermal equilibrium between sample and sample holder is secured by varnishing the sample into the hemispherical well of the sample holder. The sample holder is connected by a flexible thermal conduit to a concentric cylindrical shell to which is attached the pick-up coils and the evaporator of the liquid He³ refrigerator. The latter is of the Reich-Garwin type.⁷ The whole assembly is suspended inside a vacuum-tight can surrounded by liquid He⁴. Motion is transmitted to the sample by a

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¹ J. Owen, M. E. Browne, V. Arp, and A. F. Kip, *J. Phys. Chem. Solids* **2**, 85 (1957).

² I. S. Jacobs and R. W. Schmitt, *Phys. Rev.* **113**, 459 (1959); *Suppl. Physica* **24**, S174 (1958).

³ O. S. Lutes, International Conference on Electronic Properties of Metals at Low Temperatures, Geneva, New York, 1958 (unpublished), p. 183.

⁴ R. W. Schmitt and I. S. Jacobs, *J. Phys. Chem. Solids* **3**, 324 (1957).

⁵ It appears that coarse-grained samples do not differ significantly from single crystals in their magnetic properties. In our earlier measurements³ one of the samples (2.4 at. %) was a zone-leveled crystal. Its remanent properties were qualitatively like those of the polycrystalline samples. This furnishes support for the view that the magnetic properties are not of secondary origin but are instead characteristic of the alloy.

⁶ M. Desirant and D. Shoenberg, *Proc. Phys. Soc. (London)* **60**, 413 (1948); W. E. Henry, *Phys. Rev.* **88**, 559 (1952).

⁷ H. A. Reich and R. L. Garwin, *Rev. Sci. Instr.* **30**, 7 (1959).

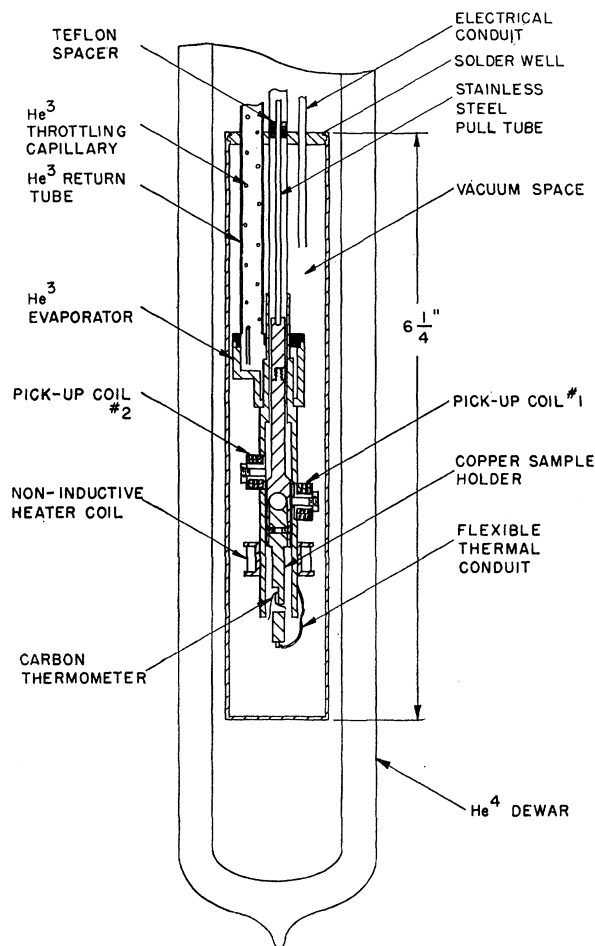


FIG. 1. Cryostat and sample chamber.

long thin-wall stainless steel pull tube which travels through a double O-ring seal at room temperature. Power is furnished by an external solenoid actuator. The response of a fluxmeter connected to the pickup coils is proportional to the magnetization of the sample, contributions from the sample holder either being negligible or constituting a small correction. The fluxmeter in use is a long-period galvanometer (Rubicon type *T*) which is highly overdamped. With this galvanometer the sensitivity of the apparatus in terms of galvanometer deflection, at scale distance 1 m, per unit magnetic moment, is $8.2 \text{ mm-gauss-erg}^{-1}$. Because of the small magnetizations characteristic of the alloys measured, amplification of the galvanometer deflection was found necessary. This was accomplished by a photoelectric system previously described.⁸ The use of this system increases the effective sensitivity of the magnetic measurement by a factor of about 100.

Temperatures in the liquid He^4 range were produced by regulating the He^4 vapor pressure while maintaining

exchange gas in the surrounding chamber. Above 4.2°K temperatures were maintained by supplying heat via the heater coil shown. Between 0.6° and 1.3°K the He^3 refrigerator was used, with the vapor pressure in the evaporator regulated by the heater.

The temperature of the samples was determined from the measured resistance of an Allen-Bradley carbon resistor, nominal 0.1 w, 33 ohms. This thermometer had been previously calibrated against the magnetic susceptibility of a compressed sphere of chromium potassium alum, occupying the position of the sample. The salt was also used in determining the absolute calibration of the fluxmeter. The susceptibility was assumed to obey Curie's law throughout the range of interest, 0.6° to 40°K . The effective Curie constant was determined at 4.2°K . Care was taken that the measuring current be kept sufficiently small at all temperatures to avoid excessive Joule heating of the thermometer.⁹ At the lowest temperatures slight frictional heating due to the motion was sometimes observed, but the resulting temperature change measured by the carbon thermometer was at all times tolerable.

Remanence Measurements

As shown previously,² the remanence may be saturated isothermally by application of a sufficiently large field, or by cooling in a smaller field from some higher temperature. In the present investigation the field-cooling method was usually used, because of two considerations. First, the fields required at low temperatures were higher than available with our magnet. Second, when operating the sample in isolation from the bath, either above 4.2°K or below 1.3°K , high field pulse techniques would be suspect because of the possibility of eddy-current heating. Saturation was achieved, therefore, by application of the maximum field, 13.3 koe, at a temperature sufficiently high for isothermal saturation, usually above the temperature of the susceptibility maximum, and then cooling to the temperature of interest. The field was then removed slowly enough to insure a negligible eddy-current effect. The residual pole-piece field was minimized by surrounding the Dewar tail with a cylindrical soft-iron shield. The residual field inside the shield was measured with a rotating coil gaussmeter during a separate experiment and found to be less than 5 oe. It thus had a negligible effect on the remanent moment measurements, since the magnetic moment due to the paramagnetic susceptibility of the sample was not appreciable in fields this small. Determinations of the saturated remanence at lower temperatures were carried out by further cooling, care being taken to insure that no cooling took place without the presence of the field.

⁸ O. S. Lutes, *Rev. Sci. Instr.* **31**, 780 (1960).

⁹ J. R. Clement and E. H. Quinell, *Rev. Sci. Instr.* **23**, 213 (1952); R. Berman, *Rev. Sci. Instr.* **25**, 94 (1954).

TABLE I. Conditions for saturating remanence.

Concentration (at. %)	T (°K)	H_I (koe)	$3.5 \times 10^3 c/T$
1.0	3.0	13.5	11.6
	4.2	8.0	8.3
1.8 ^a	4.2	14.0	15.0
4.6	10.0	12.0	16.0

^a Data taken from reference 2.

RESULTS

Saturation of Remanence

According to Jacobs and Schmitt² the field required for saturating a 1.8% sample at 4.2°K by field-cooling is about 10% of that required for isothermal saturation. For convenience we may call these fields H_F and H_I , respectively. In addition previous results³ indicate that H_I increases with increasing concentration and decreasing temperature. In order to better understand this dependence, we first of all determined the isothermal remanence curves for the 1.0% sample at 4.2° and 3.0°, and for the 4.6% sample at 10.0°K. The results are shown in Fig. 2. We may first observe from Fig. 2 that H_I depends inversely on temperature. By comparison of these results with those of Jacobs and Schmitt, we may also conclude that H_I increases with concentration. The available data can in fact be approximated within about 25% by the formula

$$H_I \cong 3.5 \times 10^3 c/T, \quad (1)$$

where c is the Mn concentration expressed as atomic fraction, and H_I is in kilo-oersteds. The extent of agreement of this relation is summarized in Table I.

Since it is evident that the higher concentrations cannot be saturated isothermally except at temperatures well above 4.2°, it is next necessary to examine the approach to saturation upon field-cooling in different fields with different starting and final temperatures. The

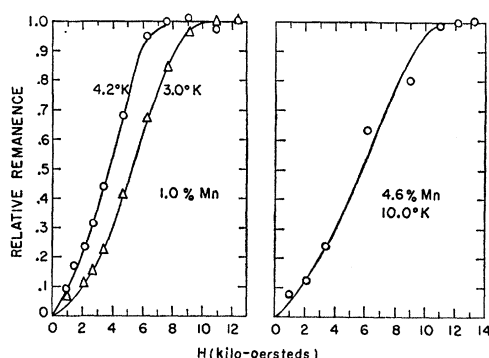


FIG. 2. Isothermal saturation of remanence. The remanent moment is shown relative to its approximate saturated value. H is the field applied and then removed prior to measurement.

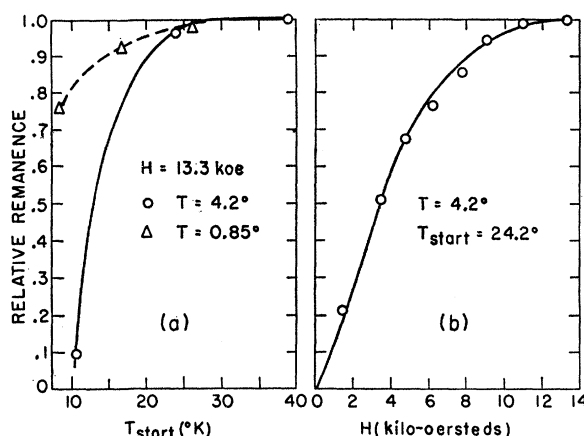


FIG. 3. Remanence after field-cooling, (a) in 13.3 koe from different starting temperatures, (b) from 24.2°K in different fields.

results of such an investigation are given in Fig. 3 for the 10% concentration. It is evident that H_F is a function of the temperature from which the sample is cooled. Figure 3(b) shows H_F to be about 14 koe for a starting temperature of 24°K. From Fig. 3(a), a field of 13.3 koe appears adequate for saturating the remanence (within 2–3%) for starting temperatures greater than 30°K, and for final temperatures of both 4.2° and 0.85°K. Comparing these numbers with Eq. (1) enables us to reach the following useful conclusion:

$$H_F \cong H_I(T_{\text{start}}). \quad (2)$$

Expressed in words, the field required for saturation by field-cooling is that required for isothermal saturation at the starting temperature, and is independent of the final temperature. Equation (2) is consistent with the interpretation of thermomagnetic remanence given by Néel¹⁰ for single domain particles. It should also be noted that Eq. (1) is in agreement with the same analysis, provided we assume a particular temperature dependence for the domain magnetization. This conclusion follows from the proportionality between coercive force and domain magnetization. If the latter is taken as inversely proportional to temperature, Eq. (1) results. This is, in fact, the approximate temperature dependence we observe for the saturated remanence, as shown in a later section.

Equations (1) and (2) are, of course, qualitative relations expressing the condition for obtaining the saturated remanence experimentally. These relations were used as a minimum condition for saturating the samples of smaller concentration. For example, the remanence data for the 1.0% alloy were obtained by field-cooling from 8°K in 13.3 koe, well above the indicated minimum field of 4.4 koe. Some idea as to limitations on the use of these relations may be obtained from

¹⁰ L. Néel, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 191.

previous results. For example, in the case of a 1.8% alloy field-cooled from 77°K, Eqs. (1) and (2) give $H_F=0.8$ koe, as compared with 1.5 koe found experimentally by Jacobs and Schmitt.² A greater difference comes from the result of Kouvel¹¹ indicating that a 30% Mn sample field-cooled in 10 koe from 300°K was not saturated, whereas Eqs. (1) and (2) give $H_F=3.5$ koe. It is not surprising that departure from these relations will occur for starting temperatures much greater than the susceptibility maximum, since at such temperatures stable remanence presumably does not exist. H_F in this case should more properly be related to some lower temperature at which domains begin to form.

Time Decay

The remanent moment decayed with time, a phenomenon also noticed in the earlier investigations.⁴ A study was made of the time decay at various concentrations and temperatures. It was found that the decay was approximately exponential in the beginning and could, therefore, be described by a time constant. Suitable corrections, generally small, of the remanence data were made for the decay. Following this early stage the rate of decay appeared to diminish with time. This behavior is illustrated in Fig. 4 for four cases in which detailed studies were made. The data are plotted on a logarithmic time scale following the work of Street and collaborators on magnetic viscosity in more concentrated Cu(Mn) alloys and in other systems.¹² The latter work has shown that changes in magnetization after application of a field frequently occur as a linear function of $\log t$. This dependence may also be characteristic of our alloys at larger values of time, as indicated in Fig. 4. In the formal analysis of viscosity effects¹² the $\log t$ dependence is associated with the presence of many activation energies, whereas exponential time decay results from a single activation energy. A possible reason

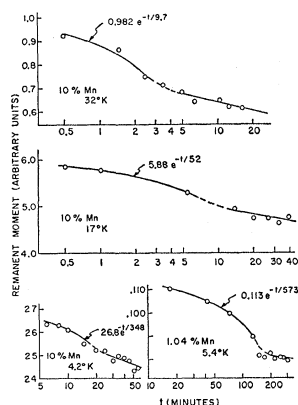


FIG. 4. Time decay of remanence. Exponential expressions apply to solid sections of curves to left of dashed portions. The approximate time constant in minutes is given by the denominator in each expression.

¹¹ J. S. Kouvel, J. Appl. Phys. **31**, 142S (1960).

¹² R. Street, J. Appl. Phys. **31**, 310S (1960); R. Street and J. C. Woolley, Proc. Phys. Soc. (London) **A62**, 562 (1949); **B63**, 509 (1950); **B69**, 1189 (1956); R. Street, J. C. Woolley, and P. B. Smith, Proc. Phys. Soc. (London) **B65**, 679 (1952).

TABLE II. Parameters of saturated remanence.

Concentration (at. % Mn)	M_{s0} (% alignment)	H_0 (koe)	T_c (°K)
0.47	1.9	3.4	5
1.04	2.7	5.3	7
4.6	5.0	14.2	25
10.0	6.9	29.0	40

for more nearly exponential decay in more dilute alloys is that the relative scarcity of complicated solute atom groupings leads to a simpler type of domain.

Temperature Dependence

The saturated remanence, designated by M_s and measured as described above, was determined as a function of temperature for Mn concentrations of 0.47, 1.04, 4.6, and 10.0 atomic percent. The results are shown in Figs. 5 and 6.¹³ The temperature dependence is evidently different from that associated with spontaneous magnetization in a ferromagnet. It is similar, instead, to the temperature dependence of paramagnetic susceptibility. This suggests a formal analysis of the data by comparison with the Brillouin function $B_J(gJ\mu_B H/kT)$.¹⁴ This function gives the degree of magnetization of a paramagnetic material for a given ratio of magnetic field to temperature. In addition to this ratio it requires for its evaluation the angular momentum quantum number, J , and the gyromagnetic ratio, g , of the magnetic entity. μ_B is the Bohr magneton, and k is Boltzmann's constant. The following relation is now assumed near $T=0$:

$$M_s/M_{s0} = B_J(gJ\mu_B H_0/kT), \quad (3)$$

where J and g are assigned values consistent with the susceptibility and spin resonance data,¹ i.e., $J=2$ and $g=2$. M_s is the remanent magnetization at temperature T , and M_{s0} is interpreted as the limiting remanent magnetization at 0°K. H_0 is the effective internal field. In Figs. 5 and 6 the remanence data are compared with Eq. (3). M_{s0} and H_0 were chosen for each concentration to give the best low-temperature agreement. This choice was made by solving simultaneously for M_{s0} and H_0 using experimental values of M_s in pairs. The appropriateness of the assumption of a limiting constant effective field is reflected in how well the curves of Figs. 5 and 6 agree with the data as $T \rightarrow 0$. Since any two points may be made to agree with Eq. (3) by proper choice of M_{s0} and H_0 , the unique determination of these two quantities requires agreement over a range of tem-

¹³ The remanence is plotted as galvanometer response per gram of sample to emphasize that this quantity is more accurately known than the absolute value of the magnetization. The latter may be easily derived by using the previously stated calibration constant, 8.2 mm-gauss-erg⁻¹. Values of the remanence in terms of percent alignment may be obtained through the following relation: M_{s0} (% alignment) = $(0.035/c) M_{s0}$ (mm/gm).

¹⁴ See, for example, C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., Chap. 9, p. 216.

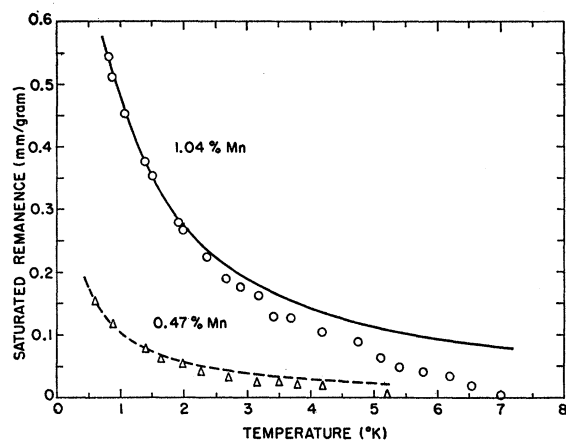


Fig. 5. Temperature dependence of saturated remanence, M_s , for 1.04% and 0.47% alloys. The saturated remanence is given in units of galvanometer deflection per gram of sample. The solid curve is the paramagnetic relation for $J=2$, $M_{s0}=0.808$ mm/gm, and $H=5.30$ koe. The dashed curve is the paramagnetic relation for $J=2$, $M_{s0}=0.251$ mm/gm, and $H=3.40$ koe.

perature including at least three points at the low-temperature end. The extent of this agreement is evident from the figures. The agreement is probably best for the 1.0% alloy, for which the Brillouin function is consistent with the data between 0.8° and 2.0°K . Table II contains the values of M_{s0} and H_0 deduced for each alloy, M_{s0} being expressed in per cent alignment (see footnote 13). It is evident that both quantities increase with Mn concentration.

DISCUSSION

Domain Size

It was shown in the preceding section that at small concentrations the temperature dependence of the saturated remanence at low temperatures could be represented by a Brillouin function with a constant field, H_0 , and a limiting remanence M_{s0} . The latter quantity must somehow represent the unbalanced moment between spins oriented parallel and anti-parallel to the previously applied field. One possible explanation of the remanence might be the statistical variation of Mn population between domains. The domain structure could then be formed in such a way that the domains having excessive numbers of Mn atoms would tend to have magnetizations aligned with the field direction, and those with deficiencies aligned opposite to the field. This structure can be described as consisting of ferromagnetic domains antiferromagnetically coupled. The number of balanced spins contributed by a domain can be approximated on this basis to be the standard deviation of the number of Mn atoms in a domain, i.e., by

$$\Delta n = [Nc(1-c)]^{1/2}, \quad (4)$$

where N is the number of lattice sites in the domain and Δn the standard deviation of Mn atoms. Since the total

TABLE III. Domain size estimated from saturated remanence.

Concentration (at. % Mn)	N	l_D (cm)
0.47	6×10^5	2×10^{-6}
1.04	1.4×10^6	1×10^{-6}
4.6	0.08×10^6	0.4×10^{-6}
10.0	0.02×10^6	0.3×10^{-6}

number of Mn atoms in the domain is given approximately by $n=Nc$, the fractional deviation is

$$\Delta n/n \cong [1/Nc]^{1/2}, \quad c \ll 1. \quad (5)$$

Equating the latter quantity to the experimentally determined fractional alignment enables us to estimate N , and thus the domain size. Denoting the linear dimension of a domain by l_D , we have

$$l_D \cong [W/A\rho cM_{s0}^2]^{1/2}, \quad (6)$$

where W and ρ are, respectively, the atomic weight and density, and A is Avogadro's number. M_{s0} is to be expressed here as fractional alignment. Table III shows N and l_D deduced in this way for the different concentrations. The domain size appears to become smaller at higher concentrations.

A picture of domain structure which has been advanced in discussions of the susceptibility behavior¹⁵ associates domain boundaries with nearest neighbor (antiferromagnetic) pairs. The Mn spins in such pairs are oppositely oriented and govern the orientations in their respective (ferromagnetic) domains. We may attempt to compare the domain size estimated from this

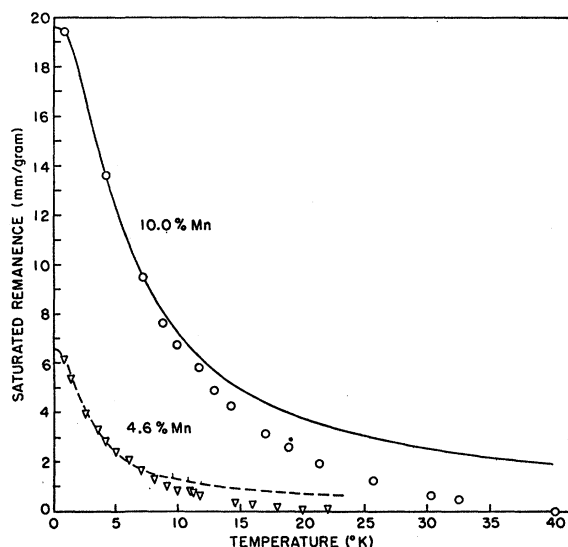


Fig. 6. Temperature dependence of saturated remanence, M_s , for 10.0% and 4.6% alloys. The solid curve is the paramagnetic relation for $J=2$, $M_{s0}=19.55$ mm/gm, and $H=29.0$ koe. The dashed curve is the paramagnetic relation for $J=2$, $M_{s0}=6.53$ mm/gm, and $H=14.2$ koe.

¹⁵ A. J. Dekker, Physica 24, 697 (1958).

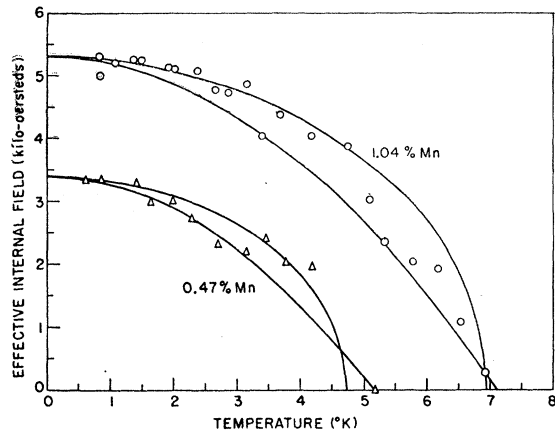


FIG. 7. Temperature dependence of effective field in 1.04% and 0.47% alloys. For each concentration the upper curve represents the relation $H_0[1 - (T/T_c)^2]^{\frac{1}{2}}$, and the lower curve represents the relation $H_0[1 - (T/T_c)^2]$, H_0 and T_c being chosen to give best agreement with the data consistent with the end points.

picture with that deduced from our data. The population density of nearest neighbor pairs in the fcc lattice (the ratio of nearest neighbor pairs to lattice sites) is given approximately by $6c^2$ for $c \ll 1$, assuming random distribution. If the distance between pairs is now taken to be the linear extent of a domain, we have

$$l_D \cong [W/6c^2 A \rho]^{\frac{1}{3}}. \quad (7)$$

Substitution in this formula gives l_D several times smaller than the value obtained from Eq. (6). For example, in the case of the 0.47% alloy Eq. (7) gives $l_D \cong 0.5 \times 10^{-6}$, as compared with 2×10^{-6} determined from Eq. (6). Stated in a different way, a domain of the size estimated from Eq. (6) contains about 60 nearest-neighbor pairs. This result suggests that the domain structure is not simply related to the incidence of Mn groupings in the alloy.

Effective Internal Field

The similarity of the low-temperature remanence curve to the magnetization of a paramagnetic material in a constant field led to the definition of an effective magnetic field, H_0 . At higher temperatures the data depart from the paramagnetic curves, as is evident from Figs. 5 and 6. This departure is in a direction indicating a decreasing effective field, which we now designate as H_T , and define by the following relation:

$$M_s/M_{s0} = B_J(gJ\mu_B H_T/kT), \quad (8)$$

where M_s is the measured moment and M_{s0} the estimated moment at 0°K, as given in Table III. The values for g , J , and μ_B are the same as before. The temperature dependence of H_T , based on the data shown in Figs. 5 and 6, is presented for each alloy in Figs. 7 and 8. The general features of the results are the systematic variation of H_0 with concentration, already discussed, and

the existence of a fairly well-defined transition temperature, T_c , at which H_T becomes zero. The shape of the curves is seen to change with concentration, with the higher concentrations developing tails. The parameters of these curves, including T_c , have been given in Table II. One of the main features of the results is the near constancy of the ratio H_0/T_c . It may also be noted that, for the smaller concentrations, T_c is approximately the temperature of the susceptibility maximum as predicted by interpolation using earlier data.¹ For the 4.6 and 10.0% alloys T_c is apparently lower than the predicted susceptibility-maximum temperature, although the breadth of the maximum and the tailing-off of H_T at these higher concentrations makes the comparison less meaningful.

It is of interest to compare the results given here with certain features of the recent Overhauser theory concerning antiferromagnetism in dilute alloys.¹⁶ According to this theory the magnetic phenomena in Cu(Mn) alloys are caused by a conduction electron spin density wave which provides an internal magnetic field of spatially-varying direction and intensity. It is possible to demonstrate a similarity between the field amplitude function $b(T)$ of the Overhauser theory and the effective field H_T , derived from our data. The former is given as follows:

$$b(T) = b(0)[1 - (T/T_c)^2]^{\frac{1}{2}},$$

where $b(0)$ is the value at 0°K. This function has been plotted in Figs. 7 and 8, with $b(0)$ and T_c chosen to agree with H_0 and T_c from our data. In addition we have shown the lower-lying parabolic relation given by

$$H(T) = H_0[1 - (T/T_c)^2].$$

The latter expression has no theoretical basis here, but is shown only for comparison. The data for the two smaller concentrations fall between these two curves. In Fig. 8 the data for the two higher concentrations fall

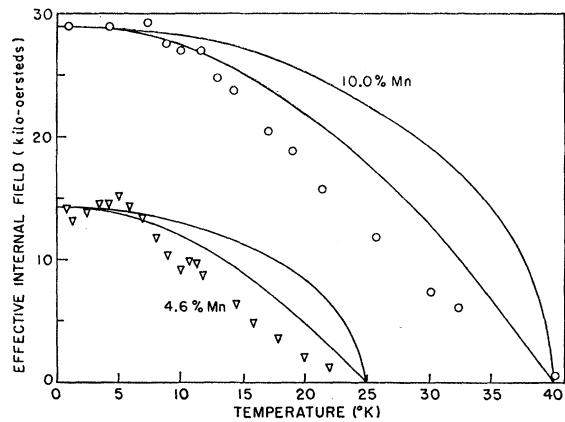


FIG. 8. Temperature dependence of effective field in 10.0% and 4.6% alloys. The curves have the same meaning as in Fig. 7.

¹⁶ A. W. Overhauser, Phys. Rev. Letters **3**, 414 (1959); J. Phys. Chem. Solids **13**, 71 (1960).

well beneath both curves except at the low-temperature extreme. In other words there appears to be a trend toward the $b(T)$ curve with decreasing Mn concentration. It should be mentioned that the transition temperatures derived from our data, and shown in Table II, are much smaller than those predicted by Overhauser from specific heat results. For example, T_c indicated from the latter for a 1 atomic per cent alloy is 27°K, as contrasted with our result of 7°K.

Concerning the magnitude of the effective field, it may be remarked that H_0 is about an order of magnitude larger than the *magnetic* field available from complete alignment of the Mn atoms. (The latter is given by $4\pi M_{\max}$, with M_{\max} equal to $n_v g J \mu_B$, n_v being the num-

ber of Mn atoms per unit volume.) This inequality is consistent with the idea that the magnetization in these alloys has its origin in exchange interactions. The possibility that these interactions take the form of a conduction-electron field tending to align the Mn atoms appears to be strengthened by the paramagnetic character of the remanent magnetization.

ACKNOWLEDGMENTS

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Impurity States in Metals

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A treatment of impurity states in metals due to Slater and Koster is extended to show the connection with the phase shift analysis of Friedel. In a simple case this allows the impurity potential to be made self-consistent. Application is made to the susceptibility and Knight shift of dilute alloys of transition metal compounds.

I. INTRODUCTION

IN a set of three papers,¹⁻³ Slater and Koster have discussed the theory of impurity states in crystals employing a Wannier function representation and using a Green's function to solve the resulting difference equations. If very restrictive conditions are placed on the problem, assuming (1) that the perturbations of only one band are important and, (2) that the perturbations caused by the impurity center are highly localized, the Green's function method gives extremely simple results. Assuming that the Wannier functions of the unperturbed problem are known, the wave functions of the electrons scattered from the impurity center can be obtained in closed form as a function of distance and energy of the incident wave.

In this particular case, the results obtained by Slater and Koster can be extended in a simple way to show the connection with the phase shift analysis of Friedel.⁴ It is possible thereby to make the scattering potential self-consistent and to obtain some simple results for charge impurities in metals. These results are particularly striking for the narrow bands and high densities of states encountered in transition element metals and

intermetallic compounds. Some clarification is also obtained of the nature of virtual states in metals and it can be seen that there is no real distinction between virtual states and bound states.

II. CONDITION OF SELF-CONSISTENCY

Following Slater and Koster, we suppose that the unperturbed lattice has a Hamiltonian H and a set of Bloch waves ψ_{nk} belonging to the n th band and \mathbf{k} th wave vector such that

$$H\psi_{nk} = E_{nk}\psi_{nk}. \quad (1)$$

We define a set of Wannier functions by the equations

$$W_n(\mathbf{r}-\mathbf{r}_i) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}_i} \psi_{nk}, \quad (2)$$

where N is the number of lattice sites in the crystal. It is easy to show that

$$HW_n(\mathbf{r}-\mathbf{r}_i) = \sum_j \epsilon_n(\mathbf{r}_j-\mathbf{r}_i) W_n(\mathbf{r}-\mathbf{r}_j), \quad (3)$$

if

$$\epsilon_n(\mathbf{r}_i) = \frac{1}{N} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_i} E_{nk}. \quad (4)$$

Let us suppose now that a perturbation V is intro-

¹ G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954).

² G. F. Koster, Phys. Rev. **95**, 1436 (1954).

³ G. F. Koster and J. C. Slater, Phys. Rev. **96**, 1208 (1954).

⁴ J. Friedel, Suppl. Nuovo cimento **7**, 287 (1958).