

## Dynamical Properties of $s$ - $d$ Interaction

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The dynamical properties of two spin systems composed of conduction electron spins and localized  $d$ -spins interacting by exchange are investigated in connection with the electron-spin resonance of  $d$ -spins with the free electron  $g$ -value. It seems to us that some basic considerations are necessary for the problem along the line of the widely accepted idea that the  $s$ - $d$  interaction itself does not lead to any relaxation time and shift. The usual adiabatic approximation is applied to this idea. A modified damping equation of the Bloch type as well as Bloch's relaxation theory are also useful, but these are not enough for a complete solution of the problem. A certain controversy involved in recent experimental and theoretical work at Berkeley concerning the electron spin resonance in Cu-Mn dilute alloy is pointed out and examined. We believe that the possibility could not be eliminated that the spin-lattice relaxation time of conduction electrons in the alloy due to mechanisms other than the  $s$ - $d$  interaction is longer than previous authors have assumed.

### § 1. Introduction

The importance of the exchange interaction between conduction electrons and localized incomplete  $d$ -shells, so-called  $s$ - $d$  interaction, has recently received increasing attention both from experimental and theoretical points of view. In particular, Yosida<sup>1)</sup> has investigated theoretically the origin of anomalous magnetic and electric properties of Cu-Mn or Ag-Mn alloys taking into account this interaction, and has given an explanation for the absence of a large paramagnetic resonance shift which was anticipated by Owen, Browne, Knight, and Kittel<sup>2)</sup> but was not found in their experiments of the electronspin resonance on manganese in copper. Yosida has also presented an explanation for the absence of a large excess Knight shift of the nuclear magnetic resonance on copper in Cu-Mn alloys, saying that the cross perturbational effects of the  $s$ - $d$  interaction and the hyperfine interaction should be responsible for the broadening of the resonance line rather than for the shift. A detailed calculation of the line width has been made by Behringer<sup>3)</sup> on this basis. Yosida<sup>4)</sup> has further given a theoretical interpretation of the anomalous electrical resistivity and magnetoresistance found in these alloys at low temperatures in terms of the effect due to the  $s$ - $d$  interaction. The success of his theory in the resistance problem may be regarded as a direct evidence of the interaction. According to these two authors the main features of Cu-Mn alloys can thus be understood fairly well if one assumes a value of the  $s$ - $d$  exchange integral in the alloys nearly equal to the one

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in free  $Mn^+$  ions. The experimental investigation of impurity states of various transition elements in copper has been extended by Sugawara<sup>5)</sup> using nuclear magnetic resonance techniques.

Owen, Brown, Arp, and Kip<sup>6)</sup> have reported the results of their experiment on the magnetic susceptibility and the electron spin resonance in those alloys. In order to explain the mechanism of the resonance anomaly found at low temperatures they argued that the polarization of conduction electron spins is highly concentrated at each manganese ion and produces the local anisotropy field for the  $d$ -core spins of manganese. In this argument they referred to Kittel and Mitchell's theory<sup>7)</sup> which states that, if the coupling of conduction electron spins with the lattice is stronger than with the  $d$ -core spins, the above mentioned local field may be effective as a shift observable in the  $d$ -core spin resonance experiment.

This idea has a close relation to Yosida's theory, because the localized character of the polarization is one of its main assertions. But Yosida's theory implies the fact, though he did not mention it explicitly, that this type of polarization can never contribute to a shift in the  $d$ -core spin resonance experiment, since in such dynamical processes the magnetization of conduction electrons does not stay at its thermal equilibrium position, but precesses following the  $d$ -core magnetization so that its direction is always kept parallel to the latter. This picture is essentially based upon the so-called adiabatic approximation.<sup>8)</sup>

However, it is not clear how Kittel-Mitchell's theory and Yosida's theory are mutually related, because the latter author did not state the significance of the spin-lattice relaxation of conduction electrons in the treatment. In fact, Yosida's treatment of minimizing the total diagonal energy involves an isothermal picture for the spin system of conduction electrons, and is therefore different from the adiabatic approximation in its original sense; it assumes implicitly the shortness of the spin-lattice relaxation of conduction electrons.

Generally speaking, the dynamical problem of the  $s$ - $d$  interaction is much more complicated than that of the nuclear relaxation through the hyperfine interaction in metals, since the time scale for the motion of the conduction electron spins may be comparable to that of the localized  $d$ -spins, so that the observable shift and broadening may not necessarily be considered in a simple analogy to the nuclear magnetic resonance in metals. In fact, we may expect that the effective shift and line width are considerably reduced from the corresponding value in the case of isothermal limit as functions of the ratio,

$$x = \frac{\text{Relaxation time through } s\text{-}d \text{ interaction}}{\text{Relaxation time through other mechanism}}.$$

This is shown in section 4.

The calculation used in that section is essentially phenomenological and has a certain ambiguity in treating the spin-lattice relaxation. Nevertheless, we regard it as a necessary step to obtain a complete understanding of the problem, because the

experimental data of the line width at paramagnetic region seem to indicate that the spin-lattice relaxation time in copper is not short enough as previous theories are applicable.

## § 2. Experimental facts and existing theories

2.1 First, we refer to the work of Owen, Browne, Knight, and Kittel,<sup>2)</sup> who made the following argument.

The polarization of conduction electrons in the substance is given by

$$M_s^\circ = \chi_p (H + \lambda M_d^\circ), \quad (2.1)$$

where  $\chi_p$  is the Pauli paramagnetic susceptibility,  $\lambda$  the molecular field coefficient of the interaction between conduction electron spins and *d*-core spins, and  $M_d^\circ$  the magnetization of total *d*-core spins along the direction of the applied constant field *H*. As is well known,  $\chi_p$  is given by

$$\chi_p = 2\mu_B^2 n(E_f), \quad (2.2)$$

where  $n(E_f)$  is the state density per unit volume at the Fermi surface of the *s*-band for one spin direction, and is equal to  $3n/4E_f$  for the free electron model,  $n$  being the number of conduction electrons per unit volume. The molecular field coefficient  $\lambda$  is expressed in terms of the zero-Fourier component  $J(0)$  of the *s-d* exchange integral as

$$\lambda = J(0)/g\mu_B^2 N, \quad (2.3)$$

$N$  being the number of Cu atoms per unit volume. Then the effective fields acting on each *d*-core spin of manganese and on each nuclear spin of copper are written as

$$H_d = \lambda M_s^\circ = \lambda \chi_p H + \lambda^2 \chi_p M_d^\circ \quad (2.4)$$

$$H_n = \alpha M_s^\circ = \alpha \chi_p H + \alpha \lambda \chi_p M_d^\circ \quad (2.5)$$

respectively, where

$$\alpha = A_0/2Ng_N\mu_N\mu_B \quad (2.6)$$

is related to the hyperfine constant of copper in the metal. Therefore, one might expect the additional resonance shifts

$$\Delta H_d^{(2)}/H = \lambda^2 \chi_p M_d^\circ / H = \lambda^2 \chi_p \chi_d \quad (2.7)$$

for the electron spin resonance, and

$$\Delta H_n^{(2)}/H = \alpha \lambda \chi_p M_d^\circ / H = \alpha \lambda \chi_p \chi_d \quad (2.8)$$

for the nuclear resonance, besides the ordinary first order shift and the Knight shift i.e.

$$\Delta H_d^{(1)}/H = \lambda \chi_p = (2/g) (n(E_f)/N) \cdot J(0) \quad (2.9)$$

$$\Delta H_n^{(3)}/H = \alpha\chi_p = (1/g_N)(\mu_B/\mu_N)(n(E_f)/N)A_0 \quad (2.10)$$

respectively. The additional shifts, (2.7) and (2.8), are directly proportional to the equilibrium value of the magnetization  $M_d^0$  which depends on the temperature and the concentration of  $d$ -cores. The ratio of these shifts to the first order shifts is given by

$$\lambda\chi_d \simeq (J(0)/3kT)(N_0/N)gS(S+1) \quad (2.11)$$

which is related to the paramagnetic susceptibility of the contributions from  $d$ -core spins, where  $N_0$  is the number of Mn ions per unit volume. Even at low concentration of manganese in copper, say one per cent, this ratio is expected to be of the order of one at 100°K. However, these additional shifts were not observed experimentally, and therefore the  $s$ - $d$  exchange interaction in the alloy looks to be much weaker than that in a free ion of manganese.

In the  $d$ -electron spin resonance, the second order shift of the form (2.7) should be observable, if the spin-lattice relaxation of conduction electrons due to the proper mechanism is shorter than the one due to the  $s$ - $d$  interaction, so that conduction electron spins may be kept at the equilibrium polarization as given by eq. (2.1).

This last assertion is due to Kittel and Mitchell's argument<sup>7)</sup> made in connection with the ferromagnetic resonance shift in ferromagnetic metals. Yosida<sup>1)</sup> did not make any argument concerning this assertion, but showed rather in a different way that the excess field (2.7) cannot contribute to a line shift in the  $d$ -electron spin resonance. The assumption made implicitly in Yosida's argument is that the second part of the polarization proportional to the molecular field coefficient  $\lambda$  in eq. (2.1) follows instantaneously the temporal change in the total magnetization of  $d$ -electron spins, so that eq. (2.1) should be replaced by the following vector equation

$$M_s(t) = \chi_p(H + \lambda M_d(t)). \quad (2.13)$$

This is illustrated in Fig. 1. One sees at once that the effective field  $\lambda^2\chi_p M_d(t)$  cannot produce a torque on  $M_d(t)$ . The difference of Kittel-Mitchell's shift and Yosida's shift is also shown there.

This interpretation comes from the following treatment in Yosida's theory. First, we take into account the diagonal part of the  $s$ - $d$  interaction with respect to the wave number  $k$  of the Bloch states, and, combining it with the kinetic energy and the Zeeman energy of conduction electrons, we minimize the total first order energy. This leads to the uniform polarization indicated by (2.1). At the same time, we obtain a gain of the polarization energy in the following form

$$\Delta H_p^{(1)} = -\frac{1}{2}\chi_p(H + \lambda M_d^z)^2, \quad (2.13)$$

which is supposed to take part in determining the motion of the  $d$ -electron magnetization. But, we must also take into account the non-diagonal part of the  $s$ - $d$  interaction so as to complete the perturbational treatment. This gives the additional

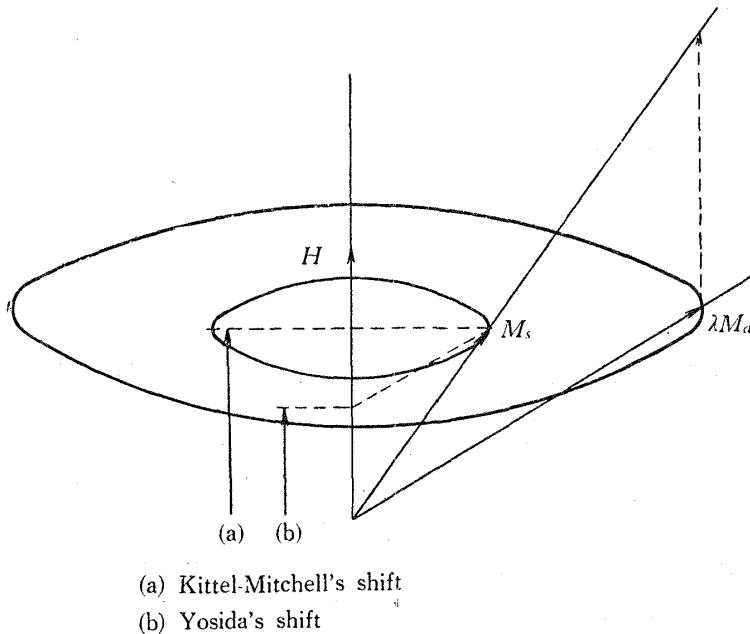


Fig. 1.

menological expression of this procedure.

2.2 Before making further examination we briefly review the experimental results and some related discussions.

(1) *The line shift and width of Mn-electron spin resonance at paramagnetic region.*

As was reported by Owen, Browne, Arp, and Kip<sup>6)</sup>, the fine structure and the hyperfine structure are absent and the observed *g*-shift is quite small, less than 1%. From the theoretical side, however, Yosida predicted that the first order shift (2.9) should be observable though the second order shift (2.7) should not. Yosida admitted that the theoretical value of this shift is several times larger than the observed shift, when one uses the free ion value of the exchange integral  $J_0$  in eq. (2.9).

The observed line width above 77°K is approximately proportional to the temperature, which is a strong indication that the spin-lattice relaxation through the *s-d* interaction is responsible for this broadening, but the observed width is only about one several tenth of the value estimated by the Korringa formula<sup>9)</sup>.

(2) *Localization of the polarization of conduction electron spins.*

The absence of the second part Knight shift (2.8) was explained by Hart<sup>10)</sup> and Yosida<sup>1)</sup> in terms of the localization of the polarization. From their argument, the second part of the uniform polarization in (2.1) is completely cancelled by the perturbation of the wave function almost everywhere just except the vicinity of the position where each *d*-core spin is located.

(3) *Static susceptibility.*

If the simple molecular field approximation is applied, we obtain the Curie-Weiss law<sup>2)</sup>

terms of the polarization energy,  $-\frac{1}{2}\chi_p(\lambda M_d^x)^2$  and  $-\frac{1}{2}\chi_p(\lambda M_d^y)^2$  of the parts of the interaction which are non-diagonal with respect to the Zeeman states but are diagonal to the Bloch states. These terms add up, together with  $\Delta H_p^{(1)}$ , to the following isotropic energy

$$\Delta H^{(1)} = -\frac{1}{2}\chi_p(H + \lambda M_d)^2, \quad (2.14)$$

which may be looked as the effective Hamiltonian for the motion of  $M_d$ . Eq. (2.12) can be regarded as a pheno-

$$\chi = \chi_p + \frac{C(1 + \lambda\chi_p)^2}{T - \theta_p} \quad (2.15)$$

where

$$C = \frac{N_0}{3k} g^2 \mu_B^2 S(S+1) \quad (2.16)$$

$$\theta_p = \frac{1}{3k} \left( \frac{N_0}{N} \frac{2n(E_f)}{N} \right) J^2(0) S(S+1). \quad (2.17)$$

The paramagnetic Curie temperature  $\theta_p$  is positive in this approximation. But, if Yosida's theory is strictly valid in explaining the absence of the second order Knight shift, we must expect that this positive  $\theta_p$  is almost cancelled out by the second order perturbation of the non-diagonal part of the  $s$ - $d$  interaction. This is because the complete expression of  $\theta_p$  obtained by the moment-expansion method, when applied to the  $s$ - $d$  interaction, is proportional to the first moment of the Cu-nuclear resonance line predicted by Yosida's formula, provided that the mean distribution of Mn atoms around an Mn atom is the same as that around a Cu atom. Therefore, the existence of positive  $\theta_p$  experimentally confirmed for the alloys of Mn concentration more than 1% must be accounted for by certain other origins.

(4) *Mn-electron spin resonance at low temperatures.*

There is a serious discrepancy between two pictures illustrated in Fig. 1 in connection with the mechanism of the anomalous shift.

(5) *Anomalous decrease of resistivity at low temperatures.*

The mechanism of the phenomenon has been explained by Yosida<sup>4)</sup> under the simple molecular field assumption. Above the Néel temperature a conduction electron is scattered by each  $d$ -core isotropically with respect to that spin states, so that the cross section is proportional to  $S(S+1)$ , whereas at absolute zero it is proportional to  $S^2$ , because  $d$ -core spins are completely ordered. He derived the corresponding resistivity difference assuming the free electron model and the free ion value of  $J(0)$ . His result is 1/3 of the observed value in Cu-Mn alloys. We note here, however, that the state density at the Fermi surface of the  $s$ -band in copper may be 1.4 or 1.9 times as large as the one expected from the free electron model<sup>11)</sup>. If we take the effective mass of the conduction electrons in copper 1.4 times as large as the true mass, the estimated value of the resistivity difference becomes more consistent, since the resistivity is proportional to the square of effective mass.

Thus the experimental facts seem to present us several problems to be re-examined more carefully. An important question is concerning the length of the spin-lattice relaxation time of conduction electrons, which determines the applicability of various pictures.

### § 3. Consideration from thermodynamical point of view

The total system under consideration is composed of three components, namely

$M_d =$  (spin-system of  $d$ -cores)

$M_s =$  (spin-system of conduction electrons)

$L =$  (translational motion of conduction electrons).

The translational motion of conduction electrons is generally very fast. Roughly speaking, it is characterized by the frequency  $E_f/\hbar$ . Therefore, the dynamical behavior of the slow spin-system may be described by the usual adiabatic approximation.

Suppose that the total Hamiltonian for the total system is given by

$$H = H_L(q) + H_M(Q) + H_I(q, Q), \quad (2.1)$$

where  $q$  and  $Q$  represent the coordinates of the fast system  $L$  and the slow spin system  $M$  respectively.  $H_L(q)$  represents the dynamical motion of the fast system, i.e. the kinetic energy of conduction electrons,  $H_M(Q)$  the Zeeman energy for the both spin-system, and  $H_I(q, Q)$  the interaction between them. Then, the principle of adiabatic approximation states that the Schrödinger equation for the two systems can be separated into two parts:

$$\{H_L(q) + H_I(q, Q)\} \phi_{nQ} = W_n(Q) \phi_{nQ} \quad (2.2)$$

$$\{W_n(Q) + H_M(Q)\} \phi_{n\tau} = E_{n\tau} \phi_{n\tau}. \quad (2.3)$$

This couple of equations states that the system  $L$  polarizes according to the instantaneous configuration  $Q$ , giving an adiabatic potential  $W_n(Q)$  which takes part in determining the motion of  $M$ . As a consequence, the heat transfer processes between  $L$  and  $M$  are neglected.

In the present problem of the  $s$ - $d$  interaction,  $H_I(q, Q)$  represents the exchange interaction between conduction electron spins and  $d$ -core spins, for which the adiabatic approximation is ideally satisfied, so far as there is no other magnetic interaction and the  $g$ -factors of conduction electrons and  $d$ -core spins are just equal to each other, so that the relation

$$[H_M, H_{s-d}] = 0 \quad (2.4)$$

is fulfilled.

In this case the frequency spectrum of  $H_{s-d}$  is a  $\delta$ -function having a sharp peak at zero-frequency on the frequency scale of  $H_M$ , so that the precessional motion in the spin-system due to the Zeeman energy does not induce any transition between the levels of adiabatic potential, or, in other words, the adiabatic approximation in this case is not an approximation. Accordingly, the  $s$ - $d$  interaction neither affects the Zeeman levels nor produces any heat transfer process from the spin-system to its surrounding, so that we do not expect any shift and any relaxation through the  $s$ - $d$  interaction in the resonance problem.

From this consideration we see that the energy minimization treated by Yosida

cannot be understood by the adiabatic approximation. In that treatment, the spin-system of conduction electrons  $M_s$  is regarded as completely in thermal equilibrium at a definite temperature  $T$  which characterizes the thermal equilibrium of the system

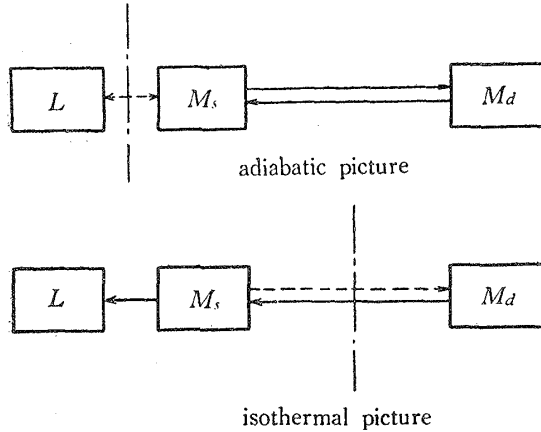


Fig. 2.

picture rises primarily in the strength of thermal contact between the systems. In the isothermal picture the transfer of heat from the system  $M_s$  to the lattice  $L$  takes place in a moment, so that the  $s$ - $d$  interaction is fully effective on the relaxation for the dynamical system  $M_d$ . For this picture, therefore, it is necessary that the spin-lattice relaxation time of conduction electrons is sufficiently short; this must be an implicit assumption in Yosida's theory.

In actual cases we may expect, more or less, an intermediate situation between the two idealized pictures, where the  $s$ - $d$  interaction may be partially effective on the shift and broadening observable in  $d$ -spin resonance.

#### § 4. Phenomenological equation for two spin systems

4.1 In order to make an interpolation between the two idealized pictures in the dynamical problems we consider a couple of phenomenological equations of the Bloch type.<sup>12)</sup> This is written as

$$\dot{M}_s = \gamma M_s \times (H + \lambda M_d) - \frac{1}{T_{sL}} (M_s - \bar{M}_s) - \frac{1}{T_{sd}} M_s + \frac{1}{T_{ds}} M_d \quad (4.1)$$

$$\dot{M}_d = \gamma' M_d \times (H + \lambda M_s) + \frac{1}{T_{sd}} M_s - \frac{1}{T_{ds}} M_d. \quad (4.2)$$

Here  $M_s$  and  $M_d$  are the total magnetization vectors of conduction electron spins and  $d$ -electron spins respectively, and  $\gamma$  and  $\gamma'$  are corresponding magneto-mechanical ratios which are assumed to be just equal to each other through the present section.

First of all we note the several assumptions required for these equations. These are as follows:

$L$ . In this sense the fast system  $L$  plays a role of heat reservoir for the dynamical system, so that we may call  $L$  a lattice system. At the same time, Yosida's picture may be called an isothermal picture for conduction electron spins. As a result of this picture, the coordinates of the conduction electron spins are completely eliminated from the dynamical equation, which necessarily leads to the first order shift (2.9) for  $d$ -spin resonance. This situation is shown in Fig. 2. The difference between the adiabatic and the isothermal



(1) The strength of thermal contact may be characterized by three time constants, namely

$T_{sL}$ : spin-lattice relaxation time of conduction electron due to the mechanism other than the  $s$ - $d$  exchange.

$T_{sd}$ : spin-lattice relaxation time of conduction electrons due to the  $s$ - $d$  exchange.

$T_{ds}$ : spin-lattice relaxation time of  $d$ -cores due to the  $s$ - $d$  exchange.

(2) It should be satisfied that

$$\dot{M}=0, \quad M=M_s+M_d, \quad (4.3)$$

when  $T_{sL}=\infty$ , i.e. zero-strength of the contact between the system of conduction electron spins and the lattice. This is because these equations should be consistent with the original equation of motion.

(3) In the equilibrium state each magnetization  $M_s$ ,  $M_d$  has a definite value  $M_s^\circ$  and  $M_d^\circ$  respectively, and the law of detailed balance

$$M_s^\circ/T_{sd}=M_d^\circ/T_{ds} \quad (4.4)$$

is satisfied.

(4) In eq. (4.1)  $\bar{M}_s$  is the final value of  $M_s$ , towards which the relaxation of  $M_s$  proceeds. For the equilibrium state eqs. (4.1) and (4.2) provide solutions

$$M_s=M_s^\circ, \quad M_d=M_d^\circ. \quad (4.5)$$

From this requirement we see that the equilibrium value of  $\bar{M}_s$  is equal to  $M_s^\circ$ . But in the non-equilibrium state it is not necessarily true to expect that

$$\bar{M}_s=M_s^\circ. \quad (4.6)$$

This is the most serious ambiguity inherent in the phenomenological treatment. In fact, there is another possibility to put

$$M_s=M_s^\circ+\chi_p\lambda(M_d-M_d^\circ) \quad (4.7)$$

which implies that the magnetization  $M_s$  is always relaxing to its instantaneous equilibrium value.\* In any case, it is important to note that the phenomenological treatment itself does not concern what are the actual values of  $M_s^\circ$  and  $M_d^\circ$ , so far as the requirements (4.4) and (4.5) are satisfied.

(5) In the non-equilibrium state the deviations of  $M_s$  and  $M_d$  from their equilibrium values are assumed to be small, so that the terms of quadratic or higher order in the deviations

$$\delta M_s=M_s-M_s^\circ, \quad \delta M_d=M_d-M_d^\circ$$

may be neglected.

Then eqs. (4.1) and (4.2) are separated into transverse and longitudinal com-

\* This standpoint is expressed by Kasuya<sup>13)</sup>. About this point we had a controversy which remains unsolved. We hope that a detail of his theory will be published in future.

ponents and are linearized for the deviations as follows:

$$\begin{aligned} \dot{M}_s^+ = & -i\gamma(H_z + \lambda M_a^\circ)M_s^+ + i\gamma(H_+ + \lambda M_d^+)M_s^\circ - \frac{1}{T_{sL}}(M_s^+ - \bar{M}_s^+) \\ & - \frac{1}{T_{sd}}M_s^+ + \frac{1}{T_{ds}}M_d^+ \end{aligned} \quad (4.8)$$

$$\begin{aligned} \dot{M}_d^+ = & -i\gamma(H_z + \lambda M_s^\circ)M_d^+ + i\gamma(H_+ + \lambda M_s^+)M_d^\circ \\ & + \frac{1}{T_{sd}}M_s^+ - \frac{1}{T_{ds}}M_d^+ \end{aligned} \quad (4.9)$$

for transverse components, where

$$M_s^\pm = M_s^x \pm iM_s^y, \quad M_d^\pm = M_d^x \pm iM_d^y, \quad (4.10)$$

and

$$H_\pm = H_1 e^{\pm i\omega t} \quad (4.11)$$

are the external oscillating field.

$$\begin{aligned} \delta \dot{M}_s^z = & -\omega_s(M_s^\circ + \delta M_s) - \frac{1}{T_{sL}}(\delta M_s^z - \delta \bar{M}_s^z) \\ & - \frac{1}{T_{sd}}\delta M_s^z + \frac{1}{T_{ds}}\delta M_d^z \end{aligned} \quad (4.12)$$

$$\delta \dot{M}_d^z = -\omega_d(M_d^\circ + \delta M_d) + \frac{1}{T_{sd}}\delta M_s^z - \frac{1}{T_{ds}}\delta M_d^z \quad (4.13)$$

for longitudinal components, where  $\omega_s$  and  $\omega_d$  have the order of magnitude  $H_1^2$ , which are taken into account in the problem of saturation.

These equations are direct extension of the nuclear relaxation in metals through hyperfine interaction, which was treated by Heitler, Teller,<sup>14)</sup> and Overhauser.<sup>15)</sup> According to their results  $T_{sd}$  and  $T_{ds}$  are given by

$$\frac{1}{T_{sd}} = \frac{2\pi}{\hbar} \frac{2n(E_f)}{N} \langle J^2 \rangle_f \frac{N_0}{N} \frac{2}{3} S(S+1) \quad (4.14)$$

$$\frac{1}{T_{ds}} = \frac{2\pi}{\hbar} \frac{2n(E_f)}{N} \langle J^2 \rangle_f \frac{n(E_f)}{N} kT \quad (4.15)$$

where  $\langle J^2 \rangle_f$  means the appropriate average of the square of the  $s$ - $d$  exchange integral over the Fermi surface. These are based on the second order perturbational theory, and satisfy the relation

$$\chi_p/T_{sd} = \chi_a/T_{ds} \quad (4.16)$$

which is to be compared to eq. (4.4). We shall come back to this point later in connection with the choice of the final value  $\bar{M}_s$  in the phenomenological equations.

4.2 Eqs. (4.8) and (4.9) are rewritten in a following form :

$$\begin{pmatrix} M_s^+ \\ M_d^+ \end{pmatrix} = -D_+ \begin{pmatrix} M_s^+ \\ M_d^+ \end{pmatrix} + i\gamma H_+ \begin{pmatrix} M_s^\circ \\ M_d^\circ \end{pmatrix}, \quad (4.17)$$

where 
$$-D_+ = i \begin{pmatrix} \omega_\tau & \omega_\beta \\ \omega_\alpha & \omega_\delta \end{pmatrix}. \quad (4.18)$$

When the oscillating field  $H_+(t)$  is inserted adiabatically at  $t = -\infty$ , the solution of eq. (4.17) is given by

$$\begin{pmatrix} M_s^+ \\ M_d^+ \end{pmatrix}_t = \int_{-\infty}^t e^{-(t-t')D_+} i\gamma H_+(t') \begin{pmatrix} M_s^\circ \\ M_d^\circ \end{pmatrix} dt', \quad (4.19)$$

which describes the resonance under the condition (4.11). The resonance frequency and the effective damping constant are determined by solving the determinantal equation

$$\det |i\omega + D_+| = 0. \quad (4.20)$$

If the two characteristic frequencies  $\omega_\pm$  of the solution satisfy the relation

$$Im(\omega_-) \gg Im(\omega_+) \quad (4.21)$$

we may neglect the heavily damped component  $e^{i\omega_-t}$  in the expression (4.19), and obtain its asymptotic form.

This becomes

$$\begin{pmatrix} M_s^+ \\ M_d^+ \end{pmatrix}_t = i\gamma H_1 \begin{pmatrix} 1 - \frac{\omega_\delta - \omega_\tau}{\omega_+ - \omega_-} & \frac{2\omega_\beta}{\omega_+ - \omega_-} \\ \frac{2\omega_\alpha}{\omega_+ - \omega_-} & 1 + \frac{\omega_\delta - \omega_\tau}{\omega_+ - \omega_-} \end{pmatrix} \int_{-\infty}^t e^{-i\omega_+(t-t') + i\omega t} \begin{pmatrix} M_s^\circ \\ M_d^\circ \end{pmatrix} dt'. \quad (4.22)$$

When the observed spin-resonance in the metal is regarded as the one due to localized *d*-core spins, only the fourth component in the matrix (4.22) is effective on the absorption, and so we obtain

$$\chi''(\omega) = Im \left[ \left( 1 + \frac{\omega_\delta - \omega_\tau}{\omega_+ - \omega_-} \right) \frac{i\gamma}{i(\omega + Re\omega_+) + Im\omega_+} \right] M_d^\circ. \quad (4.23)$$

If there is a necessity to take into account the microwave skin-effect in analysing the experimental data, one may apply Dyson's theory<sup>16)</sup> of the electron-spin resonance in metals in the case of infinite diffusion time, where the fundamental resonance frequency and the relaxation time are considered to be given by

$$\omega_{res} = -Re(\omega_+) \quad (4.24)$$

$$1/T_{2eff} = Im(\omega_+) . \quad (4.25)$$

The solution of the determinantal equation (4.20) is written as

$$\omega_{\pm} = \frac{1}{2}(\omega_{\tau} + \omega_{\delta}) \pm \frac{1}{2}[(\omega_{\tau} - \omega_{\delta})^2 + 4\omega_{\alpha}\omega_{\beta}]^{1/2} \quad (4.26)$$

where  $\omega_+$  is chosen so as to satisfy the inequality (4.21).

Now we calculate the explicit form of this frequency according to the given model.

case A.  $\bar{M} = M_s^{\circ}$

$$-D_+ = i \begin{pmatrix} \omega_{\tau} = -\gamma H_z + (i/T_{sL}) - (\gamma\lambda - i\omega)M_d^{\circ} & \omega_{\beta} = (\gamma\lambda - i\omega)M_s^{\circ} \\ \omega_{\alpha} = (\gamma\lambda - i\omega)M_d^{\circ} & \omega_{\delta} = -\gamma H_z - (\gamma\lambda - i\omega)M_s^{\circ} \end{pmatrix} . \quad (4.27)$$

Here we write

$$1/T_{sd} = \tau M_d^{\circ}, \quad 1/T_{ds} = \tau M_s^{\circ}, \quad (4.28)$$

for the sake of simplicity.

Inserting each parameter given by (4.27) into eq. (4.26),  $\omega_{\pm}$  become

$$\omega_{\pm} = -\gamma H_z - \frac{1}{2}(\gamma\lambda - i\omega)(M_s^{\circ} + M_d^{\circ}) - \frac{i}{2} \frac{1}{T_{sL}} \pm \frac{1}{2} \left[ \left\{ (\gamma\lambda - i\omega)(M_s^{\circ} + M_d^{\circ}) - \frac{i}{T_{sL}} \right\}^2 + 4(\gamma\lambda - i\omega)M_s^{\circ} \frac{i}{T_{sL}} \right]^{1/2} . \quad (4.29)$$

These may be simplified under the assumption

$$M_s^{\circ} \ll M_d^{\circ},$$

which is actually valid so far as the observed resonance is regarded as the one due to the  $d$ -core spins. These become

$$\omega_+ \approx -\gamma H_z + \frac{(\gamma\lambda - i\omega)M_s^{\circ}i/T_{sL}}{(\gamma\lambda - i\omega)M_d^{\circ} - i/T_{sL}} \quad (4.30)$$

$$\omega_- \approx -\gamma H_z - (\gamma\lambda - i\omega)M_d^{\circ} + \frac{i}{T_{sL}} \quad (4.31)$$

where the inequality (4.21) is automatically fulfilled. From eqs. (4.24) and (4.25) the shift and the broadening are given by

$$\Delta\omega = -Re \left[ \frac{(\gamma\lambda - i\omega)M_s^{\circ}i/T_{sL}}{(\gamma\lambda - i\omega)M_d^{\circ} - i/T_{sL}} \right] = \frac{(T_{sd}/T_{sL})^2}{(1 + T_{sd}/T_{as})^2 + (\gamma\lambda M_d^{\circ} T_{sd})^2} \gamma\lambda M_s^{\circ} \quad (4.32)$$

$$\frac{1}{T_{2eff}} = Im \left[ \frac{(\gamma\lambda - i\omega)M_s^{\circ}i/T_{sL}}{(\gamma\lambda - i\omega)M_d^{\circ} - i/T_{sL}} \right] = \frac{(1 + \gamma\lambda M_d^{\circ} T_{sd})^2 T_{sd}/T_{sL} + (T_{sd}/T_{sL})^2}{(1 + T_{sd}/T_{sL})^2 + (\gamma\lambda M_d^{\circ} T_{sd})^2} \frac{1}{T_{as}} . \quad (4.33)$$

In a similar way we can estimate the effective longitudinal relaxation time  $T_{1eff}$  by

assuming saturation. Under the stationary condition the left-hand sides of eqs. (4.12) and (4.13) are equated to be zero, and the deviation  $\delta M_d^z$  is solved as a term of  $H_1^2$ .

This becomes

$$\delta M_d^z = - \frac{(\omega_s M_s^\circ + \omega_d M_d^\circ) / T_{sd} + \omega_d M_d^\circ / T_{sL}}{\omega_d (1/T_{sL} + 1/T_{sd}) + 1/T_{sL} T_{ds}} \quad (4.34)$$

Here we assume that the effective power absorption of conduction electron spins from microwave is small compared with that of *d*-spins, i.e.

$$\omega_s \ll \omega_d,$$

that the solution (4.34) is approximated to

$$M_d^z = - \frac{\omega_d T_{sL} T_{ds} (1/T_{sL} + 1/T_{sd})}{1 + \omega_d T_{sL} T_{ds} (1/T_{sL} + 1/T_{sd})} M_d^\circ \quad (4.35)$$

This is compared with the usual saturation formula for one spin system, which is written as

$$M_d^z = - \frac{\omega T_1}{1 + \omega T_1} M_d^\circ$$

Therefore

$$\frac{1}{T_{1eff}} = \frac{T_{sd}}{T_{sL} + T_{sd}} \frac{1}{T_{ds}} \quad (4.36)$$

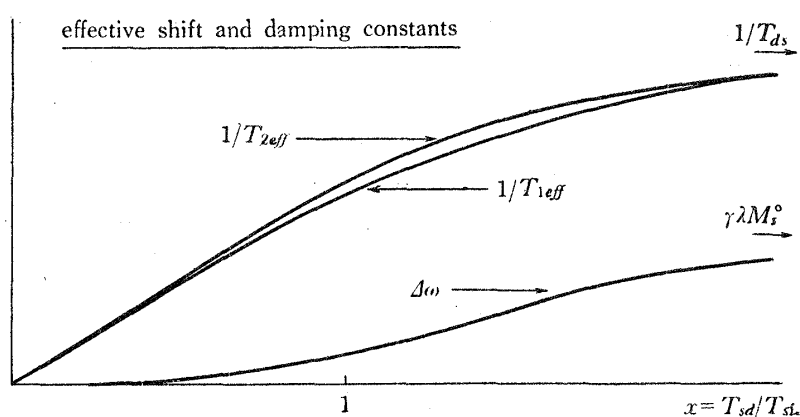


Fig. 3.

These results are graphically shown in Fig. 3 as a function of the parameter  $x = T_{sd}/T_{sL}$ .

### § 5. Discussion and summary

The results obtained in the preceding section contain two independent parameters  $x = T_{sd}/T_{sL}$  and  $M_s^\circ$ , which are unknown so long as we confine ourselves to the

phenomenological treatment. The most important question there is concerning the value of  $M_s^\circ$  which determines the shift and the relaxation time in the shortest limit of  $T_{sL}$ . When  $M_s^\circ$  assumes the value

$$\chi_p(H + \lambda M_d^\circ), \quad (5.1)$$

then eq. (4.32) gives Kittel-Mitchell's shift (2.7) in the case  $x \rightarrow \infty$ , which contradicts Yosida's theory. In this case, further, the calculation of  $T_{ds}$  in the second order perturbation of the  $s$ - $d$  exchange is no more valid because of the restriction of the detailed balance (4.4). For the consistency with that relation, we must expect

$$\frac{1}{T_{ds}} = \frac{2\pi}{\hbar} \frac{2n(E_f)}{N} \langle J^2 \rangle_f \frac{n(E_f)}{N} kT(1 + \lambda\chi_d), \quad (5.2)$$

instead of the Korringa formula (4.15). Or, in the reversed sense, the second order perturbational theory in calculating the relaxation time requires the assumption

$$M_s^\circ = \chi_p H. \quad (5.3)$$

This leads to Yosida's shift in the case  $x \rightarrow \infty$ .

This ambiguity rises in the uncertainty of the question to what extent the  $s$ - $d$  exchange field may be regarded as a fluctuating quantity and to what extent it actually contains the uniform field acting on conduction electron spins. The second order perturbational theory (4.14) and (4.15) assumes that the  $s$ - $d$  exchange produces nothing but a fluctuation, while the equilibrium value (5.1) implies that it actually acts on conduction electron spins as a uniform field like the external field.

In the present paper we cannot answer to this question, because it requires more detailed calculations from the given Hamiltonians of the spin-lattice interaction as well as of the  $s$ - $d$  exchange. Instead of this we here introduce an important idea to modify the phenomenological treatment which was proposed by Kasuya.<sup>13)</sup> This asserts that, if the  $s$ - $d$  exchange produces a uniform field steadily acting on conduction electron spins, then the spin-lattice relaxation of conduction electrons should occur as if the polarization  $M_s$  keeps its direction parallel the instantaneous field  $\chi_p(H + \lambda M_d)$  (see Fig. 1). This corresponds to

$$\text{case B.} \quad M_s = M_s^\circ + \chi_p \lambda (M_d - M_d^\circ) \quad (5.4)$$

$$M_s^\circ = \chi_p (H + \lambda M_d^\circ). \quad (5.5)$$

$$-D_+ = i \left\{ \begin{array}{ll} \omega_\gamma = -\gamma H_z + \frac{i}{T_{sL}} - (\gamma\lambda - i\omega) M_d^\circ & \omega_\delta = (\gamma - i\omega) M_s^\circ - i \left( \frac{\lambda\chi_p}{T_{sL}} \right) \\ \omega_\alpha = (\gamma\lambda - i\omega) M_d^\circ & \omega_\delta = -\gamma H_z - (\gamma\lambda - i\omega) M_s^\circ \end{array} \right\}. \quad (5.6)$$

This leads to the results just same as (4.32), (4.33), and (4.35), where the parameter  $M_s^\circ$  is replaced by  $\chi_p H$ , i.e.

$$\Delta\omega = - \frac{(T_{sd}/T_{sL})^2}{(1 + T_{sd}/T_{sL})^2 + (\gamma\lambda M_d^\circ T_{sd})^2} \gamma\lambda\chi_p H \tag{4.32'}$$

$$\frac{1}{T_{2ef}} = \frac{(1 + \gamma\lambda M_d^\circ T_{sd})^2 T_{sd}/T_{sL} + (T_{sd}/T_{sL})^2}{(1 + T_{sd}/T_{sL})^2 + (\gamma\lambda M_d^\circ T_{sd})^2} \frac{1}{T_{ds}} \tag{4.33'}$$

$$\frac{1}{T_{1ef}} = \frac{T_{sd}}{T_{sL} + T_{sd}} \frac{1}{T_{ds}} \tag{4.35'}$$

with the results of the second order perturbation theory for the relaxation time

$$\frac{1}{T_{sd}} = \frac{2\pi}{\hbar} \frac{2n(E_f)}{N} \langle J^2 \rangle_f \frac{N_0}{N} \frac{2}{3} S(S+1) \tag{4.14}$$

$$\frac{1}{T_{ds}} = \frac{2\pi}{\hbar} \frac{2n(E_f)}{N} \langle J^2 \rangle_f \frac{n(E_f)}{N} kT. \tag{4.15}$$

Here we summarize the results :

(1) For the dynamical problem such as resonance there are two entirely different pictures in treating the spin-system of conduction electrons ; i.e. adiabatic and isothermal pictures. In the adiabatic limit we do not expect any shift and any broadening of the *d*-spin resonance line through the *s-d* interaction. On the other hand, in the isothermal limit, we have two different predictions, i.e. Kittel-Mitchell's shift and Yosida's shift. As far as we know, there is no reliable answer to the question which shift is actually correct to be expected.

(2) From the phenomenological point of view based on the thermodynamical consideration it is possible to make an interpolation between two idealized pictures, i.e. between the adiabatic picture and the isothermal picture of either K-M theory and Yosida's theory. In any case the criterion of the isothermal picture is given by

$$T_{sL} < T_{sd}^* . \tag{5.7}$$

This means that the *s-d* interaction is almost ineffective on the shift as well as on the line broadening, unless the above condition is fulfilled. For instance, the time scale of Cu-Mn dilute alloys (1% Mn in Cu) can be written as follows :

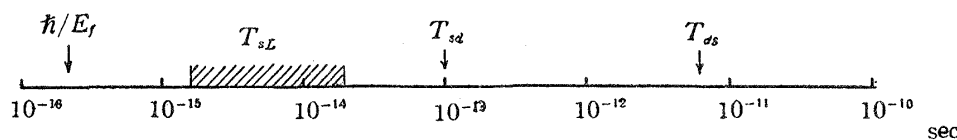


Fig. 4.

One sees that the length of  $T_{sL}$  which well satisfies the isothermal condition is fallen into a quite limited range.

(3) If one assumes that the equilibrium value of the total magnetization  $M_s^\circ$  is given by

\* Numerically this criterion does not depend on the choice of  $M_s^\circ$ .

$$M_s^\circ = \chi_p(H + \lambda M_a^\circ) \quad (5.8)$$

then the difference between K-M theory and Yosida's theory consists in the direction towards which  $M_s$  is relaxing in every moment. In both cases the calculation of the spin-lattice relaxation time based on the usual second order perturbation theory is wrong, and therefore neither of them is more convincing. To obtain a more definite conclusion it is necessary to estimate the higher order effect of the  $s$ - $d$  interaction.

In this connection it is noted that Yosida's theory implies that the magnetization of conduction electrons is spatially not uniform. This is far from the simple expression (5.8). From his picture  $M_s^\circ$  is rather only the Pauli paramagnetism  $\chi_p H$  almost everywhere just except the vicinity of each  $d$ -core, and the dynamical behavior of the localized part of the magnetization might be understood from the fact that conduction electrons adiabatically follow the  $d$ -core spins. The greatest trouble is, therefore, how to reconcile the relaxation theory with that effect of localization.

(4) We make a discussion from experimental points of view. The magnitude of the  $s$ - $d$  exchange integral previously anticipated by Berkeley group for Cu-Mn dilute alloy was about 1/10 or so of the one for free  $M_n^+$  ion because of the screening effect. This has been modified by the precise analysis of the resistivity anomaly and of the line width of the nuclear magnetic resonance. As was shown by Yosida and Behringer, the  $s$ - $d$  exchange integral in the alloy is consistent with the free ion value which is equal to

$$J_0 = 3.5 \times 10^{-13} \text{ erg.} \quad (5.9)$$

This is also confirmed by Sugawara<sup>5)</sup>.

The corresponding relaxation time  $T_{sd}$  is generally very short, which may be expected as

$$T_{sd} = 2 \times 10^{-13} f \text{ sec,} \quad (5.10)$$

where  $f$  is the atomic per cent of manganese in copper. Accordingly, the isothermal condition

$$T_{sL} < T_{sd}$$

is considerably strict even for the specimen of the lowest concentration of manganese used in the experiment. If this limiting case is valid, the shift and  $T_{2\text{eff}}$  are estimated as

$$\Delta H/H = \lambda \chi_p = 3.3 \times 10^{-2} \quad \text{by Yosida's theory} \quad (5.11)$$

$$= \lambda \chi_p (1 + \lambda \chi_a) \cong 3.4 \times f/T \quad \text{by K-M theory,} \quad (5.12)$$

where  $T$  is the absolute temperature.

$$T_{2\text{eff}} = T_{as} = 5 \times 10^{-10} T \text{ sec.} \quad \text{by Korringa formula} \\ (= 7 \times 10^{-12} \text{ sec, at } T = 77^\circ \text{K}) \quad (5.13)$$



$$=5 \times 10^{-10} T^{-1} (1 + \lambda \chi_d)^{-1} = 5 \times 10^{-12} f^{-1} \quad (5.14)$$

by assuming the K-M theory.

The shift (5.11) is several times as large as the observed shift for Cu-Mn alloy at paramagnetic region, even though about 1% experimental error is assumed. The effective relaxation time (5.13) is based on the formula (4.15). This is independent of the concentration of manganese. The observed value of  $T_{2eff}$  is about  $1 \sim 5 \times 10^{-10}$  sec. at 77°K, and is several ten times as long as the estimated value (5.13). It is even longer than the value (5.14) expected from the formula (5.2) which is consistent with the K-M theory. On the other hand, if  $T_{sL}$  is longer than  $T_{sd}$ , we may expect that the *s-d* interaction is not fully effective on these observable quantities. For instance, when  $T_{sL}$  is assumed to be 10 times as long as  $T_{sd}$ , eqs. (4.32) and (4.33) tell us that

$$\frac{\Delta H}{H} \sim \frac{1}{100} \frac{\lambda M_s^\circ}{H} \quad (5.15)$$

$$T_{2eff} \simeq 10 T_{ds} . \quad (5.16)$$

The experimental results are not quite precise so that we cannot determine whether the K-M theory or Yosida's theory suits better. But, in any way, there are considerable discrepancies between the observed data and the predicted values from these theories. In this connection it is interesting to note that the observed line width at 77°K is slightly concentration dependent, which has a tendency that the specimen of the higher concentration shows the narrower line. This may be expected from our formula (4.33) or Fig. 3, provided that  $T_{sL}$  is longer than  $T_{sd}$  and does not depend so much on the concentration of manganese.

(5) The conduction electron spin resonance in metallic copper has not yet been observed, and so the spin-lattice relaxation time of the conduction electrons in copper is regarded as considerably short compared with the one in alkali metals. Elliott<sup>17)</sup> has discussed on the basis of the spin-orbit coupling theory that  $T_{sL}$  in noble metal is about  $10^{-10}$  sec at room temperature, which seems to be still longer than the actual length of  $T_{sL}$  in copper. Further, there is a possibility that the actual length of  $T_{sL}$  in the alloy is more or less shortened from that in pure copper.

It seems to us, however, that the length of  $T_{sL}$  in the alloy less than  $10^{-13}$  sec at 77°K is too short, and is rather unrealistic. If this might be the case, much larger effect must be expected on the electrical resistivity. The plausible length of  $T_{sL}$  will be

$$T_{sL} \sim 10^{-12} \text{ sec at } 77^\circ\text{K} .$$

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