TABLE II. The states for the two donors described as states for a composite flaw.

Charge condition	Energy	No. of ways of forming state	No. of flaws
$+2$	0	1	N_{2d}
$+1$	$-E_1$ $-E_2$	2 2	N_{1d}
0	$-(E_1+E_2)$	4	N_0

ionization energies E_1 and E_2, consider the two following cases:

Case (*1*) $E_1=E_2$

$$E_{2d}=-E_1-kT\ln 4 \qquad \text{(A2.3)}$$

$$E_{1d}=-E_1. \qquad \text{(A2.4)}$$

For Case (1), the energy for binding the second electron to the flaw is the same as the first, but the entropy factor is less so that the first donor level lies higher than the second donor level by $kT\ln 4$.

Case (*2*) $E_1-E_2>kT$

$$E_{2d}\doteq -E_1-kT\ln 2 \qquad \text{(A2.5)}$$

$$E_{1d}\doteq -E_2-kT\ln 2. \qquad \text{(A2.6)}$$

For Case (2), the two donors have sufficiently different energies so that they act independently and the flaw energy levels coincide with those of the donors as corrected for spin degeneracy.†

It may also be shown that the probabilities of the various charge conditions as given by Eq. (3.7) reduce to those calculated by the usual Fermi-Dirac treatment. For example, from Eq. (3.7) we obtain

$$\begin{aligned} N_0/N_f &= [1+e^{\beta(E_{1d}-E_F)}(1+e^{\beta(E_{2d}-E_F)})]^{-1} \\ &= [1+\tfrac{1}{2}(e^{-\beta E_1}+e^{-\beta E_2}) \\ &\qquad \times e^{-\beta E_F}(1+\tfrac{1}{2}(e^{\beta E_1}+e^{\beta E_2})^{-1}e^{-\beta E_F})]^{-1} \\ &= [1+\tfrac{1}{2}e^{-\beta(E_1+E_F)}]^{-1}[1+\tfrac{1}{2}e^{-\beta(E_2+E_F)}]^{-1}. \qquad \text{(A2.7)} \end{aligned}$$

This last expression is simply the product of the probabilities given by the usual Fermi-Dirac treatment that each donor, with effective energy levels of the form $-E_1-kT\ln 2$, have an electron. The reader may easily find that similar equivalences can be established between the other charge conditions of the flaw and the corresponding states of the two donors.

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† See, for example, W. Shockley and W. T. Read, Jr., Phys. Rev. 87, 835 (1952), Appendix B.

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Anomalous Electrical Resistivity and Magnetoresistance Due to an *s-d* Interaction in Cu-Mn Alloys

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The effect of the *s-d* exchange interaction between the conduction electrons and the Mn ions on the electrical behavior of Cu-Mn alloys is investigated from the molecular-field point of view. The magnitude of the anomalous resistivity calculated with the value of the exchange integral for a free Mn^+ ion agrees with the experimental value within a factor of three. Also the temperature dependence of the resistivity obtained by the molecular-field approximation for the antiferromagnetic spin ordering is shown to be quite similar to the behavior exhibited by the alloys with more than one atomic percent Mn. For samples with lower concentration of Mn ions, however, the theoretical result shows only a monotonic decrease of the resistance below the Néel temperature. It shows neither the resistance minimum nor maximum which has been found experimentally for the very dilute alloys. The anomalous magnetoresistance calculated on the same basis is approximately proportional to the square of the magnetization and its magnitude is in good agreement with the experimental results, especially above the Néel temperature. The magnetoresistance of ferromagnetic metals is also discussed.

I. INTRODUCTION

GERRITSEN and Linde[1] have measured the electrical resistivity of noble-metal alloys such as silver and copper containing traces of the transition elements represented by manganese and iron, and have found anomalous behavior in the resistivity at low temperature. According to their experimental results, such alloys with several atomic percent Mn show an abrupt decrease of the resistivity at low temperature, and as the concentration of Mn ions becomes lower the resistivity initially rises and then decreases, exhibiting a maximum value with lowering temperature. Gerritsen[2] has also found that these alloys show an anomalous magnetoresistance accompanying the anomaly of the resistivity. Korringa and Gerritsen[3] explained this

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[1] A. N. Gerritsen and J. O. Linde, Physica 17, 573, 584 (1951).

[2] A. N. Gerritsen, Physica 19, 6 (1953).

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

anomalous behavior in electrical phenomena by introducing localized states with energy near the Fermi energy.

Recently the situation has been clarified by the experiments on the magnetic properties of Cu-Mn alloys done by Owen, Browne, Knight, and Kittel[4] and by Owen, Browne, Arp, and Kip.[5] They considered the anomaly of the magnetic properties to be attributed to the *s-d* exchange interaction between the conduction electrons and the Mn spins and discussed the effect of this interaction. Although the effect of the first-order perturbation of the *s-d* interaction was inconsistent with some of the experimental results, the situation is quite modified by the second-order perturbation, and it has been shown that apart from quantitative details, most of the magnetic properties are at least qualitatively consistent with the results predicted from the *s-d* exchange interaction.[6] Owen *et al.*[4] have also discussed the electrical resistivity and proposed a new mechanism for the anomalous resistivity due to the *s-d* interaction.

The purpose of the present paper is to calculate the anomalous resistivity due to the *s-d* interaction and to investigate to what extent this can account for the experimental results. The problem of a temperature-dependent anomalous resistivity was first treated by Elliott.[7] He calculated the anomalous resistivity of rare-earth metals due to a spin-independent interaction between conduction electrons and $4f$ ion cores some of which are excited in high-energy orbital states separated from the ground state by the crystalline Stark effect. Kasuya[8] has calculated the resistivity due to an *s-d* exchange interaction for the case of the ferromagnetic iron group and rare-earth metals and has given an alternative explanation[9] for the anomalous resistivity to that given by Mott on the basis of the band approximation for $3d$ electrons as well as $4s$ electrons. Furthermore, Schmitt[10] has developed a phenomenological theory for the resistance due to a spin-dependent interaction and discussed both resistivity and magnetoresistance of Cu-Mn alloys. The present theory will be developed along a line similar to the approaches by these authors.

We shall consider the perturbing potential consisting of the spin-dependent interaction and the spin-independent interaction between conduction $4s$ electrons and $3d$ electrons localized at impurity ions.[11] The former interaction comes from an exchange interaction and the latter comes mainly from an ordinary screened Coulomb potential around the manganese ions which are presumably in an Mn^{++} state. The lattice vibrations are neglected, and their contribution to the resistance has been subtracted out in the discussion of the experimental results. The exchange interaction can be represented as an effective potential[12] having opposite signs for electrons with $+$ and $-$ spins, so that the effective potential seen by $+$ and $-$ electrons is different. This difference in the potential gives rise to a difference in the scattering probabilities through the cross terms of the exchange interaction and the spin-independent interaction. This term is proportional to the total magnetization of the impurity Mn ions, which in the antiferromagnetic case vanishes only in the absence of an external magnetic field. The shift Φ of the Fermi sphere is inversely proportional to the total scattering probability, so that we have for $+$ and $-$ spins, respectively,

$$\Phi^{\pm}\propto 1/(W_0\mp wM).$$

Here W_0 is the sum of the transition probability due to the spin-independent potential only and that due to the spin-dependent potential only both of which are equal for $+$ and $-$ spins, and $\mp wM$ comes from the cross effect of these two interactions. M is the total magnetization of Mn ions and w is a constant. The resistivity is inversely proportional to the sum of the shifts of the Fermi sphere for $+$ and $-$ spins, so that

$$R\propto\left\{\frac{1}{W_0-wM}+\frac{1}{W_0+wM}\right\}^{-1}=\frac{W_0}{2}-\left(\frac{w^2}{2W_0}\right)M^2.$$

The extra term of the resistivity, which is proportional to M^2 and vanishes only for the case of antiferromagnetic ordering in the absence of an external magnetic field, can make an essential contribution to the magnetoresistance. The anomalous magnetoresistance of Cu-Mn alloys and similar alloys can be explained by the extra term proportional to the square of the magnetization.

In the absence of an external field, the resistivity is determined by W_0 which is the sum of a part from the exchange interaction alone and one from the screened Coulomb potential alone. The latter part is temperature-independent, whereas the former part has a monotonic temperature dependence similar to the expressions obtained by Elliott,[7] Kasuya,[8] and Schmitt.[10] Therefore, the present theory does not give rise to the resistance minimum and maximum which have been found in the resistivity-temperature curve for very low concentration of Mn in Cu. The resistance maximum occurs at somewhat higher temperature than that at which there is a specific-heat maximum.[13] In copper-tin and copper-gold alloys, a resistance minimum has also been observed. In addition the maximum and minimum cannot

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[4] Owen, Browne, Knight, and Kittel, Phys. Rev. **102**, 1501 (1956).

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[8] T. Kasuya, Progr. Theoret. Phys. Japan **16**, 58 (1956).

[9] N. F. Mott, Proc. Roy. Soc. (London) **A153**, 699 (1936).

[10] R. W. Schmitt, Phys. Rev. **103**, 83 (1956).

[11] The importance of considering the interaction between the spin-independent and spin-dependent perturbation was pointed out by Dr. V. Heine. See also discussion of reference 12.

[12] J. C. Slater, Phys. Rev. **82**, 538 (1951).

[13] Gorter, Van den Berg, and de Nobel, Can. J. Phys. **34**, 1281 (1956).

be observed for higher concentration of Mn whereas the anomalous part of the resistivity due to an *s-d* exchange interaction is large. Thus, it seems that the phenomenon of the resistance maximum and minimum is very complicated and that it cannot be attributed to an *s-d* exchange interaction only.

The experimental results concerning anomalous behavior of Cu-Mn alloys have recently been reviewed and discussed by Gorter, Van den Berg, and de Nobel,[13] Schmitt and Jacobs,[14] and Korringa.[15]

II. CALCULATIONS

The interaction between the conduction electrons and the Mn ions in Cu-Mn alloys can be expressed by

$$H=\sum_i \sum_n V(\mathbf{r}_i-\mathbf{R}_n)-2\sum_i \sum_n J(\mathbf{r}_i-\mathbf{R}_n)(\mathbf{s}_i\cdot\mathbf{S}_n), \quad (1)$$

where $\mathbf{r}_i$ and $\mathbf{R}_n$ represent the position vector of the conduction electron and that of the Mn ion, respectively. $V(\mathbf{r}_i-\mathbf{R}_n)$ is the deviation due to the impurity Mn ion from the spin-independent periodic potential, and $J(\mathbf{r}_i-\mathbf{R}_n)$ is the effective exchange integral between the conduction electron and the Mn ion. The quantities $\mathbf{s}_i$ and $\mathbf{S}_n$ represent the spin operators for the conduction electron and the Mn ion, respectively. This potential energy can be written in a form of second quantization as[6,8]

$$\begin{aligned}H=&N^{-1}\sum_{\mathbf{k}}\sum_{\mathbf{k}'} V(\mathbf{k},\mathbf{k}')e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n}(a_{\mathbf{k}'+}{}^*a_{\mathbf{k}+}+a_{\mathbf{k}'-}{}^*a_{\mathbf{k}-})\\&-N^{-1}\sum_{\mathbf{k}}\sum_{\mathbf{k}'} J(\mathbf{k},\mathbf{k}')e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n}[(a_{k'+}{}^*a_{k+}\\&-a_{k'-}{}^*a_{k-})S_n{}^\zeta+a_{\mathbf{k}'-}{}^*a_{\mathbf{k}+}S_n{}^+ +a_{\mathbf{k}'+}{}^*a_{\mathbf{k}-}S_n{}^-]. \quad (2)\end{aligned}$$

Here we denote the coordinate axes by ξ, η, and ζ and take the ζ axis as the quantization axis of spins, and $S_n{}^\pm$ represent $S_n{}^\xi\pm iS_n{}^\eta$. The quantities $a_{\mathbf{k}\pm}{}^*$ and $a_{\mathbf{k}\pm}$ are the creation and annihilation operators for the conduction electrons with the wave vector $\mathbf{k}$ and with spin parallel or antiparallel to the ζ axis, and N is the total number of lattice points. $V(\mathbf{k},\mathbf{k}')$ and $J(\mathbf{k},\mathbf{k}')$ are related to the matrix elements of $V(\mathbf{r}_i-\mathbf{R}_n)$ and $J(\mathbf{r}_i-\mathbf{R}_n)$ between two states with wave vectors $\mathbf{k}$ and $\mathbf{k}'$ as follows:

$$V(\mathbf{k},\mathbf{k}')=Ne^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n}\int \varphi_{\mathbf{k}'}{}^*(\mathbf{r})V(\mathbf{r}-\mathbf{R}_n)\varphi_{\mathbf{k}}(\mathbf{r})d\tau,$$

$$J(\mathbf{k},\mathbf{k}')=Ne^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n}\int \varphi_{\mathbf{k}'}{}^*(\mathbf{r})J(\mathbf{r}-\mathbf{R}_n)\varphi_{\mathbf{k}}(\mathbf{r})d\tau,$$

where $\varphi_{\mathbf{k}}$ represents the wave function of the conduction electron with the wave vector $\mathbf{k}$. When we approximate the wave function $\varphi_{\mathbf{k}}$ by a plane wave, these two quantities become proportional to the Fourier components of the two potentials $V(\mathbf{r})$ and $J(\mathbf{r})$. In general $V(\mathbf{k},\mathbf{k}')$ and $J(\mathbf{k},\mathbf{k}')$ depend upon $\mathbf{k}$ and $\mathbf{k}'$.

The perturbation given by (2) is regarded as the main part of the deviation from the periodic potential at a temperature low enough for the effect of the lattice vibrations to be negligible. In calculating the resistivity due to the perturbation (2), we make the following assumptions.

(1) The energy of the conduction electron can be expressed by $\hbar^2k^2/2m$, m representing an effective mass.

(2) $V(\mathbf{k},\mathbf{k}')$ and $J(\mathbf{k},\mathbf{k}')$ depend only on $|\mathbf{k}-\mathbf{k}'|$.

(3) The Mn ions can be divided into two groups containing equal numbers of ions. Mn ions belonging to one group are subjected to the field H^+ and those belonging to the other group are subjected to the field H^-. H^+ and H^- are the sum of the molecular fields and the external field.

(4) Mn ions are distributed at random and there is no interference of the scattered wave from different ions.

Now we denote the direction of the applied electric field by x which may be different from the direction of the ξ axis specified above. This electric field which is denoted below by $\mathcal{E}$, makes the distribution functions $f^\pm(E_{\mathbf{k}})$ for the conduction electrons with + and − spins deviate from their common value in the absence of an electric field, namely $f_0(E_{\mathbf{k}})$, as follows:

$$f^\pm(E_{\mathbf{k}})=f_0(E_{\mathbf{k}})-k_x\mathcal{E}\Phi^\pm(E_{\mathbf{k}})\partial f_0(E_{\mathbf{k}})/\partial E_{\mathbf{k}}, \quad (3)$$

where + and − signs represent the spin direction of the conduction electrons with respect to the ζ axis and the quantities $\Phi^\pm$ are determined in (7). Strictly, in the presence of an external magnetic field, we should use $f_0(E\pm\mu H)$ instead of $f_0(E)$, where μ is the Bohr magneton, but the error is of order $\mu H/E_f\ll 1$, E_f being the Fermi energy.

The shift of the Fermi sphere (3) gives rise to the electric current density

$$j^\pm=-\frac{1}{V}e\sum_{\mathbf{k}}\frac{\hbar k_x}{m}[f^\pm(E_{\mathbf{k}})-f_0(E_{\mathbf{k}})],$$

where V is the total volume. Inserting (3) into this expression and replacing the summation over $\mathbf{k}$ by an integration as follows:

$$\sum_{\mathbf{k}}\rightarrow\frac{V}{8\pi^3}\frac{1}{2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\int E_{\mathbf{k}}{}^{\frac{1}{2}}dE_{\mathbf{k}}\sin\theta d\theta d\varphi, \quad (4)$$

we obtain

$$j^\pm=-\frac{e}{6\pi^2}\frac{1}{\hbar}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}E_f{}^{\frac{3}{2}}\mathcal{E}\Phi^\pm(E_f), \quad (5)$$

where E_f represents the Fermi energy. Thus the electrical resistivity is given by

$$R=-\frac{6\pi^2}{e}\frac{\hbar}{E_f{}^{\frac{3}{2}}}\left(\frac{\hbar^2}{2m}\right)^{\frac{3}{2}}\{\Phi^+(E_f)+\Phi^-(E_f)\}^{-1}. \quad (6)$$

The functions $\Phi^\pm(E_{\mathbf{k}})$ are determined by the Boltzmann

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[14] R. W. Schmitt and I. S. Jacobs, Can. J. Phys. 34, 1285 (1956).

[15] J. Korringa, Can. J. Phys. 34, 1290 (1956).

equation

$$\frac{\partial f_0(E_{\mathbf{k}})}{\partial E_{\mathbf{k}}}\frac{\hbar k_x}{m}e\mathcal{E}+\left(\frac{\partial f^{\pm}}{\partial t}\right)_{\text{col.}}=0, \tag{7}$$

$(\partial f^{\pm}/\partial t)_{\text{col.}}$ being the rate of change of the distribution functions $f^{\pm}(E_{\mathbf{k}})$ due to the collisions with Mn ions. This is given by

$$\begin{aligned}(\partial f^{\pm}/\partial t)_{\text{col.}}=\textstyle\sum_{\mathbf{k}'}\{&W(\mathbf{k}_{\pm}'\rightarrow\mathbf{k}_{\pm})f^{\pm}(\mathbf{k}')[1-f^{\pm}(\mathbf{k})]\\ &-W(\mathbf{k}\pm\rightarrow\mathbf{k}'\pm)f^{\pm}(\mathbf{k})[1-f^{\pm}(\mathbf{k}')]\}\\ &+\textstyle\sum_{k'}\{W(\mathbf{k}'\mp\rightarrow\mathbf{k}\pm)f^{\mp}(\mathbf{k}')[1-f^{\pm}(\mathbf{k})]\\ &-W(\mathbf{k}\pm\rightarrow\mathbf{k}'\mp)f^{\pm}(\mathbf{k})[1-f^{\mp}(\mathbf{k}')]\}. \end{aligned}\tag{8}$$

$W(\mathbf{k}'\pm\rightarrow\mathbf{k}\pm)$, for example, represents the transition probability from a $\mathbf{k}'\pm$ state to a $\mathbf{k}\pm$ state. The first sum in this expression comes from the scattering process in which the electron spin is not reversed. Only the ζ component of the perturbation (2) contributes to this process so that the spin component S_n^{ζ} of the Mn ion does not change either. Therefore, this scattering is elastic. On the other hand, the second sum arises from the process which is accompanied by a change of the spin direction. This process is due to the ξ and η components of (2) and is inelastic.

First we shall consider the part arising from the elastic scattering. From assumption (4), the transition probability is given by the sum of the transition probability due to each Mn as follows:

$$W(\mathbf{k}'\pm\rightarrow\mathbf{k}\pm)$$
$$=\frac{2\pi}{\hbar}N^{-2}\sum_n|V(\mathbf{k}'-\mathbf{k})\mp S_n^{\zeta}J(\mathbf{k}'-\mathbf{k})|^2\delta(E_{\mathbf{k}}-E_{\mathbf{k}'}).$$

Now we denote the number of Mn ions by N_A and the probability with which S_n^{ζ} takes a value of m by $w_m^{\pm}$, where + and − mean the + and − groups of ions. Then the summation over n in the above expression can be replaced by that over m, so that

$$\begin{aligned}W(\mathbf{k}'\pm\rightarrow\mathbf{k}\pm)=\frac{2\pi}{\hbar}N^{-2}\frac{N_A}{2}\sum_m{}^{\pm}w_m^{\pm}|&V(\mathbf{k}-\mathbf{k}')\\ &\mp mJ(\mathbf{k}-\mathbf{k}')|^2\delta(E_{\mathbf{k}}-E_{\mathbf{k}'}),\end{aligned}\tag{9}$$

where the summation is taken both over m from S to $-S$ and over w_m^{+} and w_m^{-}. We get the same expression for the inverse probability. With the use of (3) and the energy conservation relation for this process, we have

$$f^{\pm}(\mathbf{k}')[1-f^{\pm}(\mathbf{k})]-f^{\pm}(\mathbf{k})[1-f^{\pm}(\mathbf{k}')]$$
$$=\mathcal{E}\Phi^{\pm}(E_{\mathbf{k}})\frac{\partial f_0(E_{\mathbf{k}})}{\partial E_{\mathbf{k}}}(k_x-k_x'). \tag{10}$$

Inserting (9) and (10) into (8) and using (4), we obtain $(\partial f^{\pm}/\partial t)_{\text{el. col.}}$ for the elastic collisions,

$$\begin{aligned}\left(\frac{\partial f^{\pm}}{\partial t}\right)_{\text{el. col.}}&=\frac{1}{4\pi\hbar}\frac{N_A}{N}\frac{V}{N}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}E_k^{\frac{1}{2}}k_x\mathcal{E}\frac{\partial f_0(E_{\mathbf{k}})}{\partial E_{\mathbf{k}}}\Phi^{\pm}(E_{\mathbf{k}})\\ &\times\sum_m{}^{\pm}w_m^{\pm}\frac{1}{2}\int_0^{\pi}\left|V\left(2k\sin\frac{\theta}{2}\right)\mp mJ\left(2k\sin\frac{\theta}{2}\right)\right|^2\\ &\times(1-\cos\theta)\sin\theta d\theta.\end{aligned}\tag{11}$$

Next we shall consider the inelastic collisions. In this case, since the ζ component of the spin of the Mn ion is changed in the internal magnetic field $H^{\pm}$, the energy of the Mn spin system changes, and the transition probability becomes

$$\begin{aligned}W(\mathbf{k}'-\rightarrow\mathbf{k}+)&=W(\mathbf{k}+\rightarrow\mathbf{k}'-)\\ &=\frac{2\pi}{\hbar}\frac{N_A}{2}N^{-2}|J(\mathbf{k}'-\mathbf{k})|^2\\ &\times\sum_m{}^{\pm}\{S(S+1)-m(m+1)\}w_{m+1}^{\pm}\\ &\times\delta(E_{\mathbf{k}}+g\mu H^{\pm}-E_{\mathbf{k}'}),\end{aligned}\tag{12}$$

$$\begin{aligned}W(\mathbf{k}'+\rightarrow\mathbf{k}-)&=W(\mathbf{k}-\rightarrow\mathbf{k}'+)\\ &=\frac{2\pi}{\hbar}\frac{N_A}{2}N^{-2}|J(\mathbf{k}'-\mathbf{k})|^2\\ &\times\sum_m{}^{\pm}\{S(S+1)-m(m+1)\}w_m^{\pm}\\ &\times\delta(E_{\mathbf{k}}-g\mu H^{\pm}-E_{\mathbf{k}'}),\end{aligned}\tag{12'}$$

where g is the g factor of the Mn^{2+} ion and μ is the Bohr magneton. With the use of (3) and the energy conservation relation, we obtain the following relations:

$$\begin{aligned}w_{m+1}^{\pm}f^{-}(E_{\mathbf{k}}')[1-f^{+}(E_{\mathbf{k}})]&-w_m^{\pm}f^{+}(E_{\mathbf{k}})[1-f^{-}(E_{\mathbf{k}}')]\\ &=w_m^{\pm}\frac{\partial f_0(E_{\mathbf{k}})}{\partial E_{\mathbf{k}}}\frac{1-f_0(E_{\mathbf{k}}')}{1-f_0(E_{\mathbf{k}})}\\ &\times\mathcal{E}\{k_x\Phi^{+}(E_{\mathbf{k}})-k_x'\Phi^{-}(E_{\mathbf{k}}')\},\end{aligned}\tag{13}$$

$$\begin{aligned}w_m^{\pm}f^{+}(E_{\mathbf{k}}')[1-f^{-}(E_{\mathbf{k}})]&-w_{m+1}^{\pm}f^{-}(E_{\mathbf{k}})[1-f^{+}(E_{\mathbf{k}}')]\\ &=w_m^{\pm}\frac{\partial f_0(E_{\mathbf{k}})}{\partial E_{\mathbf{k}}}\frac{f_0(E_{\mathbf{k}'})}{f_0(E_{\mathbf{k}})}\\ &\times\mathcal{E}\{k_x\Phi^{-}(E_{\mathbf{k}})-k_x'\Phi^{+}(E_{\mathbf{k}}')\}.\end{aligned}\tag{13'}$$

Here we have used the thermal equilibrium value for the distribution function w_m. In so far as the *s-d* exchange interaction is isotropic, w_m does not deviate from its equilibrium value. Inserting (12), (12′) and (13), (13′) into (8), replacing the summation over $\mathbf{k}$ by an integration with the use of (4), and neglecting $g\mu H^{\pm}$ compared with $E_{\mathbf{k}}$ because we need only $\Phi^{\pm}(E_{\mathbf{k}})$ at the

Fermi surface as seen from (5) and (6), we obtain

$$\left(\frac{\partial f^+}{\partial t}\right)_{\text{inel. col.}} = \frac{1}{4\pi\hbar}\frac{N_A}{N}\frac{V}{N}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} k_x \mathcal{E} \frac{\partial f_0(E_{\mathrm{k}})}{\partial E_{\mathrm{k}}} E_{\mathrm{k}}^{\frac{1}{2}} \times \sum_m{}^{\pm}\{S(S+1)-m(m+1)\}w_m{}^{\pm} \times \frac{\exp(g\mu H^{\pm}/kT)\{\exp[(E_{\mathrm{k}}-E_f)/kT]+1\}}{\exp[(E_{\mathrm{k}}+g\mu H^{\pm}-E_f)/kT]+1} \times\left\{\frac{1}{2}\int_0^\pi \left|J\left(2k\sin\frac{\theta}{2}\right)\right|^2 \sin\theta d\theta\, \Phi^+(E_{\mathrm{k}}) - \frac{1}{2}\int_0^\pi \left|J\left(2k\sin\frac{\theta}{2}\right)\right|^2 \cos\theta\sin\theta d\theta\, \Phi^-(E_{\mathrm{k}})\right\}, \tag{14}$$

$$\left(\frac{\partial f^-}{\partial t}\right)_{\text{inel. col.}} = \frac{1}{4\pi\hbar}\frac{N_A}{N}\frac{V}{N}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} k_x \mathcal{E} \frac{\partial f_0(E_{\mathrm{k}})}{\partial E_{\mathrm{k}}} E_{\mathrm{k}}^{\frac{1}{2}} \times \sum_m{}^{\pm}\{S(S+1)-m(m+1)\}w_m{}^{\pm} \times \frac{\exp[(E_{\mathrm{k}}-E_f)/kT]+1}{\exp[(E_{\mathrm{k}}-g\mu H^{\pm}-E_f)/kT]+1} \times\left\{\frac{1}{2}\int_0^\pi \left|J\left(2k\sin\frac{\theta}{2}\right)\right|^2 \sin\theta d\theta\, \Phi^-(E_{\mathrm{k}}) - \frac{1}{2}\int_0^\pi \left|J\left(2k\sin\frac{\theta}{2}\right)\right|^2 \cos\theta\sin\theta d\theta\, \Phi^+(E_{\mathrm{k}})\right\}. \tag{14'}$$

Inserting (11) and (14), (14′) into the Boltzmann Eq. (7) and putting $E_{\mathrm{k}}=E_f$, we obtain the equation which determines the shift of the Fermi sphere $\Phi^{\pm}(E_f)$ as follows:

$$\frac{\hbar e}{m}+\frac{1}{4\pi\hbar}\frac{N_A}{N}\frac{V}{N}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E_f^{\frac{1}{2}}\left\{\sum_m{}^{\pm}[S(S+1) - m(m+1)]w_m{}^{\pm}\frac{2\exp(g\mu H^{\pm}/kT)}{1+\exp(g\mu H^{\pm}/kT)} \times[A\Phi^{\pm}(E_f)-B\Phi^{\mp}(E_f)]+[\sum_m{}^{\pm} m^2 w_m{}^{\pm} D \mp 2\sum_m{}^{\pm} m w_m{}^{\pm} F+2G]\Phi^{\pm}(E_f)\right\}=0, \tag{15}$$

where

$$A=\frac{1}{2}\int_0^\pi \left|J\left(2k\sin\frac{\theta}{2}\right)\right|^2 \sin\theta d\theta,$$

$$B=\frac{1}{2}\int_0^\pi \left|J\left(2k\sin\frac{\theta}{2}\right)\right|^2 \cos\theta\sin\theta d\theta,$$

$$D=A-B, \tag{16}$$

$$F=\frac{1}{2}\int_0^\pi J\left(2k\sin\frac{\theta}{2}\right)V\left(2k\sin\frac{\theta}{2}\right)(1-\cos\theta)\sin\theta d\theta,$$

$$G=\frac{1}{2}\int_0^\pi \left|V\left(2k\sin\frac{\theta}{2}\right)\right|^2 (1-\cos\theta)\sin\theta d\theta.$$

Equations (15) are the simultaneous equations for $\Phi^{\pm}(E_f)$. We note that the shift of the Fermi sphere is different for + and − spins. Solving (15), we obtain

$$\Phi^+(E_f)-\Phi^-(E_f)=\left(\frac{2F\sum_m{}^{\pm} m w_m{}^{\pm}[\Phi^+(E_f)+\Phi^-(E_f)]}{2G+D\sum_m{}^{\pm} m^2 w_m{}^{\pm}+(A+B)\sum_m{}^{\pm}[S(S+1)-m(m+1)]w_m{}^{\pm}[1+\tanh(g\mu H^{\pm}/2kT)]}\right), \tag{17}$$

and

$$[\Phi^+(E_f)+\Phi^-(E_f)]^{-1} = -\frac{m}{8\pi e\hbar^2}\frac{N_A}{N}\frac{V}{N}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E_f^{\frac{1}{2}}\left[2G+D\{\sum_m{}^{\pm} m^2 w_m{}^{\pm}+\sum_m{}^{\pm}[S(S+1)-m(m+1)]w_m{}^{\pm}[1+\tanh(g\mu H^{\pm}/2kT)]\} - \left(\frac{4F^2(\sum_m{}^{\pm} m w_m{}^{\pm})^2}{2G+D\sum_m{}^{\pm} m^2 w_m{}^{\pm}+(A+B)\sum_m{}^{\pm}[S(S+1)-m(m+1)]w_m{}^{\pm}[1+\tanh(g\mu H^{\pm}/2kT)]}\right)\right]. \tag{18}$$

Thus, we obtain the resistivity from (6) with the use of (18) as follows:

$$R=\frac{3\pi}{4}\frac{m}{e^2}\frac{1}{\hbar E_f}\frac{V}{N}\frac{N_A}{N}\left[2G+D\{\sum_m{}^{\pm} m^2 w_m{}^{\pm}+\sum_m{}^{\pm}[S(S+1)-m(m+1)]w_m{}^{\pm}[1+\tanh(g\mu H^{\pm}/2kT)]\} - \left(\frac{4(\sum_m{}^{\pm} m w_m{}^{\pm})^2 F^2}{2G+D\sum_m{}^{\pm} m^2 w_m{}^{\pm}+(A+B)\sum_m{}^{\pm}[S(S+1)-m(m+1)]w_m{}^{\pm}[1+\tanh(g\mu H^{\pm}/2kT)]}\right)\right]. \tag{19}$$

Here, G comes from the purely spin-independent interaction, D, A, and B come from the purely spin-dependent interaction, and F comes from the cross term of these two interactions. The F term makes an essential contribution to the magnetoresistance, as shown in the next section. The result (19) is independent of the angle between the external electric field and the quantization axis of the spins.

III. COMPARISON WITH EXPERIMENTAL RESULTS

1. Electrical Resistivity

In the absence of an external magnetic field and for the antiferromagnetic ordering of Mn spins which has experimentally been found,[4,5] the total magnetization of the Mn spins vanishes and the molecular fields H^+ and H^- are equal in magnitude but opposite in sign, namely

$$\textstyle\sum_m mw_m{}^+ + \sum_m mw_m{}^- = 0, \quad H^+ + H^- = 0.$$

Therefore, the resistivity (19) can be written as

$$R = \frac{3\pi}{2}\frac{m}{e^2}\frac{1}{\hbar E_f}\frac{V}{N}\frac{N_A}{N}\left\{G + D\left[S(S+1) - \tfrac{1}{2}\sum_m{}^{\pm} mw_m{}^{\pm}\tanh\left(\frac{g\mu H^{\pm}}{2kT}\right)\right]\right\}, \quad (H_{\text{ext}}=0). \tag{20}$$

At higher temperatures than the Néel temperature, we can put $\sum_m mw_m{}^{\pm} = 0$ and $H^+ = H^- = 0$, and the resistivity becomes

$$R = \frac{3\pi}{2}\frac{m}{e^2}\frac{1}{\hbar E_f}\frac{V}{N}\frac{N_A}{N}[G + DS(S+1)], \quad (H_{\text{ext}}=0,\ T > T_N), \tag{21}$$

where the contributions from ξ, η, and ζ components of the exchange interaction are equal. Thus, the resistivity above the Néel temperature becomes independent of the temperature. Actually, even above the Néel temperature, however, the molecular fields H^+ and H^- acting on each Mn spin are not quite zero though their average values over all the Mn spins vanish. Thus, the effect of the short-range order on the resistivity would be more significant than that on the magnetic properties. This effect gives rise to a gradual increase of the resistivity even above the Néel temperature superposed on the rise of the normal resistivity due to the lattice vibrations. At temperatures below the Néel temperature the expression (20) decreases, and at absolute zero it reaches the value

$$R_{T=0} = \frac{3\pi}{2}\frac{m}{e^2}\frac{1}{\hbar E_f}\frac{V}{N}\frac{N_A}{N}(G + DS^2), \quad (H_{\text{ext}}=0,\ T=0). \tag{22}$$

The difference between the value at absolute zero and that above the Neél temperature is given by

$$\Delta R = \frac{3\pi}{2}\frac{m}{e^2}\frac{1}{\hbar E_f}\frac{V}{N}\frac{N_A}{N}DS. \tag{23}$$

If we use here the value of the Fermi energy $E_f = 1.1 \times 10^{-11}$ erg, $N/V = 8.5 \times 10^{22}$ per cc for pure copper, the free electron mass, and $S = \frac{5}{2}$, and if we estimate $(D)^{\frac{1}{2}}$ to be equal to the exchange integral for a free Mn$^+$ ion $J = 3.5 \times 10^{-13}$ erg, we obtain $\Delta R = 0.06\ \mu$ohm cm per atomic percent Mn. This value is smaller than the experimental value[10,14] $\Delta R = 0.2\ \mu$ohm cm per atomic percent Mn by a factor of 3. This means that we should take $1.7 J_0$ as a value of $D^{\frac{1}{2}}$, where J_0 is the exchange integral for a free Mn$^+$ ion.[16] Since D is really a weighted average of the square of the Fourier component of the exchange integral $J(k-k')$ as seen from (16), this agreement is satisfactory.

The functional form of (20) is similar to that obtained by Schmitt[10] for the inelastic scattering only, and its temperature dependence is described by the curve (Fig. 2, $\alpha = 0$) of his paper.[10] However, our result includes also the elastic part. Moreover, Schmitt assumed the ferromagnetic ordering of Mn spins at low temperature. In our result, the last term of (19) which vanishes in the antiferromagnetic case would give an additional important contribution in the case of ferromagnetic ordering. In the antiferromagnetic case the temperature dependence given by (20) can be fitted to the experimental result for the alloys with more than one atomic percent Mn by a suitable choice of the parameters. However, the minimum and maximum found experimentally for lower concentration cannot be explained by our result.

2. Magnetoresistance

Now we shall estimate the ratio of D to G with the use of the data obtained by Schmitt and Jacobs[14] for a sample containing 1.8 atomic percent Mn. In the absence of an external magnetic field, from (21), (22) the values of resistivity at absolute zero and above the Néel temperature are

$$\begin{aligned} R_{T=0} &= C(2 + 2S^2 D/G), \\ R(T_N) &= C[2 + 2S(S+1)D/G], \\ C &= \frac{3\pi}{4}\frac{m}{e^2}\frac{1}{\hbar E_f}\frac{V}{N}\frac{N_A}{N}G, \quad (H_{\text{ext}}=0). \end{aligned} \tag{24}$$

The corresponding experimental values are approximately $R_{T=0} = 4.6\ \mu$ohm cm and $R(T_N) = 5\ \mu$ohm cm. Inserting these values into the above expressions, we

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[16] The result (21) has also been obtained by Rodriguez (unpublished). Owen *et al.*[4] based their discussion of the resistance on this unpublished calculation but the analysis contains a numerical error so that their final estimate of the resistance should be larger by a factor of 48.

TABLE I. Experimental and calculated values of magnetoresistance for a sample containing 1.8 atomic percent Mn at 20.4°K and 2.5°K. Experimental values have been read from the curves obtained by Schmitt and Jacobs.[a, b] The double values are due to the hysteresis effect.

Magnetic field, kilo-oersteds	7.4	7.2	6.1	6.0	5.0	4.9	3.9	3.8
Temperature, °K	20.4	2.5	20.4	2.5	20.4	2.5	20.4	2.5
$(100\langle m\rangle/S)_{\mathrm{exp}}$	5.5	5.5	4.6	4.5 4.8	3.9	3.6 4.0	3.1	2.7 3.3
$-(1000\Delta R_H)_{\mathrm{exp}}$, μohm cm	9.4	13.2	6.6	9.0 9.7	4.8	6.2 7.1	2.8	3.5 4.3
$-(1000\Delta R_H)_{\mathrm{calc}}$, μohm cm	9.1	9.5	6.4	6.4 7.3	4.6	4.1 4.9	2.9	2.3 3.4

[a] See reference 14.

[b] *Note added in proof.*—The experimental values of $\langle m\rangle/s$ given in the paper of Schmitt and Jacobs[14] have been referred to an S value of 2 instead of 5/2. Therefore, the calculated values in this table should be reduced by about 35%. I should like to thank Dr. R. W. Schmitt for pointing out this fact.

obtain

$$D/G=0.045,\quad R_{T=0}=2.56C,\quad R(T_N)=2.78C. \tag{25}$$

When the magnetic field is applied, the change of the resistivity consists of two parts, one from the second term of (19) which is proportional to D and the other from the third part of (19) which is proportional to F^2. We shall see later that the former part contributes about ten percent of the latter and for the present we shall neglect the former part. Then, neglecting the small change of the denominator due to the external magnetic field in the third term of (19), we conclude that the magnetoresistance has a negative sign and is proportional to the square of the magnetization $\frac{1}{2}N_A\sum_m{}^{\pm} mw_m{}^{\pm}$. The coefficient of proportionality is large and when the magnetization is saturated, $\Delta R/R_{T=0}=-0.68$, as shown later. For a low magnetic field, the magnetoresistance is proportional to the square of the magnetic field and also to the square of the susceptibility. The susceptibility shows a maximum at the Néel temperature so that the magnetoresistance is expected to show a maximum at that temperature.

Now we shall go back to the general expression of (19). For an infinite magnetic field and any finite temperature, (19) gives

$$R_\infty=C\left(2+2S^2\frac{D}{G}-\frac{16S^2}{2+2S^2D/G}\frac{F^2}{G^2}\right),\quad (H_{\mathrm{ext}}=\infty). \tag{26}$$

The first two terms in this expression are just $R_{T=0}$ given by (24) and they are smaller than $R(T_N)$ by $2CSD/G\approx 0.22C$. The third term of (26) becomes $1.74C$, where using (16) we have put F^2/G^2 approximately equal to D/G. If we assume that the second term in (19) changes monotonically with temperature and magnetic field, then we see that its maximum change is less than ten percent of the third term of (19) when the temperature or the magnetic field is altered. This justifies the neglect of this term in the discussion above of the magnetoresistance. The value of R_∞ is estimated as about $0.82C$ and this corresponds to 32% of $R_{T=0}$. For a low magnetic field applied in the direction of the preferred axis of spins below the Néel temperature and in any direction above the Néel temperature, the change of the second term of (19) proportional to D can be shown to be proportional to H^2.

Above the Néel temperature, we can expand $w_m{}^{\pm}$ and $\tanh(g\mu H^{\pm}/2kT)$ with respect to $H^{\pm}$. Then, we see, as mentioned above, that the term linear in $H^{\pm}$ vanishes and the term quadratic in $H^{\pm}$ arises from the term

$$-\textstyle\sum_m{}^{\pm} mw_m{}^{\pm}\tanh(g\mu H^{\pm}/2kT). \tag{27}$$

Tanh$(g\mu H^{\pm}/2kT)$ can be expanded as $g\mu H^{\pm}/2kT$ for small $H^{\pm}$. On the other hand, the average magnetization $\langle m\rangle=\sum_m mw_m{}^{\pm}$ is given by the Brillouin function $SB_S(g\mu SH/kT)$. This behaves like $\frac{1}{3}S(S+1)(g\mu H/kT)$, so that for small magnetic field $\tanh(g\mu H^{\pm}/2kT)$ can be expressed as $-[3/S(S+1)](\sum_m mw_m{}^{\pm})^2$. Thus, above the Néel temperature and for a small magnetic field, we have

$$-\frac{\Delta R_H}{R_{H=0}}=\frac{1}{2+2S(S+1)D/G}\left\{\frac{3}{S(S+1)}\right.$$
$$\left.+\frac{16}{2+2S(S+1)D/G}\right\}\frac{D}{G}\langle m\rangle^2. \tag{28}$$

Here we put $F^2/G\sim D$ and $A+B\sim D$. If we use $D/G\sim 0.045$ estimated in (25), we see that the first term is only six percent of the second term. This situation would not change much below the Néel temperature. From (28), we obtain

$$-\Delta R_H=0.61\frac{\langle m\rangle^2}{S^2}R_{H=0}. \tag{29}$$

Schmitt and Jacobs[14] have measured the magnetization $\langle m\rangle$, and the magnetoresistance for the same sample. The following table shows the values of the magnetoresistance and the magnetization for a 1.8 atomic percent alloy obtained by Schmitt and Jacobs[14] and the calculated values of the magnetoresistance.

The Néel temperature of this concentration seems to be about 15°K, and the resistance at 20.4°K was calculated from (29) using the experimental values of $\langle m\rangle$. At 2.5°K the resistance was calculated from (19) neglecting the change of the second term. The agreement is quite good above T_N, but below T_N the calculated resistance is about 70% of the measured value. It is estimated that including the second term in (19) would increase this by approximately 10%. It was also implicitly assumed in using (19) to calculate the resistances below T_N shown in Table I, that the magnetic field is parallel to the preferred direction. However, it seems more reasonable to suppose that the experimental values correspond to an average over-all

TABLE II. Effective *s-d* exchange integral.

1. Anomalous g value of Mn ion[a]	$J(0)$
2. Relaxation time for Mn spin	$\left[\frac{1}{2}\int_0^\pi \left\lvert J\left(2k\sin\frac{\theta}{2}\right)\right\rvert^2 \sin\theta d\theta\right]^{\frac{1}{2}}$
3. Anomalous resistivity	$\left[\frac{1}{2}\int_0^\pi \left\lvert J\left(2k\sin\frac{\theta}{2}\right)\right\rvert^2 (1-\cos\theta)\sin\theta d\theta\right]^{\frac{1}{2}}$
4. Anomalous magnetoresistance	$\left(\frac{\frac{1}{2}\int_0^\pi J\left(2k\sin\frac{\theta}{2}\right)V\left(2k\sin\frac{\theta}{2}\right)(1-\cos\theta)\sin\theta d\theta}{\left[\frac{1}{2}\int_0^\pi \left\lvert V\left(2k\sin\frac{\theta}{2}\right)\right\rvert^2 (1-\cos\theta)\sin\theta d\theta\right]^{\frac{1}{2}}}\right)$
5. Néel temperature[a] anomalous width[b] of Cu nuclear resonance	Complicated: the precise q dependence of the Fourier component of the exchange integral determines the nature of the effective spin-coupling between spins.

[a] See reference 6.
[b] R. Behringer, Phys. Chem. Solids (to be published).

field direction, but such an average has not been calculated. In any case the resistance is independent of the direction of the applied electric field, as observed experimentally, unless higher order interactions including spin-orbit coupling are taken into account.

IV. CONCLUSIONS

The present calculation on the basis of an *s-d* interaction gives an anomalous resistivity which is smaller than the experimental value by a factor of about 3. This means that the effective exchange integral $D^{\frac{1}{2}}$ is larger than the free-ion value by a factor of 1.7. This value is quite reasonable. The temperature dependence is in good agreement with the experimental results for the alloys containing more than one atomic percent Mn. However, the present theory does not give the maximum and the minimum in the resistivity *vs* temperature curve which have been found for lower concentration. The magnetoresistance obtained here agrees quite well with the experimental values. Thus, it can be concluded that the *s-d* interaction is the essential factor for the electrical properties as well as the magnetic properties of Cu-Mn alloys, but that the phenomenon of the resistivity maximum and minimum might not be explained by this interaction only.

Table II conveniently summarizes the effective *s-d* exchange integral responsible for several quantities. For the estimation of the calculated values in this paper, it was assumed that $J(q)$ is constant and equal to the value for a free Mn^+ ion. Such an assumption makes all effective exchange integrals in this table equal to the free-ion value.

The present calculation can easily be extended to the case of ferromagnetic metals. For pure ferromagnetic metals, the perturbing potential does not include any spin-independent part so that we have no contribution from the cross term in (19). Moreover, when all the localized *d*-spins of the ions are in the same spin state, the potential becomes periodic and there is no elastic scattering. Hence subtracting out the mean magnetization of each atom, we can replace $\sum m^2 w_m$ in the second (elastic) term of (19) by $\sum(m-\langle m\rangle)^2 w_m$ and putting $N_A=N$, we obtain the resistivity due to *s-d* interaction for ferromagnetic metals as

$$R=\frac{3\pi}{2}\frac{m}{e^2}\frac{1}{\hbar E_f}\frac{V}{N}D\{\sum_m(m-\langle m\rangle_{\mathrm{Av}})^2 w_m+\sum_m[S(S+1) -m(m+1)]w_m[1+\tanh(g\mu H/2kT)]\}, \quad (30)$$

where H is the sum of the internal field and the external field. The interesting fact about this expression is that the expansion of (30) with respect to the external field below the Curie temperature includes a term linear in the external field in contrast to the antiferromagnetic case. Thus, we can expect a decrease of resistance proportional to the external field for ferromagnetic metals from the same *s-d* interaction mechanism.

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