PHYSICAL REVIEW VOLUME 106, NUMBER 5 JUNE 1, 1957

Magnetic Properties of Cu-Mn Alloys

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(Received February 18, 1957)

The polarization of conduction electrons due to *s-d* interaction in CuMn alloys is investigated. The uniform polarization due to the first order perturbed energy corresponding to the Fröhlich-Nabarro and Zener mechanism is shown to be completely modified by the first order perturbation of the wave functions and the polarization is concentrated in the neighborhood of the Mn ions. At the same time it is shown that the Fröhlich-Nabarro interaction is included in the Ruderman-Kittel result as one component. The electronic *g*-value of Mn ions and the Knight shift of the Cu-nuclei are also discussed from this point of view.

I. INTRODUCTION

PROBLEMS concerning the hyperfine interaction between conduction electrons and nuclear spins in metals were first treated by Fröhlich and Nabarro.[1] They investigated the uniform polarization of the conduction electrons due to the first-order perturbed energy. Ruderman and Kittel[2] and Bloembergen and Rowland[3] treated the effect of the second order perturbation and explained the anomalous broadening of the absorption line in the nuclear magnetic resonance in metals by the indirect $\mathbf{I}\cdot\mathbf{I}$ coupling arising from the second order perturbation.

In transition metals and in alloys including transition metal ions the interaction between the conduction electrons and the *d*-electrons can be treated in a completely parallel way to the hyperfine interaction in metals. Zener[4] proposed a mechanism of polarizing the conduction electrons by the exchange interaction with the *d*-electrons of the paramagnetic ions. This is the mechanism due to the first order perturbation and corresponds to the Fröhlich-Nabarro treatment. In connection with the problems of metallic ferromagnetism, Kasuya[5] carefully investigated the interaction between the conduction electrons and the localized *d*-electron spins, including the second order effect.

Recently, Owen, Browne, Knight, and Kittel[6] have made experiments on the magnetic properties of Cu-Mn alloy systems and have discussed the effects of the exchange interaction between the conduction *s*-electrons and the localized *d*-electrons of the Mn ions. According to their discussions, the first-order effect of the *s-d* interaction corresponding to the Zener mechanism should give rise to a large extra Knight shift of the Cu nuclear spins and a large electronic *g*-value of the Mn spins on account of the uniform polarization of the conduction electrons. The effect of the uniform polarization of the conduction electrons, however, has not been observed in their experiments.

The purpose of the present paper is to investigate the contribution of the second-order effect corresponding to the Ruderman-Kittel mechanism to the hyperfine interaction in metals and its relation to the first order effect. A partial solution of this problem can be found in Kasuya's paper[5] though he did not explicitly mention this problem.

On the other hand, according to the Friedel theorem the perturbing potential due to the impurities added in the metal is completely screened out except in the neighborhood of the impurities. Friedel[7] and Bloembergen and Rowland[8] explained by this theorem that the Knight shift of Tl^{205} in Tl metal including less than three percent tin is the same as that in pure Tl metal.

Recently Hart[9a] also discussed the localization of the polarization around the manganese atoms and hence the absence of an additional copper Knight shift. He pointed out that we must have a localization of the polarization independent of the particular model or mechanism envisaged. This follows directly from a general result due to Friedel (when properly formulated), and in fact the present calculation furnishes an illuminating illustration of Friedel's result.

II. POLARIZATION OF CONDUCTION ELECTRONS

In this section we shall consider the polarization of the conduction electrons due to the *s-d* exchange interaction. The Hamiltonian of the *s-d* interaction has been given by Kasuya[5] and by Mitchell[9b] as follows:

$$-N^{-1}\sum_{\mathbf{k}}\sum_{\mathbf{k}'}\sum_n J(\mathbf{k}-\mathbf{k}')\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n] \times\{(a_{k'+}^*a_{k+}-a_{k'-}^*a_{k-})S_n^z + a_{k'+}^*a_{k-}S_n^- + a_{k'-}^*a_{k+}S_n^+\}, \quad (2.1)$$

where N is the total number of lattice points and $J(\mathbf{k}-\mathbf{k}')$ is the exchange integral between a conduction

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electron and the *d*-core spin of the Mn ion. The exchange integral may be written

$$J(\mathbf{k}-\mathbf{k}')=N\int\frac{e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n}\phi_{k'}^*(\mathbf{r}_1)\phi_d^*(\mathbf{r}_2-\mathbf{R}_n)\phi_k(\mathbf{r}_2)\phi_d(\mathbf{r}_1-\mathbf{R}_n)}{r_{12}}d\tau_{12}, \tag{2.2}$$

where $\mathbf{k}$ and $\mathbf{k}'$ are the wave vectors of the conduction electron, $\mathbf{R}_n$ represents the position of the Mn ion and $\mathbf{S}_n$ represents its spin operator. $a_{k\pm}^*$ and $a_{k\pm}$ are the creation and annihilation operators for the electrons with wave vector $\mathbf{k}$ and + or − spin.

The z axis is taken as the axis of quantization of the electron spins and the state of the system is specified by giving the number of electrons of each spin for each value of $\mathbf{k}$. The *s-d* interaction expressed by (2.1) has the following diagonal element:

$$-N^{-1}J(0)(n_+-n_-)\sum_n S_n^z, \tag{2.3}$$

where n_+ and n_- represent the total number of electrons of + and − spin. This diagonal energy becomes lower as n_+-n_- increases, and tends, therefore, to polarize the conduction electrons.

The Fermi energies for electrons with + and − spins are given by

$$E_f^\pm=(\hbar^2/2m)k_m^{\pm 2}\mp N^{-1}J(0)\sum_n S_n^z, \tag{2.4}$$

where $k_m^\pm$ are, respectively, the maximum wave vectors of + and − spins and they are related to $n_\pm$ by the following equations:

$$n_\pm=(V/6\pi^2)k_m^{\pm 3}. \tag{2.5}$$

Now let us denote the maximum wave vector for the unpolarized state by k_m and the total number of electrons by $2n=n_++n_-$. Then we have

$$n=(V/6\pi^2)k_m^3. \tag{2.6}$$

If we put

$$k_m^\pm=k_m\pm\Delta k, \tag{2.7}$$

we get

$$E_f^\pm=E_f\pm 2E_f(\Delta k/k_m)\mp N^{-1}J(0)\sum_n S_n^z, \tag{2.8}$$

where E_f represents the Fermi energy of the unpolarized spin system. Similarly we obtain, for n_+ and n_-,

$$n_\pm=n\pm 3n(\Delta k/k_m). \tag{2.9}$$

Δk is determined by the condition that E_f^+ and E_f^- should be equal to each other. This gives

$$\Delta k/k_m=[N^{-1}J(0)/2E_f]\sum_n S_n^z. \tag{2.10}$$

Inserting (2.10) into (2.9) we obtain the following expression for $n_\pm$:

$$n_\pm=n\pm(3n/2E_f)N^{-1}J(0)\sum_n S_n^z. \tag{2.11}$$

The change of the total kinetic energy is given by

$$\Delta E=(E_f/6n)(n_+-n_-)^2. \tag{2.12}$$

The result (2.11) can also be obtained by minimizing the sum of (2.3) and (2.12) with respect to (n_+-n_-). The polarization expressed by (2.11) is that given by Fröhlich and Nabarro[1] and Zener.[4] Here it should be noted that this polarization arising from the first-order perturbation of the energy is proportional to $N^{-1}J(0)/E_f$ and, as will be shown below, that from the first-order perturbation of the wave function has the same order of magnitude. The first-order energy including the change of the kinetic energy is given by

$$-(3n/2E_f)[N^{-1}J(0)\sum_n S_n^z]^2. \tag{2.13}$$

This energy is proportional to $[N^{-1}J(0)]^2/E_f$, and has the same order as the second order perturbed energy.

Next, we shall calculate the change of the density of the + and − spins due to the first-order perturbation of the wave function. The first-order perturbed wave function of the conduction electron is given by

$$\phi_{\mathbf{k}}=\phi_{\mathbf{k}}^0+\sum_{\mathbf{k}'}\frac{\mathcal{H}_{k'k}}{E_{\mathbf{k}}-E_{\mathbf{k}'}}\phi_{\mathbf{k}'}^0. \tag{2.14}$$

With the use of (2.1) as $\mathcal{H}$ and approximating $\phi_{\mathbf{k}}^0$ with the plane wave $(1/V)^{\frac{1}{2}}e^{i\mathbf{k}\cdot\mathbf{r}}$, we obtain

$$\phi_{\mathbf{k}\pm}=\phi_{\mathbf{k}\pm}^0-\frac{2m}{\hbar^2}N^{-1}\sum_{\mathbf{k}'}{}'\frac{J(\mathbf{k}-\mathbf{k}')}{k^2-k'^2}\sum_n e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n}$$

$$\times\{\pm S_n^z\phi_{\mathbf{k}'\pm}^0+S_n^\pm\phi_{\mathbf{k}'\mp}^0\}, \tag{2.15}$$

where + and − express the plus and minus spins, respectively, and the prime attached to the summation means to exclude the term $\mathbf{k}=\mathbf{k}'$. The densities of ± spins can be obtained by calculating the quantities

$$\sum_S\sum_{\mathbf{k}}^{\mathbf{k}_m^\pm}\phi_{\mathbf{k}\pm}^*\phi_{\mathbf{k}\pm}$$

by means of (2.15) as follows:

$$\rho_\pm(r)=\frac{1}{V}\sum_{\mathbf{k}}^{\mathbf{k}_m^\pm}\mp\frac{2m}{V\hbar^2}N^{-1}\sum_{\mathbf{k}}^{\mathbf{k}_m^\pm}\sum_{\mathbf{k}'}{}'\frac{J(\mathbf{k}-\mathbf{k}')}{k^2-k'^2}$$

$$\times\sum_n\{e^{i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{r}-\mathbf{R}_n)}+e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{r}-\mathbf{R}_n)}\}S_n^z. \tag{2.16}$$

The first term in (2.16) is written with the use of (2.11) as

$$\frac{1}{V}\sum_{\mathbf{k}}^{\mathbf{k}_m^\pm}=\frac{1}{V}n_\pm=\frac{1}{V}\left\{n\pm\frac{3n}{2E_f}N^{-1}J(0)\sum_n S_n^z\right\}. \tag{2.17}$$

Now we put $\mathbf{k}-\mathbf{k}'=\mathbf{q}$ and, when we perform an integration over **k**, the second terms in (2.16) become

$$\pm\frac{2m}{VN\hbar^2}\frac{V}{16\pi^2}\sum_{\mathbf{q}}{}' J(\mathbf{q})\left\{k_m^{\pm}+\frac{4k_m^{\pm 2}-q^2}{4q}\ln\left|\frac{2k_m^{\pm}+q}{2k_m^{\pm}-q}\right|\right\}$$
$$\times\sum_n\{e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_n)}+e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_n)}\}S_n^z.$$

Here, if we consider the relation (2.6), (2.16) can be written as

$$\rho_{\pm}(r)=\frac{n}{V}\pm\frac{3n}{2E_f}\frac{1}{V}N^{-1}J(0)\sum_n S_n^z\pm\frac{1}{8}\frac{3n}{E_f}\frac{N^{-1}}{V}$$
$$\times\sum_{\mathbf{q}}{}' J(\mathbf{q})f(q)\sum_n\{e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_n)}+e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_n)}\}S_n^z \quad (2.18)$$

and

$$f(q)=1+\frac{4k_m^2-q^2}{4k_mq}\ln\left|\frac{2k_m+q}{2k_m-q}\right|. \quad (2.19)$$

We have neglected the difference between $k_m^{\pm}$ and k_m in $f(q)$. In the expression (2.18), the second term is the polarization coming from the first-order perturbation of the energy and it is uniform over the metal. The third term comes from the first-order perturbation of the wave function and has the same order of magnitude as the second term.

The term $\mathbf{q}=0$ which is omitted from the summation of the third term can easily be shown to be just equal to the second term because $f(0)$ is equal to 2. Therefore, we finally obtain

$$\rho_{\pm}(r)=\frac{n}{V}\pm\frac{1}{8}\frac{3n}{E_f}\frac{N^{-1}}{V}\sum_{\mathbf{q}} J(\mathbf{q})f(q)$$
$$\times\sum_n S_n^z[e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_n)}+e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_n)}], \quad (2.20)$$

where the summation should be taken over all **q**-values including $\mathbf{q}=0$. We wish to emphasize that the expression (2.20) includes both the first order effect considered by Fröhlich and Nabarro and the second order effect considered by Ruderman and Kittel.

Here, if we put $J(\mathbf{q})=\text{const}$, we can perform the integration over **q** in (2.20) as

$$N^{-1}\sum_{\mathbf{q}} f(q)e^{i\mathbf{q}\cdot\mathbf{R}}=-24\pi(n/N)F(2k_mR), \quad (2.21)$$

$$F(x)=(1/x^4)(x\cos x-\sin x), \quad (2.22)$$

and we obtain

$$\rho_{\pm}(r)=\frac{n}{V}\mp\frac{1}{V}\frac{(3n)^2}{E_f}2\pi J(0)N^{-1}\sum_n F[2k_m|\mathbf{r}-\mathbf{R}_n|]S_n^z. \quad (2.23)$$

Equation (2.22) is the same as the function obtained by Ruderman and Kittel. This expression becomes infinite as r tends to R_n. This is due to the approximation of $J(\mathbf{q})=\text{constant}$. In actuality, $J(\mathbf{q})$ would decrease with **q**. Noting that the function $f(q)$ abruptly decreases near $q=2k_m$, and putting $J(\mathbf{q})f(q)=2J(0)$ for $q<2k_m$ and $J(\mathbf{q})f(q)=0$ for $q>2k_m$, we obtain

$$\rho_{\pm}(r)=\frac{n}{V}\mp\frac{1}{V}\frac{4(3n)^2}{E_f}J(0)N^{-1}$$
$$\times\sum_n 2k_m|\mathbf{r}-\mathbf{R}_n|F[2k_m|\mathbf{r}-\mathbf{R}_n|]S_n^z. \quad (2.24)$$

This ρ has a finite value at $r=R_n$. The polarization given by (2.23) and (2.24) oscillates and rapidly vanishes as $r-R_n$ tends to infinity. Therefore, the polarization of the conduction electrons is concentrated in the neighborhood of the impurity center and the uniform polarization given by Fröhlich and Nabarro[1] is completely modified.

In the next section we shall give a formal discussion of the copper nuclear resonance, but already we can see qualitatively at this stage that there will be no additional Knight shift as expected by Owen *et al.* The Knight shift for a copper nucleus is proportional to $\Delta\rho=\rho_+-\rho_-$ at the nucleus and since the polarization of the conduction band is localized there is no additional contribution to $\Delta\rho$ (besides the Pauli spin paramagnetic effect) at a copper nucleus far away from the manganese atoms.

III. EFFECTIVE HAMILTONIAN OF Cu-NUCLEAR SPIN AND Mn-ELECTRONIC SPIN SYSTEM

In the preceding section, it has been shown that the uniform polarization of the electron spins due to the first-order perturbation of the energy is completely modified by the perturbation of the wave function and the polarization is concentrated in the vicinity of the impurity center. In this section we shall derive the effective Hamiltonian of the spin system consisting of Mn-*d* core spins and Cu-nuclear spins.

Now taking the z-axis as the direction of the magnetic field, the total Hamiltonian for this spin system can be written as follows:

$$\mathcal{H}=\tfrac{1}{2}a\sigma_z^2-\beta_eH\sigma_z-g\beta_eH\sum_n S_n^z-g_N\beta_NH\sum_n I_n^z$$
$$-N^{-1}\sum_{\mathbf{k}}\sum_{\mathbf{k}'}J(\mathbf{k}-\mathbf{k}')\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n]$$
$$\times\{(a_{k'+}^*a_{k+}-a_{k'-}^*a_{k-})S_n^z$$
$$+a_{k'+}^*a_{k-}S_n^-+a_{k'-}^*a_{k+}S_n^+\}$$
$$+\tfrac{1}{2}N^{-1}\sum_{\mathbf{k}}\sum_{\mathbf{k}'}A(\mathbf{k}-\mathbf{k}')\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n]$$
$$\times\{(a_{k'+}^*a_{k+}-a_{k'-}^*a_{k-})I_n^z$$
$$+a_{k'+}^*a_{k-}I_n^-+a_{k'-}^*a_{k+}I_n^+\}. \quad (3.1)$$

Here, σ_z is twice the z-component of the total spin of the conduction electrons and is equal to n_+-n_- and the first term represents the change of the kinetic energy of the free electrons. The quantity a is given by

$$a=E_f/3n. \quad (3.2)$$

I_n represents the nuclear spin operator of Cu and the second, the third and the fourth terms in the first line are the Zeeman energy of the conduction electrons, Mn-spins and Cu-nuclear spins, respectively. The fifth term expresses the *s-d* interaction given by (2.1), and the sixth term represents the hyperfine interaction between conduction electrons and Cu-nuclear spins.

The diagonal energy of (3.1) is given by

$$\tfrac{1}{2}a\sigma_z^2-\sigma_z[\beta_eH+N^{-1}J(0)\textstyle\sum_n S_n^z-\tfrac{1}{2}N^{-1}A(0)\textstyle\sum_n I_n^z]$$
$$-g\beta_eH\textstyle\sum_n S_n^z-g_N\beta_NH\textstyle\sum_n I_n^z. \quad (3.3)$$

The z-component of the total spin of conduction electrons $\frac{1}{2}\sigma_z$ can now be determined by minimizing the diagonal energy (3.3) with respect to σ_z as follows:

$$\sigma_z=\frac{1}{a}[N^{-1}J(0)\textstyle\sum_n S_n^z-\tfrac{1}{2}N^{-1}A(0)\textstyle\sum_n I_n^z+\beta_eH]. \quad (3.4)$$

This polarization σ_z corresponds to the uniform polarization due to the Fröhlich-Nabarro mechanism. Inserting (3.4) into (3.3), we get the first order perturbed energy as

$$-\frac{1}{2a}\beta_e^2H^2-\frac{1}{2a}N^{-2}J(0)^2(\textstyle\sum_n S_n^z)^2-\frac{1}{8a}N^{-2}A^2(0)(\textstyle\sum_n I_n^z)^2$$
$$+\frac{1}{2a}N^{-2}J(0)A(0)(\textstyle\sum_n S_n^z\cdot\textstyle\sum_n I_n^z)$$
$$-\left[g\beta_eH+\frac{1}{a}N^{-1}J(0)\beta_eH\right]\cdot\textstyle\sum_n S_n^z$$
$$-\left[g_N\beta_NH-\frac{1}{2a}N^{-1}A(0)\beta_eH\right]\textstyle\sum_n I_n^z. \quad (3.5)$$

The calculation for the second order perturbed energy can be performed along the same line as in Kasuya's paper.[5] In our case, however, the second order terms consist of three parts, the first comes from the *s-d* interactions alone, the second from the *s-I* interaction alone and the third from the cross term of these two kinds of interactions. We shall begin with the first part. This part $H_{S\cdot S}^{(2)}$ is expressed as

$$H_{S\cdot S}^{(2)}=N^{-2}\sum_{\mathbf{k}}\sum_{\mathbf{k}'}\sum_{n}\sum_{m}|J(\mathbf{k}-\mathbf{k}')|^2\frac{\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{nm}]}{(\hbar^2/2m)(k^2-k'^2)}$$
$$\times\{f^+(k)[1-f^+(k')]+f^-(k)[1-f^-(k')]\}S_n^zS_m^z$$
$$+N^{-2}\sum_{\mathbf{k}}\sum_{\mathbf{k}'}\sum_{n}\sum_{m}|J(\mathbf{k}-\mathbf{k}')|^2\frac{\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{nm}]}{(\hbar^2/2m)(k^2-k'^2)}$$
$$\times\{f^-(k)[1-f^+(k')]S_m^+S_n^-$$
$$+f^+(k)[1-f^-(k')]S_m^-S_n^+\}, \quad (3.6)$$

where the primed summation $\sum'$ over $\mathbf{k}$ for the z component means to exclude $\mathbf{k}=\mathbf{k}'$. In ordinary temperature, the Fermi distribution function for + and − spins $f^\pm(k)$ can be put equal to 1 for $k<k_m$ and zero for $k>k_m$. Then we have

$$H_{S\cdot S}^{(2)}=\frac{2m}{\hbar^2}N^{-2}\sum_{\mathbf{k}=0}^{\mathbf{k}_m}\sum_{\mathbf{k}'=0}^{\infty}{}'\sum_{n}\sum_{m}|J(\mathbf{k}-\mathbf{k}')|^2$$
$$\times\frac{\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{nm}]}{k^2-k'^2}\cdot 2S_n^zS_m^z$$
$$+\frac{2m}{\hbar^2}N^{-2}\sum_{\mathbf{k}=0}^{\mathbf{k}_m}\sum_{\mathbf{k}'=0}^{\infty}\sum_{n}\sum_{m}|J(\mathbf{k}-\mathbf{k}')|^2$$
$$\times\frac{\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{nm}]}{k^2-k'^2}\cdot 2(S_n^xS_m^x+S_n^yS_m^y). \quad (3.7)$$

Integrating with respect to $\mathbf{k}$ and keeping $\mathbf{k}-\mathbf{k}'=\mathbf{q}$ constant, (3.7) becomes

$$H_{S\cdot S}^{(2)}=-\frac{3n}{4E_fN}N^{-1}\{\sum_{nm}\sum_{\mathbf{q}}{}'|J(\mathbf{q})|^2f(q)e^{i\mathbf{q}\cdot\mathbf{R}_{nm}}S_n^zS_m^z$$
$$+\sum_{nm}\sum_{\mathbf{q}}|J(\mathbf{q})|^2f(q)e^{i\mathbf{q}\cdot\mathbf{R}_{nm}}(S_n^xS_m^x+S_n^yS_m^y)\}. \quad (3.8)$$

This expression has been obtained by Kasuya.[5]

Similarly we obtain the **I·I** interaction and **I·S** interaction as follows:

$$H_{I\cdot I}^{(2)}=-\frac{3n}{16E_f}N^{-2}\{\sum_{nm}\sum_{\mathbf{q}}{}'A(\mathbf{q})^2f(q)e^{i\mathbf{q}\cdot\mathbf{R}_{nm}}I_n^zI_m^z$$
$$+\sum_{nm}\sum_{\mathbf{q}}A(\mathbf{q})^2f(q)e^{i\mathbf{q}\cdot\mathbf{R}_{nm}}(I_n^xI_m^x+I_n^yI_m^y)\} \quad (3.9)$$

and

$$H_{I\cdot S}^{(2)}=+\frac{3n}{4E_f}N^{-2}\{\sum_{nm}\sum_{\mathbf{q}}{}'A(\mathbf{q})J(\mathbf{q})f(q)e^{i\mathbf{q}\cdot\mathbf{R}_{nm}}I_n^zS_m^z$$
$$+\sum_{nm}\sum_{\mathbf{q}}A(\mathbf{q})J(\mathbf{q})f(q)$$
$$\times e^{i\mathbf{q}\cdot\mathbf{R}_{nm}}(I_n^xS_m^x+I_n^yS_m^y)\}. \quad (3.10)$$

In these three expressions, the summation with a prime does not include $\mathbf{q}=0$. The $\mathbf{q}=0$ terms become just equal to the second, third, and fourth terms in (3.5) which come from the first order perturbation of the energy. Thus, we obtain as the total energy up to the second order

$$-\frac{1}{2a}\beta_e^2H^2-\left[g\beta_eH+\frac{1}{a}N^{-1}J(0)\beta_eH\right]\sum_n S_n^z$$
$$-\left[g_N\beta_NH-\frac{1}{2a}N^{-1}A(0)\beta_eH\right]\sum_n I_n^z$$
$$-\frac{3n}{4E_f}N^{-2}\sum_{nm}\sum_{\mathbf{q}}J(\mathbf{q})^2f(q)e^{i\mathbf{q}\cdot\mathbf{R}_{nm}}(\mathbf{S}_n\cdot\mathbf{S}_m)$$
$$-\frac{3n}{16E_f}N^{-2}\sum_{nm}\sum_{\mathbf{q}}A(\mathbf{q})^2f(q)e^{i\mathbf{q}\cdot\mathbf{R}_{nm}}(\mathbf{I}_n\cdot\mathbf{I}_m)$$
$$+\frac{3n}{4E_f}N^{-2}\sum_{nm}\sum_{\mathbf{q}}A(\mathbf{q})J(\mathbf{q})f(q)$$
$$\times e^{i\mathbf{q}\cdot\mathbf{R}_{nm}}(\mathbf{I}_n\cdot\mathbf{S}_m). \quad (3.11)$$

Here, the first-order energy has been combined with the second-order energy as the $\mathbf{q}=0$ term of the Fourier components. This corresponds to the fact that the uniform polarization due to the first-order perturbation of the energy has been modified by the first-order perturbation of the wave function as seen before. (3.11) represents the effective Hamiltonian for the spin system. There, the first term expresses the energy decrease due to the polarization of the conduction electrons by the external field. The second and the third terms give the Zeeman energy of Mn-spins and and Cu-nuclear spins, respectively. Each of them consists of two parts; one comes from the external field and the other comes from the polarization of the conduction electrons. This part has a close analogy with the orbital contribution for the g-value of the paramagnetic ions in the crystalline field. The last three parts of (3.11) express the indirect interactions among Mn spins and Cu-nuclear spins. If we neglect the $\mathbf{q}$-dependence of $J(\mathbf{q})$ and $A(\mathbf{q})$ in these terms, we can perform the summation with respect to $\mathbf{q}$ and we obtain

$$\left(\frac{3n}{N}\right)^2\frac{2\pi}{E_f}J(0)^2\sum_{nm}F(2k_mR_{nm})(\mathbf{S}_n\cdot\mathbf{S}_m)$$
$$+\left(\frac{3n}{N}\right)^2\frac{\pi}{2E_f}A(0)^2\sum_{nm}F(2k_mR_{nm})(\mathbf{I}_n\cdot\mathbf{I}_m)$$
$$-\left(\frac{3n}{N}\right)^2\frac{2\pi}{E_f}A(0)J(0)\sum_{nm}F(2k_mk_{nm})(\mathbf{I}_n\cdot\mathbf{S}_m). \quad (3.12)$$

The second interaction is the Ruderman-Kittel interaction. Here it should be emphasized that the Ruderman-Kittel interaction given by (3.12) is all that should be considered, the Fröhlich-Nabarro interaction being only a part of the former interaction. In this sense the Zener theory of ferromagnetism in metals is incomplete and it is to be regarded as a limiting case in which the Fourier coefficient of the exchange integral $J(\mathbf{q})$ has a finite value only in the vicinity of $\mathbf{q}=0$.

IV. ELECTRONIC g-VALUE OF Mn IONS AND Cu-NUCLEAR KNIGHT SHIFT

From (3.11) we can see that the deviation of the g-value of the Mn ions from that of free ions becomes

$$\Delta g=(3n/E_f)N^{-1}J(0). \quad (4.1)$$

Using the values of $E_f=1.1\times10^{-11}$ erg for pure copper and $J(0)=3.5\times10^{-13}$ erg for a free Mn^+ ion[6] we obtain $\Delta g/g=2.4\times10^{-2}$. This is somewhat larger than the experimental value.[10] However, this is independent of temperature and the external field and seems to be consistent with the experiment considering the approximation used here.

The deviation of the g-value from 2 found in ferromagnetic metals has first been explained in terms of the s-d interaction by Kittel and Mitchell.[11] From our standpoint, this deviation of the g-value is also given by (4.1) and it is independent of both temperature and microwave frequency.

The nuclear Knight shift of Cu is given by

$$\Delta H/H=-(3n/2E_f)N^{-1}A(0)\beta_c/g_N\beta_N. \quad (4.2)$$

This expression coincides with the ordinary Knight shift in pure copper. Besides this, the nuclear spin is subjected to the additional internal field arising from the indirect $\mathbf{I}\cdot\mathbf{S}$ interaction presented by the last term of (3.12). This internal field is expressed as

$$\Delta H=-\frac{|\langle S_z\rangle|}{g_N\beta_N}\left(\frac{3n}{N}\right)^2\frac{2\pi}{E_f}A(0)J(0)\sum_m F(2k_mR_{nm}), \quad (4.3)$$

where the electronic Bohr magneton is negative and the average of S_z becomes negative. This field decreases as $1/R_{nm}^3$ as the position of Cu departs from the Mn ion. This is due to the fact that the polarization of conduction electrons is concentrated near the impurity Mn ion. Therefore, for almost all the Cu-nuclei in the very dilute Cu-Mn alloy the polarization of the conduction electrons is ineffective: only the Cu-nuclei situated in the neighborhood of a Mn-ion are subjected to a finite effective field due to the electronic polarization. For a face-centered cubic lattice, (4.3) becomes negative for nearest neighbor distance and positive for the next nearest neighbors. Thus, we expect that the center of the nuclear resonance line does scarcely shift from that for pure copper and that the line shape becomes asymmetric. The first moment of the resonance line can easily be calculated and it becomes negative. This fact seems to be related to the slight diamagnetic shift found by the experiment. The line breadth due to this kind of the indirect $\mathbf{S}\cdot\mathbf{I}$ interaction has been calculated by Behringer[12] and he obtained reasonable agreement with the experimental value. He also calculated a histogram and found that the center of the peak shows scarcely any shift.

V. CONCLUSIONS

The uniform polarization of the conduction electrons due to the exchange interaction with the Mn ions expected by the Fröhlich-Nabarro and Zener mechanism is strongly influenced by the first order perturbation of the wave function corresponding to the Ruderman-Kittel mechanism and it is concentrated around the Mn ions. Corresponding to this situation, the Fröhlich-Nabarro interaction is completely included in the Ruderman-Kittel result. This point of view is corrobo-

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rated by the fact that the experimental results on the electronic g-value of the Mn ions and the Knight shift of the Cu-nuclei can be qualitatively accounted for.

However, there still remain difficult problems concerning the properties shown by Cu-Mn alloys. The important one is that of the antiferromagnetic transition. The writer believes that the essential interaction between Mn spins is the Ruderman-Kittel interaction. A difficulty lies in the statistical problem concerning the dilute and randomly distributed spin system. Another difficulty which is more essential is in calculating the actual $\mathbf{q}$-dependence of $J(\mathbf{q})$. The positive paramagnetic Curie temperature and the occurrence of the antiferromagnetic ordering may be explained by the special $\mathbf{q}$-dependence of $J(\mathbf{q})$.

ACKNOWLEDGMENTS

The author would like to express his deepest thanks to Professor C. Kittel for his helpful discussions and continual interests through this work. Thanks are also due to Mr. R. Behringer, Dr. V. Heine, Dr. C. McCombie and Professor M. Ruderman for their valuable discussions, and to Dr. E. W. Hart for communicating his results prior to publication. Also the author wishes to express his thanks for the grant from the National Carbon Research Laboratories and that under the Fulbright Smith-Mundt Acts which have made his stay at the University of California possible. The work has been assisted in part by the Office of Naval Research, the Signal Corps, and the Air Force Office of Scientific Research.

PHYSICAL REVIEW VOLUME 106, NUMBER 5 JUNE 1, 1957

Photoconduction in KBr and KI Containing F Centers*

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(Received February 25, 1957)

Photoconductivity in potassium bromide and potassium iodide containing F centers has been investigated at 80°K. The product of the quantum yield and unit range has been measured over the spectral range from 2.0 to 5.8 ev with F-center concentrations between 10^{15} and 10^{17} cm^{-3}. Evidence is presented that the mechanism for the production of photoelectrons depends upon the photon energy and the concentration of F centers. Two mechanisms for the production of photoelectrons are suggested by the data: the ionization of F centers by excitons and direct optical ionization of F centers.

INTRODUCTION

The pure alkali halides do not exhibit photoconductivity but the absorption of photons by F centers in these crystals excites an internal photocurrent.[1,2] Taft and Apker have shown that the absorption of photons by the first fundamental band which lies near 2000 A will yield *photoemission* from the alkali halides *if F centers are present.*[3] It appears that photon absorption by the first fundamental band produces an excited nonconducting state of the crystal and that the excitons can ionize F centers.

These experiments suggest that *photoconductivity* occurs in alkali halides containing F centers on irradiation in the first fundamental absorption band. The present experiments investigate the dependence of this process on the energy of the absorbed photon and the concentration of F centers. Additional information has been obtained concerning the origin of the photoconductivity excited by irradiation in the spectral region occupied by the high-energy tail of the F band.[4]

MATERIALS

Potassium bromide and potassium iodide crystals were obtained from the Harshaw Chemical Company. Potassium iodide crystals were also grown by the Kyropoulos method from Baker's Analyzed Grade of the salt. Thallium absorption bands at 285 and 236 mμ were observed in the Harshaw potassium iodide at 80°K. The concentration of thallium was estimated as approximately one part per million. The thallium absorption bands were not detectable in the home grown potassium iodide crystals. The photoconductive behavior of the two types of potassium iodide crystals was similar.

F-CENTER PREPARATION

F centers were prepared by heating the crystals for 12 hours in potassium vapor. The temperature of the crystals was 570°C and the desired vapor pressure of potassium was obtained by maintaining the tempera-

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* Partially supported by the Office of Scientific Research, U. S. Air Force and the Office of Naval Research, Department of the Navy.

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