

# Theory of Magnetic Exchange-Lattice Relaxation in Two Organic Free Radicals\*

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A calculation of the spin-lattice relaxation rate is made for conditions appropriate to certain organic free radicals with exchange-narrowed paramagnetic resonance lines, at temperatures well above the Néel temperature. The relaxation is supposed to be a two-step process: 1. Energy is transferred from the "Zeeman" system to the "exchange" system by spin-spin relaxation. 2. The energy is then transferred from the "exchange" system to the lattice. It is the rate of energy transfer in the latter process which is here computed, assuming that the exchange-lattice coupling is due to (a) the variation of exchange energy when the distance between two adjacent spins is changed or (b) the corresponding variation of magnetic dipolar energy. The calculation shows that in the case of diphenyl picryl hydrazyl (DPPH) and bisdiphenylene phenyl allyl (BDPA) the exchange-lattice relaxation rate above liquid nitrogen temperatures is rapid enough (under the usual experimental conditions) to make the experimental spin-"lattice" relaxation time equal to the Zeeman-exchange relaxation time and hence temperature independent, as experimentally observed.

## I. INTRODUCTION

BLOEMBERGEN and Wang<sup>1</sup> measured the spin-lattice relaxation time  $T_1$  in the organic free radical diphenyl picryl hydrazyl (DPPH) at a frequency of 10 kMc/sec and at two temperatures, 77° and 300°K. They explained the equality of  $T_1$  at these two temperatures by suggesting that the spin system and lattice may be regarded as three heat reservoirs (see Fig. 1).<sup>2</sup> Microwave power is put into the Zeeman system; the experimentally observed  $T_1$  is the time required for this energy to be dissipated in the exchange system. The Zeeman system is supposed to be weakly coupled to the lattice and the exchange system (relatively) strongly coupled. The Zeeman-exchange relaxation, being a spin-spin relaxation effect, should give a temperature independent relaxation time for temperatures well above the Néel temperature of the material—about 1°K in the case of DPPH. A similar equality of  $T_1$  at 77° and 300°K has been observed in bisdiphenylene phenyl allyl (BDPA).<sup>3</sup>

The Zeeman-exchange relaxation time depends on the magnitude of the dipolar and exchange energies; a calculation using reasonable estimates of these quantities agrees in order of magnitude with the experimental  $T_1$  in DPPH and BDPA.<sup>4</sup> But the question of how energy is transferred from the exchange system to the lattice does not seem to have been carefully investigated. One possibility is that a change in the exchange integral when the distance between adjacent spins is altered provides an exchange-lattice coupling. This mechanism is treated in some detail in Secs. IV to VI below. Bloembergen and Wang<sup>1</sup> suggested that the same dipolar interaction which connects Zeeman and ex-

change systems may also serve to connect the exchange with the lattice. This mechanism is considered in Sec. VII. Comparison with the results of published experimental  $T_1$  measurements is found in Sec. VIII. The entire calculation is restricted to temperatures well above the Néel temperature of the free radical in question.

## II. ENERGY TRANSFER BETWEEN RESERVOIRS

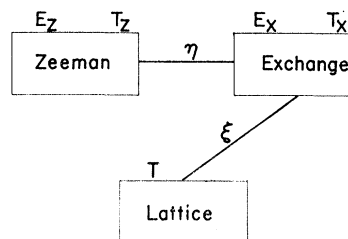
Referring to Fig. 1, assume the Zeeman, exchange, and lattice systems are individually in approximate thermal equilibrium at the temperatures  $T_z$ ,  $T_x$ , and  $T$ , respectively. Let  $E_z$  and  $E_x$  be the Zeeman and exchange energies, respectively, which are given in the high-temperature limit for spin  $\frac{1}{2}$  by

$$\begin{aligned} E_z &= \text{const} - a/kT_z, \\ E_x &= \text{const} - b/kT_x, \\ a &= \frac{1}{4}N(g\beta H)^2, \\ b &= \frac{3}{8}NZJ^2, \end{aligned} \quad (1)$$

where  $N$  is the number of spins in the crystal,  $g$  the electron  $g$  factor (very nearly isotropic in DPPH and BDPA),  $\beta$  the Bohr magneton,  $H$  the external magnetic field, and the exchange interaction between a spin and each of its  $Z$  nearest neighbors is of the form  $2JS_i \cdot S_j$ .

Let the energy per unit time flowing from the Zeeman to the exchange system be  $\eta(1/kT_x - 1/kT_z)$  and from exchange to lattice  $\xi(1/kT - 1/kT_x)$ . For sufficiently high temperatures we expect  $\eta$ , which refers to the spin-spin relaxation, to be temperature independent, whereas

FIG. 1. Schematic diagram of the Bloembergen-Wang three-reservoir model. The  $E$ 's are energies, the  $T$ 's are temperatures, and  $\eta$  and  $\xi$  are energy transfer constants defined in the text.



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<sup>1</sup> N. Bloembergen and S. Wang, Phys. Rev. **93**, 72 (1954).

<sup>2</sup> For a further discussion of the three-reservoir model, see J. H. Van Vleck, Nuovo cimento Suppl. **6**, 1081 (1957).

<sup>3</sup> J. P. Goldsborough, M. Mandel, and G. E. Pake, Phys. Rev. Letters **4**, 13 (1960). M. Mandel (private communication) states that the values given in Table I of this reference are for measurements at 10 kMc/sec, not 24 kMc/sec.

<sup>4</sup> G. E. Pake (private communication).

$\xi$ , as shown in the subsequent calculation, depends on the lattice temperature  $T$ . If an energy per unit time  $W$  is introduced (by an external rf field) to the Zeeman system, one finds, for steady-state conditions,

$$W = \eta \left( \frac{1}{kT_x} - \frac{1}{kT_z} \right) = \xi \left( \frac{1}{kT} - \frac{1}{kT_x} \right), \quad (2)$$

or

$$\frac{1}{kT_z} = \frac{1}{kT} - \left( 1 + \frac{\eta}{\xi} \right) \frac{W}{\eta}. \quad (3)$$

In order to obtain the Bloembergen-Wang result—temperature independence of  $T_1$ —it is necessary that  $1/T_z$  (which is proportional to the component of magnetization in the direction of the static magnetic field) depend on  $W$  only through  $\eta$ , which will be the case if  $\eta/\xi \ll 1$ . The argument may also be stated in terms of relaxation times. Let  $\tau_1$  be the Zeeman-exchange relaxation time, i.e.,  $\tau_1$  is the characteristic time in which, for constant  $T_x$  and  $W=0$ ,  $1/T_z$  relaxes to its equilibrium value. Similarly let  $\tau$  be the exchange-lattice relaxation time.

$$\tau_1 = a/\eta, \quad \tau = b/\xi. \quad (4)$$

The experimentally observed  $T_1$  is equal to  $\tau_1$ , and hence temperature independent, provided the following condition holds:

$$\eta/\xi = (a\tau/b\tau_1) \ll 1. \quad (5)$$

Conversely, the temperature independence of the experimental  $T_1$ , in a given temperature range, indicates that  $\tau_1 = T_1$ . Then  $\eta$  may be computed from the experimental  $T_1$  using (1) and (4). In the remainder of the paper  $\eta$  and  $\xi$  will be referred to as “energy transfer constants.”

### III. RELAXATION RATES FROM TRANSITION PROBABILITIES

With reference to Fig. 2, let  $i$  and  $j$  be any two levels of the exchange system, with energies  $E_i$  and  $E_j$  and occupation probabilities  $P_i$  and  $P_j$ , respectively. Likewise let  $\alpha$  and  $\beta$  be levels in the lattice (phonon) system with energies  $E_\alpha$ ,  $E_\beta$  and occupation probabilities  $Q_\alpha$ ,  $Q_\beta$ . Consider an elementary process in which the exchange system goes from  $i$  to  $j$  and the lattice from  $\beta$  to  $\alpha$ . We assume  $P_i$  satisfies the rate equation,<sup>5</sup>

$$(dP_i/dt)_{j\beta\alpha} = W(ji, \alpha\beta) [P_j Q_\alpha - P_i Q_\beta], \quad (6)$$

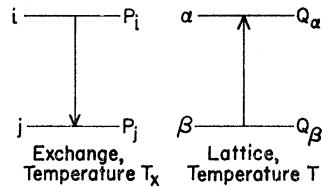


FIG. 2. Diagram representing an elementary process in which energy is transferred from the exchange system to the lattice.

<sup>5</sup> If one writes a rate equation, (6) is a sensible form for it to take. We prefer to regard (6) as one of the assumptions of our calculation, rather than discussing the not-so-simple problem of justifying it starting from Schrödinger's equation.

where the subscripts on the derivative denote that fraction of  $dP_i/dt$  due to the process in question;  $W(ji, \alpha\beta)$  is the transition probability for the elementary process, given that the exchange and lattice are initially in states  $i$  and  $\beta$ , respectively, and will vanish unless the energies satisfy the relation  $E_i - E_j \approx E_\alpha - E_\beta$ . The inverse probability  $W(ij, \beta\alpha)$  is equal to  $W(ji, \alpha\beta)$ .<sup>6</sup>

Further assume that  $E_i - E_j$  is much less than  $kT$  or  $kT_x$ , i.e., the energy transferred in the elementary process is much less than  $kT$ . For thermal equilibrium we have

$$\begin{aligned} P_j/P_i &\approx 1 + (E_i - E_j)/kT_x, \\ Q_\alpha/Q_\beta &\approx 1 - (E_\alpha - E_\beta)/kT. \end{aligned} \quad (7)$$

Inserting these expressions into (6) and using the definition of the exchange-lattice energy transfer constant  $\xi$ , one obtains

$$\begin{aligned} &\xi \left( \frac{1}{kT_x} - \frac{1}{kT} \right) \\ &= \frac{dE_x}{dt} = \sum_{i>j} \sum_{\beta>\alpha} (E_i - E_j) \left( \frac{dP_i}{dt} \right)_{j\beta\alpha} \\ &\approx \left( \frac{1}{kT_x} - \frac{1}{kT} \right) \sum_{i>j} \sum_{\beta>\alpha} (E_i - E_j)^2 P_i Q_\beta W(ji, \alpha\beta). \end{aligned} \quad (8)$$

A comparison of (8) with (6) yields the following simple rule: The exchange-lattice energy transfer constant  $\xi$  may be obtained by multiplying the probability of occurrence of an elementary process by the square of the energy transferred in this process, and then summing the result over all processes which increase the lattice energy.

Above the Néel temperature it is reasonable to assume that different pairs of spins contribute incoherently to the exchange-lattice relaxation. Hence the energy transferred in an elementary process should be on the order of a few times  $J$  or less, and the simple rule for computing  $\xi$  will hold provided  $kT \gg J$ , i.e., for temperatures well above the Néel temperature.

### IV. METHOD OF CALCULATION

The exchange Hamiltonian  $\mathcal{H}_{ex}$  is expanded in a power series as follows:

$$\mathcal{H}_{ex} = 2 \sum_{\langle jk \rangle} J(\mathbf{x}_{jk}) \mathbf{S}_j \cdot \mathbf{S}_k = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2 + \cdots, \quad (9)$$

$$\mathcal{H}_0 = 2J \sum_{\langle jk \rangle} \mathbf{S}_j \cdot \mathbf{S}_k, \quad (10)$$

$$\mathcal{H}_1 = \sum_{\langle jk \rangle} \mathbf{S}_j \cdot \mathbf{S}_k \sum_s 2 \left( \frac{\partial J(\mathbf{x}_{jk})}{\partial x_{jk}^s} \right) u_{jk}^s, \quad (11)$$

$$\mathcal{H}_2 = \sum_{\langle jk \rangle} \mathbf{S}_j \cdot \mathbf{S}_k \sum_{rs} \left( \frac{\partial^2 J(\mathbf{x}_{jk})}{\partial x_{jk}^r \partial x_{jk}^s} \right) u_{jk}^r u_{jk}^s, \quad (12)$$

<sup>6</sup> Since both exchange and lattice levels are considered explicitly, there are no Boltzmann factors appearing in the  $W$ 's. See, e.g., A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), p. 267.

where  $\langle jk \rangle$  denotes an adjacent pair of spins, each pair to be counted in the sum only once;  $\mathbf{x}_{jk}$  is the vector joining spins  $j$  and  $k$ ;  $\mathbf{u}_{jk}$  is the difference between  $\mathbf{x}_{jk}$  and its equilibrium value; and the Cartesian components of  $\mathbf{x}_{jk}$  and  $\mathbf{u}_{jk}$  are denoted by superscripts. The derivatives of  $J(\mathbf{x}_{jk})$ , as well as  $J$  itself in (10), are evaluated at the equilibrium value of  $\mathbf{x}_{jk}$ .  $\mathcal{H}_0$  is regarded as the unperturbed exchange Hamiltonian and  $\mathcal{H}_1$  and  $\mathcal{H}_2$  the perturbations connecting  $\mathcal{H}_0$  with the lattice. The vector  $\mathbf{u}_{jk}$  is an operator in the lattice system and may be written as a linear combination of phonon creation and destruction operators.

To find the transition probabilities due to  $\mathcal{H}_1$  and  $\mathcal{H}_2$  we employ a method quite analogous to that used in computing nuclear spin-lattice relaxation in liquids.<sup>7</sup> In the latter case one deals with the nuclear spins with known Zeeman energy levels, and the lattice—the translational motion of molecules in the liquid—for which the energy levels are not known. The dipolar Hamiltonian, which acts as a perturbation connecting spins and lattice, consists of products of spin operators with lattice operators (the relative positions of molecules). The lattice operators are treated as random functions of the time, and only their correlation spectra appear in the transition probabilities for the spins.

For the exchange-lattice relaxation considered here, the phonon energy levels are known, but the exchange energy levels are not known. Hence the spin operators in Eqs. (11) and (12), in analogy with position and angles in the case of nuclear relaxation, are regarded as random functions of the time, and only the correlation spectra of these operators appear in the phonon absorption and emission probabilities. The correlation spectra are computed quantum mechanically, in contrast to the case of nuclear relaxation in a liquid where the spectra are usually computed classically.

## V. SINGLE PHONON PROCESSES

Let  $W_{fq}$  be the emission probability per unit time for a phonon in branch  $f$  with wave vector  $\mathbf{k}_q$  and angular frequency  $\omega_{fq}$ , due to a particular pair of spins  $\langle jk \rangle$ . The usual perturbation formula gives

$$W_{fq} = \frac{1}{\hbar^2 t} \left| \int_0^t \langle n_{fq} + 1 | \mathcal{O}_{jk} | n_{fq} \rangle \times [\mathbf{S}_j(\tau) \cdot \mathbf{S}_k(\tau)] \exp(i\omega_{fq}\tau) d\tau \right|^2, \quad (13)$$

where  $\mathcal{O}_{jk}$  is the coefficient of  $\mathbf{S}_j \cdot \mathbf{S}_k$  in (11) and  $n_{fq}$  is the number of phonons initially in the  $fq$  mode. Define

$$F(\omega) = \frac{1}{t} \left| \int_0^t \mathbf{S}_j(\tau) \cdot \mathbf{S}_k(\tau) e^{i\omega\tau} d\tau \right|^2, \quad (14)$$

<sup>7</sup> See, for instance, E. R. Andrew, *Nuclear Magnetic Resonance* (Cambridge University Press, New York, 1955), p. 228.

which may be written as

$$F(\omega) = \int_{-\infty}^{\infty} f(t) \cos(\omega t) dt, \quad (15)$$

where  $f(t)$  is the autocorrelation function for  $\mathbf{S}_j(t) \cdot \mathbf{S}_k(t)$  and is given in the high-temperature limit,  $kT \gg J$ , by

$$f(t) = \langle \exp(i\mathcal{H}_0 t/\hbar) \mathbf{S}_j \cdot \mathbf{S}_k \exp(-i\mathcal{H}_0 t/\hbar) \mathbf{S}_j \cdot \mathbf{S}_k \rangle, \quad (16)$$

where the angular brackets  $\langle \rangle$  denote the trace of the quantity inside the brackets divided by the trace of unity. Equation (15) follows from (14) upon taking a statistical average, provided  $f(\tau)$  approaches zero in a time short compared to the time  $t$  in (14).<sup>8</sup>

Equation (16) involves an approximation in that the total Hamiltonian for the spins—Zeeman plus dipolar plus exchange—has been replaced in the exponentials by the exchange Hamiltonian  $\mathcal{H}_0$ . The Zeeman Hamiltonian commutes with  $\mathbf{S}_j \cdot \mathbf{S}_k$  so need not be included. The dipolar energy is small compared to the exchange energy in materials (such as DPPH and BDPA) with strong exchange narrowing of the paramagnetic resonance line, and hence its contribution to the correlation function may be neglected.

We expect that  $W_{fq}$  will be negligibly small for phonon energies greater than a few times  $J$  (as mentioned at the end of Sec. III), or, in other words, that  $F(\omega)$  will be negligibly small for  $|\omega| > \omega_1$ , where  $\omega_1$  is of the order of a few times  $J/\hbar$ . Since it substantially simplifies the calculation, we shall assume that

$$\hbar\omega_1 \ll k\Theta, \quad (17)$$

where  $\Theta$  is the lattice Debye temperature. Condition (17) is probably satisfied for DPPH and BDPA since the Néel temperature for these materials is of the order of 1 to 5°K and the Debye temperature of the order of 40 or 50°K.

The displacement  $\mathbf{u}_{jk}$  may be expanded in lattice normal modes<sup>9</sup>:

$$\mathbf{u}_{jk} = \left( \frac{\hbar}{2M} \right)^{\frac{1}{2}} \sum_q \sum_{f=1}^3 \frac{d_{fq}^\dagger \boldsymbol{\epsilon}_{fq}}{(\omega_{fq})^{\frac{1}{2}}} [\exp(i\mathbf{k}_q \cdot \mathbf{x}_j) - \exp(i\mathbf{k}_q \cdot \mathbf{x}_k)] + \text{Hermitian conjugate}, \quad (18)$$

where  $M$  is the crystal mass;  $d_{fq}^\dagger$  is the creation operator and  $\boldsymbol{\epsilon}_{fq}$  the unit polarization vector (a complex quantity) for the phonon  $fq$ ; and  $\mathbf{x}_j$  and  $\mathbf{x}_k$  are the equilibrium positions of spins  $j$  and  $k$ , respectively. The nonzero matrix elements for  $d_{fq}^\dagger$  are:

$$\langle n_{fq} + 1 | d_{fq}^\dagger | n_{fq} \rangle = (n_{fq} + 1)^{\frac{1}{2}}. \quad (19)$$

<sup>8</sup> For a very illuminating discussion of the entire procedure, see reference 6, Chap. VIII.

<sup>9</sup> See, for example, P. G. Klemens, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 1.

The polarization vectors satisfy the orthogonality relations

$$\begin{aligned}\sum_s (\epsilon_{fq}^s) (\epsilon_{gq}^s)^* &= \delta_{fg}, \\ \sum_f (\epsilon_{fq}^s) (\epsilon_{fq}^t)^* &= \delta_{st}.\end{aligned}\quad (20)$$

The following approximations are made in treating the phonon modes<sup>10</sup>:

(a) The phonons are treated as if the material were homogeneous and isotropic. The velocity difference between longitudinal and transverse phonons is neglected.

(b) Variation of phonon velocity with frequency is neglected.

(c) The phonon wavelength is assumed to be much larger than the distance between adjacent spins.

(d) A simple Debye spectrum is assumed, with the cutoff frequency chosen so that the number of phonon modes is three times the number of molecules in the crystal. Thus only acoustical modes are considered.

Approximations (b), (c), and (d) are probably justified in the case of single-phonon processes since, by condition (17), the phonon energy is small compared to  $k\Theta$ .

Combining (11), (13), (14), and (18), and using the long-wavelength approximation (c), one obtains

$$\begin{aligned}W_{fq} &= \frac{2}{\hbar M} F(\omega_{fq}) \frac{n_{fq} + 1}{\omega_{fq}} [\mathbf{k}_q(\mathbf{x}_j - \mathbf{x}_k)]^2 \\ &\quad \times \sum_{st} \epsilon_{fq}^s (\epsilon_{fq}^t)^* \frac{\partial J(\mathbf{x}_{jk})}{\partial x_{jk}^s} \frac{\partial J(\mathbf{x}_{jk})}{\partial x_{jk}^t}.\end{aligned}\quad (21)$$

Let  $\xi_i$  be the fraction of the energy transfer constant  $\xi$  due to single-phonon processes. Using the prescription of Sec. III we may write

$$\xi_i = \frac{1}{2} NZ \sum_{fq} (\hbar \omega_{fq})^2 W_{fq}, \quad (22)$$

where the factor  $\frac{1}{2}NZ$  is the number of separate pairs of spins. It is assumed that  $\xi_i$  may be obtained by adding the transition probabilities computed for each pair of spins, i.e., coherence effects between different pairs of spins are neglected.

By assumptions (a) and (d),  $\omega_{fq}$  is independent of  $f$ . The summation over wave vectors  $q$  in (22) is replaced by an integral over  $\omega = \omega_{fq}$ , for which the density of states is given by

$$\begin{aligned}\rho(\omega) &= V\omega^2 / (2\pi^2 v^3) \quad \text{for } 0 \leq \omega \leq \omega_0 \\ &= 0 \quad \text{for } \omega > \omega_0, \\ \omega_0 &= v(6\pi^2 N/V)^{1/3},\end{aligned}\quad (23)$$

where  $V$  is the volume of the crystal,  $v$  is the "average" speed of sound, and  $N$  is the number of molecules, which is equal to the number of spins in DPPH and BDPA.

<sup>10</sup> With respect to these approximations our calculation follows very closely that of I. Waller, *Z. Physik* **79**, 370 (1932). The same or similar approximations are found in calculations by J. H. Van Vleck, *Phys. Rev.* **57**, 426 (1940) and R. D. Mattuck and M. W. P. Strandberg, *ibid.* **119**, 1204 (1960).

Note that the Debye temperature  $\Theta$  is equal to  $\hbar\omega_0/k$ . The quantity  $[\mathbf{k}_q(\mathbf{x}_j - \mathbf{x}_k)]^2$  is replaced by its average over all angles  $a^2\omega^2/3v^2$ , where  $a$  is the distance between adjacent spins. The thermal-equilibrium value is used for  $n_{fq}$ :

$$n_{fq} = [\exp(\hbar\omega_{fq}/kT) - 1]^{-1}. \quad (24)$$

In Eq. (21),  $n_{fq} + 1$  may be replaced by the high-temperature approximation:

$$n_{fq} \approx kT/\hbar\omega_{fq}. \quad (25)$$

Inserting (21) in (22) and using the above approximations, one obtains

$$\begin{aligned}\xi_i &= \left(\frac{Z}{6\pi^2}\right) \frac{N K V a^2 k T}{M v^5} \int_0^\infty \omega^4 F(\omega) d\omega, \\ K &= \sum_s \left(\frac{\partial J(\mathbf{x}_{jk})}{\partial x_{jk}^s}\right)^2,\end{aligned}\quad (26)$$

where  $\omega_0$  has been replaced by  $\infty$  in the upper limit of the integral in accordance with condition (17).

The functional form of  $J(\mathbf{x}_{jk})$  is not known. We assume that if  $\mathbf{x}_{jk}$  is close to its equilibrium value the following approximation may be used:

$$J(\mathbf{x}_{jk}) = \text{const} \times \exp(-\lambda |\mathbf{x}_{jk}|), \quad (27)$$

giving  $K = \lambda^2 J^2$ . The integral over  $\omega$  is evaluated in Appendix A for some simple lattices and found to be proportional to  $(Z-1)^2$ . Finally we have

$$\xi_i = \frac{3}{2\pi} Z(Z-1)^2 J^6 \frac{N V \lambda^2 a^2}{M v^5 \hbar^4} k T. \quad (28)$$

## VI. TWO PHONON PROCESSES

In a single-phonon process only phonons with energy of the order of  $J$  or less are utilized in the relaxation process; by condition (17) these occupy but a small part of the phonon spectrum. A two-phonon process in which a phonon of energy  $\gg J$  is absorbed and one of slightly higher energy emitted,<sup>11</sup> although less probable than the single-phonon process, utilizes the entire phonon spectrum and hence may be of importance for the relaxation, especially at higher temperatures where the higher energy modes are appreciably excited.

Let  $W_{fq;gp}$  be the probability per unit time for absorption of a phonon in mode  $gp$  and simultaneous emission of a phonon in mode  $fq$ , due to a single pair of spins  $\langle jk \rangle$ .

$$\begin{aligned}W_{fq;gp} &= \frac{1}{\hbar^2 t} \left| \int_0^t \langle n_{fq} + 1, n_{gp} - 1 | \mathcal{O}_{jk} | n_{fq}, n_{gp} \rangle \right. \\ &\quad \times [\mathbf{S}_j(\tau) \cdot \mathbf{S}_k(\tau)] \exp[i(\omega_{fq} - \omega_{gp})\tau] d\tau \left. \right|^2,\end{aligned}\quad (29)$$

<sup>11</sup> Following Waller, reference 10, we omit as unimportant the processes in which two phonons are emitted or absorbed.

where  $\mathcal{O}_{jk}$  is the coefficient of  $\mathbf{S}_j \cdot \mathbf{S}_k$  in (12). Let  $\xi_{ii}$  be that fraction of the energy transfer constant  $\xi$  due to the two-phonon processes:

$$\xi_{ii} = \frac{1}{2}NZ \sum_{qp}' \sum_{fg}' (\omega_{fq} - \omega_{gp})^2 W_{fq;gp}, \quad (30)$$

where the summation  $\sum'$  is restricted to cases where  $\omega_{fq} > \omega_{gp}$ , in accordance with the prescription in Sec. III.

The same procedures used to evaluate (22) are employed with (30), including the long wavelength approximation (c) and the high-temperature limit (25). One would not at first expect either approximation to be very good. However, as shown in Appendix B, the long-wavelength approximation overestimates  $\xi_{ii}$  by a factor of 3 or less, whereas the high-temperature approximation overestimates  $\xi_{ii}$  by a factor of 2 or less even at a temperature as low as one-third the Debye temperature. These factors are not large in view of the other approximations entering the calculation, but, as partial compensation, the expression for  $\xi_{ii}$  in (31) and (33) contains an extra factor of  $\frac{1}{3}$ . Writing  $\omega'$  for  $\omega_{fq}$  and  $\omega$  for  $\omega_{gp}$ , one obtains

$$\xi_{ii} = \frac{\frac{1}{3}Z}{72\pi^4} \frac{NV^2La^4}{M^2v^{10}} k^2 T^2 \times \int_0^{\omega_0} d\omega \int_{\omega}^{\omega_0} d\omega' \omega^2 \omega'^2 [(\omega' - \omega)^2 F(\omega' - \omega)], \quad (31)$$

for  $T > \frac{1}{3}\Theta$ , and

$$L = \sum_{rs} \left( \frac{\partial^2 J(\mathbf{x}_{jk})}{\partial x_{jk}^r \partial x_{jk}^s} \right)^2.$$

Substituting  $\Omega$  for  $\omega' - \omega$ , the integral in (31) may be approximated by

$$\left( \int_0^{\omega_0} \Omega^2 F(\Omega) d\Omega \right) \left( \int_0^{\omega_0} \omega^4 d\omega \right), \quad (32)$$

since, by condition (17),  $F(\Omega)$  is nonzero only for values of  $\Omega$  much less than  $\omega_0$ . The integral of  $F(\Omega)$  in (32) is evaluated in Appendix A. One obtains  $L = \lambda^4 J^2$  by using (27) and neglecting terms of order  $(\lambda a)^{-2}$ . Finally one obtains

$$\xi_{ii} = \frac{Z(Z-1)}{40} \left( \frac{\pi V}{6N} \right)^{\frac{1}{3}} \frac{J^4 N^3 \lambda^4 a^4}{\hbar^2 M^2 v^5} k^2 T^2, \quad (33)$$

for  $T > \frac{1}{3}\Theta$ .

An additional contribution to the two-phonon process may be obtained using only the term  $\mathcal{H}_1$  in (9) but going to second order in perturbation theory. Processes involving high-energy phonons are permitted since energy need not be conserved in the intermediate state. Let  $\mathcal{H}_{\text{eff}}$  be the "effective" Hamiltonian which when used in first-order perturbation theory yields the second order

effects of  $\mathcal{H}_1$ . In order of magnitude one has

$$\mathcal{H}_{\text{eff}} \sim (\mathcal{H}_1)^2 / \Delta \sim (J/\Delta) \mathcal{H}_2, \quad (34)$$

where  $\Delta$  is the difference in energy between the initial and intermediate state. By condition (17) the great majority of phonons have energies  $\gg J$ ; for these phonons  $\Delta$  is essentially the phonon energy. Thus we conclude that the processes induced by  $\mathcal{H}_{\text{eff}}$  are of negligible importance, since they are of order  $(J/\Delta)^2$  less probable than those induced by  $\mathcal{H}_2$ .

## VII. RELAXATION BY MEANS OF THE DIPOLE INTERACTION

The dipolar Hamiltonian  $\mathcal{H}_d$  may be written, neglecting interaction between nonadjacent spins, as

$$\mathcal{H}_d = g^2 \beta^2 \sum_{\langle jk \rangle} \frac{1}{|\mathbf{x}_{jk}|^3} \times \left[ \mathbf{S}_j \cdot \mathbf{S}_k - \frac{3}{|\mathbf{x}_{jk}|^2} (\mathbf{S}_j \cdot \mathbf{x}_{jk})(\mathbf{S}_k \cdot \mathbf{x}_{jk}) \right]. \quad (35)$$

In analogy with  $\mathcal{H}_{\text{ex}}$  in Eq. (9),  $\mathcal{H}_d$  may be expanded in a Taylor series in a sum of products of spin operators with phonon operators. The spin operators are regarded as random functions of the time. The correlation functions are of the form (taking a typical example)

$$f_{xy;xy}(t) = \langle \exp(i\mathcal{H}_0 t / \hbar) S_{jx} S_{ky} \times \exp(-i\mathcal{H}_d t / \hbar) S_{jx} S_{ky} \rangle, \quad (36)$$

where the subscripts  $x, y$  denote the Cartesian components of the spin operators, and the  $\mathcal{H}_0$  appearing in the exponentials is, just as in (16), the exchange Hamiltonian given by Eq. (10). The dipolar Hamiltonian is not included in  $\mathcal{H}_0$  because it is small, and the Zeeman Hamiltonian is omitted because we are only interested in the exchange-lattice relaxation and not in the direct Zeeman-lattice relaxation.<sup>12</sup>

The exchange-lattice energy transfer constant due to the dipolar interaction,  $\xi_d$ , is computed using the methods and approximations of Secs. V and VI, with the exception of Eq. (27). Since the dependence of the dipolar energy on the distance between spins is given explicitly by (35), no further assumptions are needed. The details of the calculation will not be presented here. For the single-phonon process one obtains

$$\xi_{di} = 4.2 Z(Z-1)^2 \frac{NV}{Mv^5} \left( \frac{J}{\hbar} \right)^4 \left( \frac{g^2 \beta^2}{a^3} \right)^2 kT, \quad (37)$$

<sup>12</sup> I. Waller, reference 10, has computed the direct Zeeman-lattice relaxation due to the dipolar interaction. However, there may also be interference between the Zeeman-lattice and exchange-lattice relaxation. Equations (37) and (38) should still be correct in order of magnitude provided the Zeeman energy is comparable to or smaller than the exchange energy.

TABLE I. Physical properties of crystalline DPPH (benzene) and BDPA.

	DPPH	BDPA
Debye temperature ( $^{\circ}\text{K}$ ) <sup>a</sup>	50	42
Exchange $J/k$ ( $^{\circ}\text{K}$ ) <sup>a</sup>	0.45	1.2
Density (g/cc) <sup>b</sup>	1.36	
Molecular weight <sup>c</sup>	472	496
Speed of sound (cm/sec)	$1.4 \times 10^5$	
Distance between adjacent spins (cm)	$8 \times 10^{-8}$	

<sup>a</sup> Reference 14.<sup>b</sup> M. Sternberg, *Compt. rend.* **240**, 990 (1955).<sup>c</sup> Including benzene.

and for the two-phonon process

$$\xi_{dii} = 4.0 Z(Z-1) \left( \frac{\pi V}{6N} \right)^{\frac{1}{3}} \frac{N^3}{M^2 v^5} \left( \frac{J}{\hbar} \right)^2 \times \left( \frac{g^2 \beta^2}{a^3} \right)^2 k^2 T^2, \quad (38)$$

for  $T > \frac{1}{3}\Theta$ . [The  $Z$  dependence of (37) is an approximate but fairly close fit to results obtained by evaluating derivatives of the correlation functions for a linear chain, a square lattice, and a simple cubic lattice. The  $Z$  dependence of (38) is exact in the same three cases.]

Equations (37) and (38) differ from the corresponding (28) and (33) in only two respects: (i) A factor of  $J^2$  in (28) and (33) has been replaced by  $(g^2 \beta^2 / a^3)^2$ ; (ii) the factor  $\lambda^2 a^2$  in (28) has been replaced by 9 and  $\lambda^4 a^4$  in (33) by 160.

### VIII. COMPARISON WITH EXPERIMENT

Some of the physical constants of DPPH and BDPA needed for numerical estimates of the exchange-lattice energy transfer constant  $\xi$  are found in Table I. The magnetic properties of DPPH depend somewhat on the type of solvent from which it is crystallized.<sup>13</sup> Data in Table I refer to DPPH crystals containing one benzene molecule per DPPH molecule. Specific heat measurements at liquid helium temperatures<sup>14</sup> provide values for  $\Theta$  and  $J$ . Actually only  $J\sqrt{Z}$  is determined by the specific heat. Since, however, corresponding factors of  $Z$  or  $Z-1$  appear in (28) and (33), no great error will result from setting  $Z$  equal to 6.

The value of  $J$  for DPPH computed from low-temperature specific heat data is in violent disagreement with susceptibility measurements made between room temperature and  $77^{\circ}\text{K}$ .<sup>15</sup> In this range the susceptibility, corrected for diamagnetism, is proportional to  $(T+\theta)^{-1}$  where  $\theta \approx 20^{\circ}\text{K}$ . In view of this fact it is probably best to regard the estimate of  $J$  for DPPH in Table I as merely

<sup>13</sup> J. J. Lothe and G. Eia, *Acta Chem. Scand.* **12**, 1535 (1958).<sup>14</sup> J. P. Goldsborough, M. Mandel, and G. E. Pake, *Proceedings of the Seventh International Conference on Low-Temperature Physics*, Toronto, 1960 (University of Toronto Press, Toronto, 1960), p. 702.<sup>15</sup> W. Duffy, Jr. (unpublished).TABLE II. Values of the energy transfer constants  $\xi$  and  $\eta$  in units of  $\text{erg}^2 \text{sec}^{-1} \text{mole}^{-1}$  for  $T$  in  $^{\circ}\text{K}$ .

	DPPH	BDPA
$\xi_i$	$1 \times 10^{-3} T$	$4 \times 10^{-1} T$
$\xi_{di}$	$4 \times 10^{-9} T$	$2 \times 10^{-7} T$
$\xi_{ii} (T > 15^{\circ}\text{K})$	$2 \times 10^{-8} T^2$	$1 \times 10^{-3} T^2$
$\xi_{dii} (T > 15^{\circ}\text{K})$	$5 \times 10^{-12} T^2$	$4 \times 10^{-11} T^2$
$\xi = \xi_i + \xi_{ii}$ at $77^{\circ}\text{K}$	0.2	40
$\xi = \xi_i + \xi_{ii}$ at $300^{\circ}\text{K}$	2	200
$\eta$ ( $H = 3600 \text{ oe}$ ) at $77^{\circ}$ and $300^{\circ}\text{K}$	$1 \times 10^{-2}$	$7 \times 10^{-3}$

a lower limit. The value of  $a$  for DPPH is chosen so that the crystal volume is  $Na^3$ , and represents a reasonable guess in the absence of detailed knowledge of the crystal structure. The speed of sound is estimated using the Debye temperature and the density. The BDPA crystals also contain one benzene molecule per BDPA molecule.<sup>16</sup> We assume the density and speed of sound are about the same as in DPPH. The susceptibility of BDPA above  $77^{\circ}\text{K}$  gives a value of  $6 \pm 4^{\circ}\text{K}$  for  $\theta$ ,<sup>15</sup> in reasonable agreement with specific heat data. Since the exchange interaction results from the overlap of wave functions of adjacent atoms, a reasonable value for  $\lambda$  is about  $2 \times 10^8 \text{ cm}^{-1}$ .<sup>17</sup>

Computed values of  $\xi_i$ ,  $\xi_{ii}$ ,  $\xi_{di}$ , and  $\xi_{dii}$  are found in Table II together with experimental values of the Zeeman-exchange energy transfer constant  $\eta$  calculated from the published data on  $T_1$  by use of Eqs. (1) and (4). From reference 3, the values of  $T_1$  at  $77^{\circ}\text{K}$  (and at room temperature) for a frequency of 10 kMc/sec are: DPPH (benzene),  $5 \times 10^{-8} \text{ sec}$ ; BDPA,  $1 \times 10^{-7} \text{ sec}$ . The value for DPPH agrees with that found in reference 1 ( $6 \times 10^{-8} \text{ sec}$ ). Values of  $\xi$  in Table II are significant only in a very rough order of magnitude, due to the rather severe approximations made in the theoretical derivation. From the experimental evidence, viz., the temperature independence of  $T_1$ , it is clear that  $\xi$  is much larger than  $\eta$ , i.e., the "bottleneck" in energy transfer is between the Zeeman and exchange systems, at least for temperatures above  $77^{\circ}\text{K}$ . Table II shows that the value of  $\xi$  we have calculated is much larger than the experimental value of  $\eta$  for BDPA, and at least of the same order of magnitude as  $\eta$  for DPPH, at  $77^{\circ}\text{K}$  and above. (Of course, if the value of  $J$  for DPPH substantially exceeds the value in Table I—as the susceptibility measurements seem to indicate—then the theoretical estimate for  $\xi$  should be correspondingly increased.) Thus it appears that our theoretical estimate does not contradict the experimental evidence. The dipolar contribution to  $\xi$  seems to be smaller than the direct exchange contribution by a factor of roughly  $10^6$ , and hence it is probably unimportant in the exchange-lattice relaxation.

In addition to the acoustical modes, to which the

<sup>16</sup> C. F. Koelsch, *J. Am. Chem. Soc.* **79**, 4439 (1957).<sup>17</sup> This is the order of magnitude found for exchange coupled pairs in ruby. M. J. Weber *et al.*, *Bull. Am. Phys. Soc.* **6**, 141 (1961); M. J. Weber (private communication).

above calculation is restricted, there are, of course, a large number of optical modes which, together with anharmonic effects and hindered rotations, may be a significant cause of relaxation at higher temperatures.

It may be possible to observe the exchange-lattice relaxation directly by steady-state saturation measurements at higher microwave frequencies (for which  $\eta$  is larger) or by going to lower temperatures (for which  $\xi$  is smaller). Unfortunately, steady-state saturation measurements at liquid helium temperatures<sup>3</sup> are impaired by lattice heating, due to the low specific heat of the lattice and imperfect thermal contact between the crystals and the helium bath.<sup>18</sup> It is still possible the exchange-lattice relaxation may be directly observed at some temperature between 4 and 77°K.

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#### APPENDIX A. SECOND AND FOURTH MOMENTS FOR $F(\omega)$

Inverting the transform (15), we obtain

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) \cos(\omega t) d\omega. \quad (\text{A1})$$

Let  $g$  and  $h$  be the second and fourth derivatives of  $f(t)$ , respectively, evaluated at  $t=0$ . Note that  $F(\omega) = F(-\omega)$ . By differentiating (A1), we find

$$\begin{aligned} \int_0^{\infty} \omega^2 F(\omega) d\omega &= -\pi g, \\ \int_0^{\infty} \omega^4 F(\omega) d\omega &= \pi h. \end{aligned} \quad (\text{A2})$$

By expanding in a power series the exponentials in (16) and rearranging some terms, it may be shown that

$$\begin{aligned} f(t) &= \langle (\mathbf{S}_j \cdot \mathbf{S}_k)^2 \rangle + \frac{t^2}{2! \hbar^2} \langle [\mathcal{H}_0, \mathbf{S}_j \cdot \mathbf{S}_k]^2 \rangle \\ &+ \frac{t^4}{4! \hbar^4} \langle [\mathcal{H}_0, [\mathcal{H}_0, \mathbf{S}_j \cdot \mathbf{S}_k]]^2 \rangle + \dots \end{aligned} \quad (\text{A3})$$

The commutators are evaluated for spin  $\frac{1}{2}$  appropriate for DPPH and BDPA. One finds

$$-g = \frac{3}{4} (Z-1) (J/\hbar)^2, \quad (\text{A4})$$

<sup>18</sup> M. Mandel, G. E. Pake, and J. P. Goldsborough, *Bull. Am. Phys. Soc.* **6**, 141 (1961).

provided two adjacent spins have no nearest neighbors in common. The fourth derivative,  $h$ , depends on the particular lattice assumed and not just the number of nearest neighbors. We evaluate  $h$  for three simple cases:

$$\begin{aligned} h &= 9(J/\hbar)^4, \text{ linear chain,} \\ &= 82\frac{1}{2}(J/\hbar)^4, \text{ square lattice,} \\ &= 234(J/\hbar)^4, \text{ simple cubic lattice.} \end{aligned} \quad (\text{A5})$$

All three cases are represented quite well by the simple formula

$$h \approx 9(Z-1)^2 (J/\hbar)^4. \quad (\text{A6})$$

#### APPENDIX B. HIGH-TEMPERATURE AND LONG-WAVELENGTH APPROXIMATIONS FOR $\xi_{ii}$

If the long-wavelength and high-temperature approximations are not made, the integral in (31) becomes

$$\left(\frac{\hbar}{kT}\right)^2 \int_0^{\omega_0} d\omega \int_{\omega}^{\omega_0} d\omega' \omega \omega' g(\omega) g(\omega') n(\omega) [n(\omega') + 1] \times [(\omega' - \omega)^2 F(\omega' - \omega)], \quad (\text{B1})$$

with

$$n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$$

and

$$\begin{aligned} g(\omega) &= \frac{6v^2}{a^2} \langle 1 - \cos(a\omega u/v) \rangle \\ &= \frac{6v^2}{a^2} \left( 1 - \frac{v}{a\omega} \sin \frac{a\omega}{v} \right), \end{aligned}$$

where  $u$  is the cosine of the angle between the vectors  $\mathbf{k}_q$  and  $\mathbf{x}_{jk}$ , and  $\langle \rangle$  denotes an average over all angles. In the long-wavelength limit,  $g(\omega)$  becomes  $\omega^2$ . The same approximation used to obtain (32) from (31) (which only requires  $k\Theta \gg J$ ) yields

$$\left(\frac{\hbar}{kT}\right)^2 \int_0^{\omega_0} \omega^2 [g(\omega)]^2 n(\omega) [n(\omega) + 1] d\omega. \quad (\text{B2})$$

The integral over  $F(\Omega)$ , identical to that in (32), is a constant factor and hence irrelevant to the present discussion.

First the high-temperature approximation is used for  $n(\omega)$  in order to obtain an upper limit on the error due to the long-wavelength approximation. (That it is actually an upper limit is apparent from the fact that the high-temperature approximation for  $n(\omega)$   $[n(\omega) + 1]$  is an overestimate of the population of the high-frequency modes, which are the modes for which the long-wavelength approximation breaks down.)

Assume for purposes of estimation a simple cubic lattice; then from (23) one finds  $\omega_0 = 3.90v/a$ . In the high-temperature limit, (B2) becomes, if one drops constant factors and replaces  $\omega$  by  $xv/a$ ,

$$U = \int_0^{3.90} \left( 1 - \frac{\sin x}{x} \right)^2 dx = 1.78. \quad (\text{B3})$$

The long-wavelength approximation is obtained by expanding the integrand in a power series in  $x$  and using only the lowest nonvanishing term. The result is  $U=5.0$ . Hence the long-wavelength approximation leads to a result which, in the limit of high temperatures, is too large by roughly a factor of 3.

Next the long-wavelength approximation is used to obtain an upper estimate on the error due to the high-temperature approximation. If one drops constant factors and replaces  $\hbar\omega/kT$  by  $y$ , the relevant integral becomes

$$I = T^5 \int_0^\theta y^6 (\cosh y - 1)^{-1} dy, \quad (B4)$$

where  $\theta = \Theta/T$ . Since the integrand satisfies the inequalities

$$y^4 \theta^2 (\cosh \theta - 1)^{-1} \leq y^6 (\cosh y - 1)^{-1} \leq 2y^4 \quad (B5)$$

in the range  $0 \leq y \leq \theta$ ,  $I$  satisfies the inequalities

$$\frac{1}{2} \theta^2 [\cosh \theta - 1]^{-1} \leq I/I' \leq 1, \quad (B6)$$

where  $I'$  is the high-temperature limit of  $I$ , obtained by replacing the integrand of (B4) by  $2y^4$ . For  $\theta=3$ , i.e.,  $T=\frac{1}{3}\Theta$ , (B6) shows that  $I'$  overestimates  $I$  by at most a factor of 2.

## Localized Moments in Metals

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A simple model is used to study the occurrence of localized magnetic moments in dilute alloys. The phenomenon is treated as a scattering problem in which conduction electrons scatter from impurity potentials. Under appropriate circumstances the scattering amplitude may show a resonance—corresponding to a virtual level of the impurity. It is shown that if such a level is sufficiently sharp and lies close enough to the Fermi level, the impurity atom will develop an exchange potential that polarizes neighboring electrons. The potentials for spin-up and spin-down electrons are determined by a pair of coupled equations, whose solutions are discussed in a number of interesting cases.

### I. INTRODUCTION

IN recent publications Matthias, *et al.*<sup>1</sup> have discussed the remarkable behavior of dilute ( $\sim 1\%$ ) solutions of Fe in various  $4d$  elements and alloys. From susceptibility measurements they demonstrate that in certain of these solvents the Fe atoms possess a localized magnetic moment, whereas in others they do not. Study of a wide variety of such alloys leads them to a plot of the magnitude of the localized moment versus atomic number in the  $4d$  series that shows three maxima—one at the beginning of the series, one in the vicinity of Mo, and one near Rh and Pd—separated by regions in which the Fe atoms are unpolarized. Anderson,<sup>2</sup> following the ideas of Friedel,<sup>3</sup> has proposed a simple model to explain this behavior. He considers a localized level (representing a  $d$  state of the Fe atom) immersed in a sea of mobile electrons (representing the band of the  $4d$  element or alloy). The one-electron portion of the Hamiltonian is chosen to include the energies of the localized and running wave (Bloch) states, as well as off-diagonal matrix elements that couple the two. It is

also assumed that there is a Coulomb energy of the form  $Un_{d\uparrow}n_{d\downarrow}$ , where  $n_{d\uparrow}$  and  $n_{d\downarrow}$  are the number of electrons with spin up and spin down in the localized level. In this model the coupling between the Bloch waves and the localized state broadens the latter—making it into a virtual level of the type discussed by Friedel. Whether or not this virtual level carries a moment is then determined by its position and width in comparison to the Coulomb energy. If it lies close to the Fermi level and is narrow (compared to  $U$ ) it will be split by the Coulomb interaction and thus polarize, but in other cases it remains unmagnetized. Thus one has a picture in which the occurrence of a localized moment depends sensitively on the position and width (which is proportional to the density of states) of the virtual level. By assuming that these quantities vary smoothly throughout the  $4d$  series, it is then possible, in a qualitative way, to understand the behavior of the Fe moment.

In this paper we wish to consider the problem of the localized moments—again using an exceedingly simple model—from a somewhat different point of view. We consider it as a scattering problem in which the conduction electrons of the  $4d$  elements scatter from the potential due to a (single) iron impurity atom. In this language (see Friedel), the virtual level manifests itself as a maximum in the impurity scattering cross section

<sup>1</sup> B. T. Matthias, M. Peter, H. J. Williams, A. M. Clogston, E. Corenzwit, and R. C. Sherwood, *Phys. Rev. Letters* **5**, 542 (1960). A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood (to be published).

<sup>2</sup> P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).

<sup>3</sup> J. Friedel, *Suppl. Nuovo cimento* **7**, 287 (1958).