a shallow minimum in its variation with $\Delta\mathcal{E}$ (or composition) in the competition region.

IV. CONCLUSIONS

The room temperature magnetoresistance data for the germanium-silicon alloys can be explained by a conduction band of [111] spheroids for alloys with less than ten percent silicon in germanium. However, the data for alloys of ten to seventeen percent silicon show a different anisotropy, not in accord with the assumption of one set of spheroids. These data are fitted satisfactorily by a conduction band made up of two sets of spheroids, with an energy separation varying with composition—one set having four [111]-oriented spheroids, the other having six [100]-oriented spheroids. This is in agreement with the alloy band structure suggested by Herman[6] to explain the variation with composition of the optical band gap.[7]

This analysis does not yield unique values for the effective masses of the spheroids. However, the effective masses which fit the data for germanium and silicon satisfy the magnetoresistance symmetry condition for the ten to seventeen percent silicon alloys.

An analysis of the data to yield the energy separation of the two bands as a function of composition depends sensitively on the scattering behavior in the alloys. If the scattering in each band is assumed independent of the other, the observed Hall mobility in the competition region is only about two-thirds that expected from an analysis of the magnetoresistance. The mobilities can be correlated with the magnetoresistance if some interband scattering is assumed. Such scattering lowers the band mobilities but leaves the magnetoresistance symmetry conditions unchanged.

The author is indebted to Professor H. Brooks, Dr. F. Herman, and Dr. R. H. Parmenter for informative discussions on the problems of energy band structure and scattering processes.

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Electron and Nuclear Spin Resonance and Magnetic Susceptibility Experiments on Dilute Alloys of Mn in Cu*

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Dilute alloys of Mn in Cu are expected to show marked effects of the exchange interaction between the $3d^5$ ion core electrons of the Mn atoms and the $4s$ conduction electrons of the crystal. The simple model leads to the prediction of indirect exchange ferromagnetism; electronic Knight shift of the electron spin resonance line; nuclear Knight shift of the copper nuclear resonance; electron spin relaxation by the coupling with the conduction electrons; and a contribution to the electrical resistivity by the Elliott-Schmitt mechanism. The observed width of the electron spin resonance line suggests that the *sd* exchange interaction may be of the order of 0.2 of the interaction in the free ion. The dilute alloys appear to be antiferromagnetic, but with a ferromagnetic interaction also present which is rather stronger than calculated on the indirect exchange model. An unexpected experimental result is that the nuclear Knight shift is unaffected by the presence of Mn, suggesting that the conduction electron magnetization by the *sd* coupling is less than 1/50 of what might be expected.

It occurred to us that it might be profitable to study by electron spin resonance methods the electronic properties of metallic alloys. We were particularly interested in observing the effect on the conduction electrons of the host metal when a low concentration of a second component is added. For several reasons it was decided to emphasize at the beginning the study of dilute solutions of manganese in copper: (a) The conduction band of copper is believed to have a simple structure, containing $4s$ electrons with an approximately isotropic effective mass nearly equal to the free electron mass. (b) The presence of paramagnetic solute ions permits the application to the problem of powerful magnetic methods, including susceptibility determination; line width, intensity, and position in electron and nuclear spin resonance; and neutron diffraction.[1] (c) It was anticipated that a ferromagnetic coupling between Mn ions might result from an indirect exchange coupling[2] via the conduction electrons. (d) There was some

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[1] Neutron diffraction studies of the Cu—Mn system are being carried out at the Argonne National Laboratory under the direction of Dr. S. Sidhu, to whom we are indebted for interest and cooperation.

[2] The idea is based on the observed exchange energy difference ${}^5S-{}^7S=9473$ cm^{-1} of the $3d^54s$ configuration of free Mn$^+$. A Mn^{++} ion is viewed as magnetizing the $4s$ conduction electrons, which in turn magnetize other Mn^{++} ions by the same interaction. Similar mechanisms have been proposed by H. Fröhlich and F. R. N. Nabarro, Proc. Roy. Soc. (London) **A175**, 382 (1940); C. Zener, Phys. Rev. **81**, 440 (1951); see also M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954). The application to the Cu—Mn problem was suggested independently by J. Fisher (unpublished).

evidence[3] from susceptibility measurements that at sufficiently low concentrations the Mn dissolves in the copper in the simple configuration $3d^5$ with the ground state ^6S appropriate to the Mn^{++} ion. That is, the manganese has a half-filled $3d$ shell with five parallel electron spins. It was presumed that the two $4s$ electrons of the Mn join the common $4s$ conduction band of the alloy.

Some features of the results are these: (1) The magnitude of the ferromagnetic part of the coupling is reasonable when one uses the free-atom exchange energy. (2) The dilute alloys are antiferromagnetic at low temperature. (3) The expected large electronic Knight shift in the electron spin resonance of the Mn ions is absent. (4) The expected large change in the nuclear Knight shift of the copper nuclei does not occur. (5) The electron resonance line width is considerably narrower than expected on the Heitler-Teller-Korringa[4] mechanism translated to the present interaction using a coupling constant deduced from the known spectroscopic energy level scheme of free Mn^+ ions.

A possible conclusion is that the conduction electrons are not magnetized substantially by interaction with the Mn ions. It might be as if the Mn dissolved as a neutral atom, or a negative ion. This result is unexpected to us, but it is not out of line with metallurgical experience of the phase diagrams of manganese alloys. It is also possible that the actual magnitude of the sd interaction is not too far from expectation on the Mn^{++} model, but the spin order of the s electrons may be destroyed to produce local equilibrium.

In the present paper we shall summarize the interpretation of the experiments which have been performed. A detailed discussion of the electron resonance and static magnetic susceptibility measurements will be given in a subsequent publication by Owen, Browne, Arp, and Kip.[5]

I. ELEMENTARY CONSEQUENCES OF A 4s-3d EXCHANGE INTERACTION IN A METAL

We first consider what would happen if the magnetic behavior of the solid were dominated by an $s-d$ exchange interaction

$$\mathcal{H}'=A\mathbf{S}\cdot\mathbf{s}, \tag{1}$$

where $\mathbf{S}$ refers to a manganous ion in the state ^6S and $\mathbf{s}$ refers to an electron in the $4s$ conduction band. All the numerical estimates in this section will be made using the value of A deduced from the spectral terms of the free ion.

It is a reasonable deduction from previous susceptibility determinations that the greater part of the manganese in the alloys is in the electronic state $^6S_{\frac{5}{2}}$. This state is known to have $g=2.0$ in many salts, in agreement with the spin assignment $S=5/2$. In the alloy with Cu we must picture the Mn as bathed in the sea of conduction electrons of the $4s$ band, the normal conduction band of pure copper. Spectroscopic measurements on the free ion Mn^+ give, for the configuration $3d^54s$, the separation

$$^5S_2-{}^7S_3=9473\ \mathrm{cm}^{-1}. \tag{2}$$

It seemed not at all unlikely that there would persist in the solid solution a splitting of the same order of magnitude. The splitting (2) corresponds to a frequency of the order of

$$\Delta\nu\cong-3\times10^{14}\ \mathrm{sec}^{-1}, \tag{3}$$

and

$$\begin{aligned} A/h&=\Delta\nu/(S+\tfrac{1}{2})\cong-1\times10^{14}\ \mathrm{sec}^{-1};\\ A&=-7\times10^{-13}\ \mathrm{erg}. \end{aligned} \tag{4}$$

These values will be referred to below as the free-atom values of the exchange interaction, although they really refer to the Mn^+ ion.

We must consider the possibility that there may exist a crystal field splitting of the Mn ion in the cubic environment of the surrounding copper atoms. The state ^6S through mixing of higher states can split in a cubic field into two levels, one fourfold and the other twofold degenerate. The splitting was too small to be observed[6] for Mn^{++} ions in solid solution in cubic ZnS crystals. In metallic copper the conduction electrons help screen the crystal field. It is not surprising that one can neglect the crystal field splitting of Mn in Cu in our electron spin resonance results.

Ferromagnetism

The exchange interaction between a $3d^5$ core and the $4s$ conduction electrons will tend to magnetize the $4s$ band parallel to the spin of the ion core. In turn, the magnetization of the $4s$ band thus induced will tend to magnetize the other Mn^{++} ions parallel to the spin of the original Mn^{++} ion. There is therefore a cooperative effect which will lead to ferromagnetic ordering of the spin system at a sufficiently low temperature.

The ferromagnetic interaction discussed here was first introduced by Fröhlich and Nabarro[7] in their consideration of the possibility of nuclear ferromagnetism in metals. The $\mathbf{I}\cdot\mathbf{s}$ hyperfine coupling of the nuclear magnetic moment to the conduction electrons leads to estimated Curie temperatures in the range 10^{-8} to 10^{-6} °K, according to the particular nucleus. Zener[8] has used the present model in his discussion of the magnetic properties of the transition metals.

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[3] E. Kronqvist, Arkiv Mat. Astron. Fysik **34B**, No. 7 (1947); L. Néel, J. phys. 3, 160 (1932).

[4] W. Heitler and E. Teller, Proc. Roy. Soc. (London) **A155**, 637 (1936); J. Korringa, Physica **16**, 601 (1950).

[5] Owen, Browne, Arp, and Kip (to be published); see also Owen, Browne, and Kip, Phys. Rev. **100**, 965(A) (1955).

[6] W. D. Hershberger and H. N. Leifer, Phys. Rev. **88**, 714 (1952); K. A. Müller, Helv. Phys. Acta **28**, 450 (1955).

[7] H. Fröhlich and F. R. N. Nabarro, Proc. Roy. Soc. (London) **A175**, 382 (1940).

[8] C. Zener, Phys. Rev. **81**, 440 (1951).

Molecular Field Derivation of Curie Point

Let M_A be the magnetization of the solute atoms and M_e the magnetization of the conduction electrons. The effective magnetic field acting on the conduction electrons and arising from the exchange interaction with the solvent atoms will be written as

$$\mathbf{H}_e=\lambda\mathbf{M}_A, \tag{5}$$

and, similarly,

$$\mathbf{H}_A=\lambda\mathbf{M}_e. \tag{6}$$

These expressions are consistent, as the interaction energy density may be written as $-\lambda\mathbf{M}_A\cdot\mathbf{M}_e$, as $-\mathbf{H}_A\cdot\mathbf{M}_e$, or as $-\mathbf{H}_e\cdot\mathbf{M}_A$. We may evaluate λ by comparison of the first expression for the energy density with Eq. (1) written for a single elementary interaction. As $\bar{M}_A=2\mu_BN_A\bar{S}$ and $\bar{M}_e=2\mu_BN_e\bar{s}$, we have for the energy density

$$-4\lambda N_AN_e\mu_B{}^2\mathbf{S}\cdot\mathbf{s}=AN_A\mathbf{S}\cdot\mathbf{s}, \tag{7}$$

so

$$\lambda=-A/4\mu_B{}^2N_e. \tag{8}$$

Now from the Pauli paramagnetic susceptibility

$$M_e=3N_e\mu_B{}^2H_e/2kT_F, \tag{9}$$

while from the Curie law

$$M_A=N_Ap^2\mu_B{}^2H_A/3kT, \tag{10}$$

where $p^2=g^2S(S+1)$, and T_F is the Fermi temperature. Substituting (5) and (6) in (9) and (10), we have

$$\begin{aligned}(2kT_F)M_e-3N_e\mu_B{}^2\lambda M_A&=0;\\ \lambda N_Ap^2\mu_B{}^2M_e-3kTM_A&=0.\end{aligned} \tag{11}$$

These equations have a nontrivial solution at a temperature T_c such that

$$\begin{vmatrix} 2kT_F & 3N_e\mu_B{}^2\lambda \\ \lambda N_Ap^2\mu_B{}^2 & 3kT_c \end{vmatrix}=0,$$

or

$$\begin{aligned}kT_c&=\frac{3N_eN_Ap^2\mu_B{}^4\lambda^2}{6E_F}\\ &=\frac{S(S+1)A^2}{8E_F}\cdot\frac{N_A}{N_e}\\ &=\frac{1}{8}\frac{S(S+1)}{(S+\frac{1}{2})^2}\frac{(h\Delta\nu)^2}{E_F}\frac{f}{100},\end{aligned} \tag{12}$$

where f is the concentration of Mn in atomic percent. This agrees with the Fröhlich-Nabarro result obtained in another way. Here E_F is the Fermi energy of the conduction electrons. For copper we calculate $E_F=1.1\times10^{-11}$ ergs, using $m^*=m$. With the free-ion value of A given in Eq. (4), we have

$$T_c=3.5f\,°\mathrm{K}, \tag{13}$$

for f atomic percent Mn in Cu.

Conduction Electron Magnetization

From Eqs. (5) and (9), we have

$$M_e=(3N_e\mu_B{}^2/2kT_F)(H+\lambda M_A). \tag{14}$$

Now, from Eq. (8), for Mn in Cu, we estimate

$$\lambda\approx7\times10^{-13}/(4\times10^{-40}\times10^{23})\approx20\,000. \tag{15}$$

For $T\gg T_c$ and $\mu_BH/kT\ll1$, we have

$$M_e\approx(1.0\times10^{-6})[1+(1.2f\times10^2/T)]H; \tag{16}$$

thus for concentrations above one percent at temperatures below 100°K the magnetization of the conduction electrons would be expected to be dominated by the $s-d$ exchange interaction.

The usual nuclear Knight shift of the copper nuclei is proportional to M_e, the magnetization of the conduction electrons. According to Eq. (16) an alloy containing 0.1 atomic percent of Mn should have at 2°K a Knight shift six times larger than the shift in pure copper. The nuclear Knight shift should be a very sensitive indicator of the s-band magnetization.

Electronic g-Shift

One would expect, as discussed by Kittel and Mitchell[9] in connection with ferromagnetic relaxation, that the interaction $A\mathbf{S}\cdot\mathbf{s}$ will contribute to the electron spin resonance line width and lead also to a shift in the position of the electron resonance line. The effects are well known in nuclear resonance in metals where the hyperfine interaction $a\mathbf{I}\cdot\mathbf{s}$ plays the role of our exchange interaction $A\mathbf{S}\cdot\mathbf{s}$.

The effective internal field acting on the Mn ions from the $s-d$ interaction at $T\gg T_c$ is

$$H_A=\lambda M_e\approx2\times10^{-2}[1+(1.2f\times10^2/T)]H, \tag{17}$$

using the results of Eqs. (15) and (16). For a 5% alloy,

$$H_A\approx12H/T; \tag{18}$$

thus one expects an *electronic* Knight shift or g-shift

$$\Delta H/H=\Delta g/g\approx12/T \tag{19}$$

for this alloy; here T is in deg K.

Electron Spin Relaxation

Among the mechanisms leading to a line width or relaxation in nuclear spin resonance is the Heitler-Teller-Korringa mechanism[10] in which a simultaneous flip of nuclear and conduction electron spins occurs through the hyperfine $a\mathbf{I}\cdot\mathbf{s}$ interaction. A similar

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[9] C. Kittel and A. H. Mitchell, Phys. Rev. **101**, 1611 (1956). It is well known that an electron exchange interaction is not supposed to contribute to a line width or a shift; however, if the conduction electrons relax rapidly against the lattice the injunction does not apply and we observe in effect the resonance of the Mn ions alone. In the present problem we believe the 4s electrons may be relaxed rapidly in comparison with other relevant quantities.

[10] See reference 4; for an elementary derivation see D. Pines and C. P. Slichter, Phys. Rev. **100**, 1014 (1955).

process will occur for the Mn ion cores through the $s-d$ interaction $A\mathbf{S}\cdot\mathbf{s}$.

The result for the relaxation time of the Mn ions due to the conduction electron interaction is

$$1/T_1=9\pi kTA^2/16\hbar E_F^2. \tag{20}$$

We have for Mn in Cu, using the free-ion value of A,

$$1/T_1=T\times10^9\ \text{sec}^{-1}, \tag{21}$$

where T is in deg K.

Electrical Resistivity

It is known that dilute alloys of Mn in Cu show an increase in the electrical resistivity[11] with increasing temperature at low temperature. The extra resistivity mechanism has been associated by Korringa and Gerritsen,[12] Elliott,[13] and Schmitt[13] with collisions between conduction electrons and Mn ions; in these collisions spin flips occur under the influence of the interaction $A\mathbf{S}\cdot\mathbf{s}$. For this mechanism every conduction electron collision relaxation event is accompanied by relaxation of the Mn ion spin direction according to Eq. (20) above. This mechanism does give a resistivity maximum (or minimum) at low temperatures; such effects are still essentially unexplained.

By the principle of detailed balance the conductivity relaxation time τ is given by

$$N_{\text{eff}}/\tau=N_A/T_1, \tag{22}$$

where N_{eff} is the effective number of conduction elections and N_A the number of Mn atoms, both per unit volume. Now in terms of the conduction electron concentration N_e,

$$N_{\text{eff}}\approx8(kT/E_F)N_e, \tag{23}$$

as only electrons within a range of the order of kT of the Fermi surface participate in collisions. The factor 8 is found in an unpublished calculation by S. Rodriguez. Using the results (20) through (23), we have

$$\frac{1}{\tau}\approx\frac{9\pi A^2}{16\hbar E_F}\left(\frac{N_A}{8N_e}\right). \tag{24}$$

With our previous choice of numerical values for Mn in Cu,

$$1/\tau\approx1\times10^{11}f\ \text{sec}^{-1}, \tag{25}$$

where f is in atomic percent.

The associated resistivity from this mechanism would be

$$\rho=m/N_e e^2\tau\approx0.005\ \mu\text{ohm-cm/atomic percent}. \tag{26}$$

We note in passing that the exchange coupling mechanism is a new mechanism for conduction electron spin relaxation in metals, and that if the mechanism were fully effective for a particular impurity species it would be necessary to exercise extreme precautions to purify the metal with respect to that species. One impurity atom in 10^3 could give a conduction electron line width of the order of a hundred oersteds.

II. EXPERIMENTAL RESULTS

Magnetic Susceptibility

Previous determinations of the magnetic susceptibility of dilute Cu$-$Mn alloys were carried out largely at room temperature and above. The susceptibility had been observed to obey a Curie-Weiss law,

$$\chi=C/(T-\theta), \tag{27}$$

which led to the expectation that the alloys would be ferromagnetic at $T<\theta$. We observe instead that the dilute alloys become dominantly antiferromagnetic near a transition temperature $T_N>\theta$. Below T_N the susceptibility decreases. Results are summarized in Table I. A slight remanent magnetization is observed below below the Néel temperature; this is not uncommon in other antiferromagnetics and is discussed in a separate publication of Owen, Browne, Arp, and Kip.[5]

The occurrence of a positive T_N and positive θ suggests that nearest neighbor Mn$-$Mn interactions are antiferromagnetic and next nearest neighbor Mn$-$Mn interactions are ferromagnetic. The strength of the ferromagnetic interaction is not incompatible with Eq. (13) for the indirect exchange-conduction electron mechanism; in fact the ferromagnetic term is rather stronger than calculated. The presence of antiferromagnetism clearly suggests that direct overlap or superexchange interactions are very important. It is rather surprising that a dilute alloy such as the 1.4% Mn alloy should have a well defined antiferromagnetic transition. This suggests that a certain degree of spatial order may perhaps occur among the Mn ions. It is possible that direct exchange may be the responsible antiferromagnetic interaction. Friedel has suggested privately that the range of overlap may be greater in the metal than for free ions.

The fact that our observed values of the Curie constant C are smaller than calculated from the chemical analyses and the assumed $S=5/2$ state causes us some concern; the deficiency may be due to incomplete solution of the Mn, or the ion may have $S=2$. This

TABLE I. Summary of susceptibility determinations [C_0 is calculated for Mn^{++} ions using chemical analyses of Mn content].

Atomic percent of Mn in Cu	Relative Curie constant C/C_0	Curie temperature θ °K	Transition region $\sim T_N$ °K	Critical field at 4°K H_c kilo-oersteds
11.1	0.62	100	80 to 120	4.4
5.6	0.77	37	40 to 60	2.5
1.4	0.73	7	10 to 13	1.07
0.029	0.70	0 ± 0.5	<4	0

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[11] See, for example, A. N. Gerritsen and J. O. Linde, Physica **18**, 877 (1952).

[12] J. Korringa and A. N. Gerritsen, Physica **19**, 457 (1953).

[13] R. J. Elliott, Phys. Rev. **94**, 564 (1954); R. W. Schmitt, Phys. Rev. (to be published).

state would give $g \cong 2$ provided the doubly degenerate levels were lowest and the crystal field splitting large. The exchange interaction is large.

Electron Spin Resonance

Electron spin resonance has been observed in connection with this research in alloys of Mn with Cu, Ag, and Mg. We discuss here the results for the Mn−Cu alloys. A typical resonance line is shown in Fig. 1.

We may ask whether the ferromagnetic part of the exchange interaction pattern revealed by the susceptibility studies may not be caused by indirect exchange via the conduction electrons. If this were true we would expect the g-shift above the Curie temperature to be at least as large as that deduced from Eq. (17), as the ferromagnetic Curie temperature θ is larger than that predicted by Eq. (13); thus the appropriate molecular field constant λ would be larger than the value 20 000 used in all of our estimates above. However, in all alloys the g-value is quite close to the free spin value 2.00 at all temperatures above the Néel temperatures T_N. In the 5.6% alloy Eq. (19) would predict a g-shift of more than 15% at 77°K, while any observed shift is less than 1 or 2%, the uncertainty being caused by the shape and width of the absorption line. The calculated shift goes essentially as λ^2 or A^2; thus we may infer the actual value of λ or A is not more than perhaps $\frac{1}{3}$ of the assumed value which was based on the free atom value.

When $T \ll T_N$, the resonance field H satisfies $H^2 = H_0^2 - H_c^2$, where H_c is a parameter whose value slowly increases as T is lowered. Here H_0 is the resonance field for a free spin with $g=2$. Values of H_c in Table II give shifts $H_0 - H$ about three times larger at 3 cm than at 1-cm wavelength. Such a resonance condition is expected for an antiferromagnet with critical field H_c less than the applied field H. The susceptibility data are consistent with the Mn ions being distributed approximately equally over two sublattices A and B with antiferromagnetic coupling $A-A$ and $B-B$. This model gives an antiferromagnetic transition regardless of the relative strengths of the couplings. The appropriate antiferromagnetic resonance condition for a single crystal at $T=0$ is

$$H^2 = H_0^2 - H_c^2, \tag{28}$$

where the critical field $H_c = (2H_E H_a)^{\frac{1}{2}}$, as given by Nagamiya and Kittel. The exchange field H_E relates here only to the $A-B$ interaction. We estimate anisotropy field H_a to be ≈ 60 oersteds. In polycrystalline specimens the resonance line was observed to be broader than in single crystals, in agreement with expectation. For random orientation of polycrystals the position of maximum absorption is still given approximately by Eq. (28). No resonance is seen in the 10 Mn−90 Cu alloy at 3 cm and 4°K because here $H_0 < H_c$, as determined at 1 cm. We see then that the remarkable behavior of the resonance line below the Néel temperature is consistent with the theory of antiferromagnetic resonance; other explanations, however, may be possible.

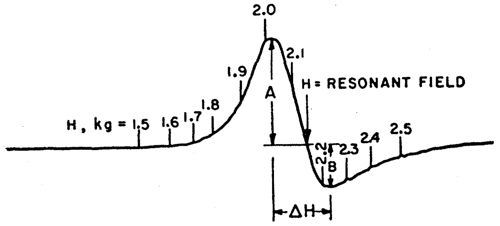

FIG. 1. Derivative of absorption *versus* magnetic field for single crystal of Cu+5.6% Mn at 4°K, λ=3.28 cm. The free spin resonance field is $H_0 = 3.26$ kilo-oersteds.

TABLE II. Summary of electron spin resonance results on polycrystals.

Atom percent of Mn in Cu	Wave-length $X \approx 3.30$ cm $K \approx 1.30$ cm	H_0 oersteds	Line shift[a] $(H_0 - H)$ oersteds 4°K	Line shift[a] $(H_0 - H)$ oersteds 2°K	Line width ΔH[b] oersteds 77°K	Line width ΔH[b] oersteds 4 and 2°K
11.1	K	8170	1290	1600	210	650
	X	3250	no resonance observed		160	···
5.6	K	8250	395	490	170	220, 300
	X	3250	1170	1370	180	450
1.4	K	8240	75	100	···	100
	X	3240	185	240	360	130
0.1	X	3250	0	0	···	100

[a] Above the transition point $(T > T_N)$, $H_0 - H \approx 0$.
[b] ΔH = peak to peak separation of derivative of absorption line.

The observed line width at temperatures $T \gg T_N$ is not incompatible with a relation $1/T_1 \propto T$, where T_1 is the spin-lattice relaxation time and T is the absolute temperature, as suggested by Eq. (20) for relaxation by interaction with conduction electrons. At 77°K the widths correspond to times T_2 close to 2×10^{-10} sec. If we assume $T_1 = T_2$, the relation (21) leads us to expect $T_2 \approx 10^{-11}$ sec at this temperature. This suggests that the interaction constants λ and A may be of the order of $\frac{1}{5}$ of the values calculated for the free ion. We have in this section tried to use experimental data which may be free from hyperfine broadening and exchange narrowing, but our selection may not be entirely successful.

The line width at low temperatures shows signs of antiferromagnetic effects and also signs of the motional and exchange narrowing of the hyperfine $\mathbf{S} \cdot \mathbf{I}$ interaction of the Mn.

Nuclear Spin Resonance

The position and width of the electron spin resonance line led to the conclusion that the $s-d$ exchange interaction was rather smaller in the metal than in the free atom. A study of the Knight shift of the copper nuclear spin resonance in these alloys was undertaken as an independent check on the magnitude of the conduc-

TABLE III. Properties of the Cu^{63} nuclear resonance line. Frequencies in kc/sec.

Sample	Temperature (°K)	Δf_0	f_1	f_2	f_5	Error
Pure Cu	4.2, 77, 300	⋯	3.7	6.3	8.0	±0.1
Cu−Mn	300	−0.3	3.8	6.9	9.3	±0.3
Cu−Mn	77	−0.5	4.2	7.6	10.5	±0.5
Cu−Mn	4.2	−0.5	7.6	18.0	27.8	±0.5
Cu−Mn	1.7	−0.7	9.8	28.5	44.9	±1
Cu−Mn	1.2	−1.0	12.7	34.0	55.1	±1

tion electron magnetization. According to Eq. (16), the Knight shift of the Cu nuclear resonance in an 0.03% alloy at 1.2°K should be larger by a factor of four than the usual Knight shift of about 10 kc/sec at 5980 kc/sec in pure copper. The observed results show, however, that under these conditions the line is not shifted by more than 10% of the normal Knight shift, and the 10% can be accounted for approximately as a demagnetization correction. The sign of the shift is opposite to that expected for the $s-d$ interaction, but agrees with that expected from demagnetization.

The extra shift as calculated from Eq. (14) is linear in the exchange coupling constant, suggesting in this example that λ and A are not greater than 1/50 of the free-atom value. The line is slightly asymmetric, so the limit may be somewhat larger, possibly 1/20.

The nuclear magnetic resonance of Cu^{63} was observed in an unannealed alloy of 0.029 atomic percent manganese in copper. The results are compared in Table III with those for pure copper, at several temperatures. The magnetic field was 5200 oersteds and the corresponding resonance frequency 5980 kc/sec.

The data were taken with a recording spectrometer. Each resonance line is a plot of $d\chi''/df$, where χ'' is the absorptive part of the rf susceptibility, and f is the radiofrequency. We let Δf_0 be the center frequency of a line relative to the center of the pure copper line at the same temperature; f_1 is the frequency at the peak of the derivative relative to the center; f_2 is the frequency deviation at the point where the line has fallen to an amplitude one-half as great as for f_1; f_5 is the frequency deviation from the center for the point at one-fifth maximum amplitude. Values for these quantities are displayed in Table III.

It may be seen that the resonance frequency in the alloy is not significantly different from the value for pure copper. At all temperatures the center of the line in the alloy appears to be slightly lower in frequency. However, the variation is within the error of measurement. At the high temperatures the errors arise because the signal-to-noise ratio is poor. At the lower temperatures, the signal-to-noise is very good, but the lines are so broad that it is hard to determine the exact center. At all temperatures the lines in the alloy are slightly asymmetric, which contributes to the error. The pure copper line was symmetrical. There was no evidence for appreciable rf saturation or for effects attributable to particle size.

The line widths in the alloy indicate the existence of a magnetic interaction between the copper and the dissolved manganese. At the low temperatures, the line changes from the nearly Gaussian shape of pure copper to one closely approximating a Lorentz shape. If we take f_5 as a measure of the interaction, we find the following temperature dependence between 1.2 and 4.2°K: $f_5(\mathrm{kc/sec}) = 17 + 46/T$. This indicates the existance of two broadening mechanisms, only one of which depends on temperature. In the range of higher temperatures, the temperature coefficient is apparently higher, and the residual width agrees well with that of pure copper. Further measurements at a different magnetic field suggest that the line width is a function of H/T, as would be expected if the width is related to the net Mn ion magnetization.

We note that the rapid relaxation of the spin of the manganese atom will cause copper nuclear widths to be motionally narrowed for all mechanisms coupled to the spin direction of the manganese atom. This applies as long as the net magnetization of the Mn is negligible but at low temperatures and high fields the Mn is appreciably magnetized and there is a significant contribution to the width. According to unpublished calculations by Robert Behringer, the dipolar interaction is not large enough to account for more than about 20% of the observed broadening. We infer that it is necessary to invoke a local perturbation of the s electron spin distribution, a pertubration tied to the direction of the spin of the Mn ion. We would expect the exchange interaction to lead to a local magnetization perturbation, similar to the mechanism proposed by Ruderman and Kittel[2] for nuclear interactions in metals.

Electrical Resistivity

The electrical resistivity of dilute alloys of Mn in Cu has been studied by Gerritsen and Linde,[14] among others. The presence of the Mn causes a temperature-independent resistivity increase of about 3 μohm-cm/atomic percent. There are two further features at low temperatures: there is a gradual increase of about 0.2 μohm-cm/atomic percent as the temperature is increased, and a peak in the resistivity of about the same magnitude. It is tempting to ascribe the gradual increase to the spin relaxation mechanism, but Eq. (26) calculated for the free atom value of the sd interaction is only 1/40 as large as the observed gradual increase. We have no explanation of this discrepancy, but suggest that it may be connected with the phenomena of the resistivity minimum. The temperature-independent resistivity of 3 μohm-cm/atomic percent is probably caused by ordinary alloy potential scattering.

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[14] A. N. Gerritsen and J. O. Linde, Physica **18**, 877 (1952).

III. INTERPRETATION

The width and temperature dependence of the electron spin resonance line suggest that the actual strength of the $s-d$ interaction may be of the order of $\frac{1}{5}$ the free-atom value. Such a factor might easily appear on going from the free atom to the metal; in particular, the other conduction electrons will screen the *sd* interaction. We estimate that screening alone will reduce the interaction by a factor $\frac{1}{3}$ to $\frac{1}{2}$. We probably cannot have $A(\text{exp})/A(\text{calc})>\frac{1}{3}$ without causing a perceptible g-shift, although it may also be that the Kittel-Mitchell argument[9] does not apply here. We must probably look to other interactions for the source of the strong ferromagnetic coupling evident in the susceptibility data. We consider now only the problem of the nuclear Knight shift, which suggests $A(\text{exp})/A(\text{calc})<1/50$.

Is this small value real or apparent? If it is real we need another temperature-dependent mechanism to account for the width of the electron spin reasonance line. Granted this, how would we account for $A(\text{exp}) <0.02A(\text{calc})$? When a Mn atom enters the copper lattice it might lose (on simple models) 2, 1, or 0 of its 4*s* electrons to the conduction band, retaining 0, 1, or 2, respectively; it might also become a negative ion. We can probably account for the observed weakness of the $3d-4s$ interaction if the Mn retains both 4*s* electrons, entering the lattice as neutral manganese. In this event the conduction electrons of the copper would suffer an exchange repulsion at the manganese atom, thereby reducing the overlap with the $3d^5$ core of the manganese. Further, a neutral manganese atom will act effectively as a charge $-|e|$ relative to the Cu^+ ions of the periodic lattice; thus the conduction electrons experience also an ordinary Coulomb repulsion. A negative ion would also have the same effect, but probably would not be consistent with the properties of electron reasonance line.

We can also argue on other grounds against the possibility that manganese enters the lattice as Mn^{++}, contributing two electrons to the 4*s* conduction band of the alloy. If this occurred, then Mn in Cu would be expected to behave like Zn in Cu with respect to the dependence of the crystal structure on Zn or Mn concentration. Actually the phase diagram of the Cu$-$Mn system is entirely unlike that of the Cu$-$Zn system. The Cu$-$Mn phase diagram is very simple and shows no signs of the orderly elaborate sequence of phases as a function of electron concentrations as discussed by Hume-Rothery and Jones, in particular for alloys of copper with the elements just beyond it in the periodic table.

We then have an argument for Mn^0 and another argument against Mn^{++}. It seems a little unlikely that Mn^+ would help us. This can be looked at as a $3d^5$ core screened by one bound 4*s* electron. On this model there would still be a strong exchange interaction (although of opposite sign) with the conduction electrons; in fact, the state of parallel spin requires approximate promotion of a conduction electron to the 4*p* band because of the exclusion principle.

There is also a possibility that the theory of the Fröhlich-Nabarro-Zener effect is not entirely applicable to dilute alloys. There is something uncomfortable about the thought that according to the simple first-order theory a single manganese atom will cause in principle a uniform magnetization to exist throughout the metal, for a perfect lattice. Second-order perturbation theory will cause the uniformity to be disturbed in the neighborhood of the manganese atom, but it is not evident that the uniform magnetization at large distances will be reduced greatly. We have considered several other mechanisms, such as spin flip on collision with phonons or impurities, but we have not been able to show positively that a mechanism exists which will reduce by an order of magnitude the uniform magnetization calculated from the first-order energy perturbation.

We would like to emphasize that the explanation suggested by Kittel and Mitchell[9] for the apparent low value (~0.01 ev) of the $s-d$ interaction in ferromagnetic alloys such as the Fe$-$Ni system is not applicable here. They were able to invoke d electron screening because in the Fe$-$Ni system there is a high concentration of holes in the d band. The present problem is quite different, and we have had to propose different explanations.

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