[16] T. Tabata, R. Ito, and S. Gkabe, Ann. Rep. Rad. Center Osaka Prefect. 9, 34 (1968).

[17] T. Tabata, R. Ito, S. Okabe, and Y. Fujita, Ann. Rep. Rad. Center Osaka Prefect. 10, 34 (1969).

[18] M. J. Berger and S. M. Seltzer (private communication); calculation carried out with program ETRAN developed at the National Bureau of Standards. The basic features of this program are described in Refs. 5, 8, and 10.

[19] T. Tabata, Phys. Rev. 162, 336 (1967).

[20] D. Harder and H. Metzger, Z. Naturforsch. 23a, 1675 (1968).

[21] P. J. Ebert, A. F. Lauzon, and E. M. Lent, Phys. Rev. 183, 422 (1969).

[22] M. J. Berger and S. M. Seltzer, National Aeronautics and Space Administration Report No. NASA SP-3012, 1964 (unpublished).

[23] O. Blunck, Z. Physik 131, 354 (1952).

[24] J. A. Lonergan, C. P. Jupiter, and G. Merkel, J. Appl. Phys. 41, 678 (1970).

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Stochastic Theory of Line Shape: Off-Diagonal Effects in Fine and Hyperfine Structure*

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An extension of the stochastic model of relaxation effects is used to derive a theory of the line shape of fine and hyperfine structure. The theory is developed for Mössbauer spectra, but can be readily applied in related fields such as perturbed angular correlations, electron and nuclear spin resonance, and optical spectroscopy. Previous stochastic-model theories of hyperfine spectra have used a semiclassical fluctuating-field approach which inherently restricts the hyperfine Hamiltonian to matrix elements which are diagonal with respect to the electronic states. In the present theory, these restrictions are removed by using a quantum-mechanical treatment of the combined electronic-nuclear system, wherein the relaxation enters as random instantaneous transitions between electronic states. This allows inclusion of the effects of off-diagonal electronic hyperfine matrix elements (e.g., the pseudoquadrupole interaction). A model for the relaxation is presented which allows all the transition rates to be specified independently, as is necessary to treat finite temperatures. Two examples are used to illustrate the the theory and to compare it with other theories.

I. INTRODUCTION

Numerous stochastic[1-5] and *ab initio*[6-10] treatments of the effects of time-dependent perturbations on Mössbauer line shapes have appeared in recent years. Many of these theories are derived from similar developments in magnetic resonance[11-13] or perturbed angular correlations,[14-16] and they are applicable in many other line-shape problems as well. In this paper, we present a generalization of the stochastic theories to cover a class of situations not previously discussed.[17]

A simple illustration shows the type of extension made. In stochastic treatments of Mössbauer line shape, the hyperfine interaction between the nuclear spin and the electronic spin is replaced by an interaction between the nuclear spin and randomly varying external magnetic and electric fields.[18] The randomly varying fields represent the effect of a relaxing electronic spin on the nucleus. This type of treatment is only valid, however, if the electronic part of the hyperfine interaction has no off-diagonal matrix elements, since an external magnetic field has no such elements. Thus, such a treatment is reasonable for a hyperfine interaction of the form aI_zS_z, since the electronic relaxation causes a time dependence to be induced in S_z, which is a diagonal operator. If the interaction is of the form $a\vec{I}\cdot\vec{S}$, however, we may not replace $\vec{S}$ by a varying external field. The appropriate time-varying field would be of the form $\vec{h}(t) = a\langle\psi(t)|\vec{S}|\psi(t)\rangle$. Since, in the stochastic model, $\psi(t)$ jumps instantaneously from one electronic state to another, $\vec{h}(t)$ only takes on the values $a\langle i|\vec{S}|i\rangle$, and the off-diagonal matrix elements $\langle i|\vec{S}|j\rangle$ would be ignored. These matrix elements are important when the splitting of the electronic levels is not large compared with the hyperfine splitting. Our approach here is to treat the entire nucleus-electron system quantum mechanically. The effects of electronic relaxation are then introduced by additional terms in the Hamiltonian which have random properties and which are capable of inducing transitions between the different electronic levels. Previous stochastic treatments are recovered in the cases where the electronic part of the hyperfine interaction is diagonal. The results derived here are similar to those found in the *ab initio* calculations of Afanas'ev and Kagan[6] and Gabriel, Bosse, and Rander,[8] and it is of interest to note that the same formal expressions are obtained in the stochastic and the *ab initio* treatments. Stochastic theories have the advantage, in some cases, of greater physical clarity and the insight which they afford into the broadening mechanisms. Our theory is, in essence, a quantum-mechanical version of Brownian motion[19] or shot-noise[20] phenomena, with the emitting atom or nucleus acting as the detector.

Effects of the type discussed here are ordinarily not found in magnetic resonance problems, since an external magnetic field which "quenches" the off-diagonal matrix elements of the hyperfine interaction is usually present in such experiments. There are, however, occasions in Mössbauer effect, perturbed angular correlation, and light-scattering experiments when the results derived here are of practical value.

The central result of the paper is contained in Eqs. (24) and (27), which give an expression for the line shape of radiation emitted by a system governed by a Hamiltonian such as Eq. (1). In Sec. II, we derive these expressions and enumerate the assumptions used in the derivation. In Secs. III and IV, we illustrate the utility of the results with some simple examples, and we discuss the form of the transition operator which appears in the formula. In a later paper we will apply the formalism to the analysis of experimental Mössbauer data.

II. FORMAL SOLUTION

We adopt a physical picture in which the system (consider for concreteness a nucleus coupled to an atomic spin) is subject to sudden pulses at random instants of time. The effect of these pulses is to cause transitions between the levels of the system. A simple example is that of electronic spin-lattice relaxation. At random instants of time the system is "hit" by phonons, some of which cause transitions between different states of the system. In the stochastic model the pulses are assumed to occur instantaneously, and in between pulses the system is assumed unperturbed. In accordance with this picture the Hamiltonian is taken in the form

$$\mathcal{H} = \mathcal{H}_0 + \sum_i V_i \,\delta(t - t_i) \; . \qquad (1)$$

The instants t_i are assumed random with a Poisson distribution, and the V_i are quantum-mechanical operators which we assume uncorrelated from one instant to the next. In our example we would have $\mathcal{H}_0 = a\vec{I}\cdot\vec{S}$, and $V_i = \vec{h}_i \cdot \vec{S}$, where $\vec{h}_i$ is a magnetic field which varies in magnitude and direction from one instant to the next.

We want to calculate the line shape of radiation emitted by a system governed by a Hamiltonian of the form of Eq. (1). This may be expressed as the Fourier or Laplace transform of a correlation function,[5] so we consider the evaluation of

$$F(p) = \int_0^\infty dt\, e^{-pt} \left(\langle A^\dagger(0) A(t)\rangle\right)_{\mathrm{av}} , \qquad (2)$$

where A is an operator for emission or absorption of radiation, $p = \frac{1}{2}\Gamma - i\omega$, with Γ the natural linewidth of the nuclear excited state. The angular brackets $\langle \cdots \rangle$ denote an average over the initial states of the emitter, and the round brackets $(\cdots)_{\mathrm{av}}$ denote an average over the stochastic properties of the Hamiltonian, Eq. (1).

The time dependence of a wave function governed by Eq. (1) is given by

$$\psi(t) = U(t)\psi(0), \qquad (3)$$

where

$$U(t) = U_0(t - t_n)\, T_n \cdots T_2\, U_0(t_2 - t_1)\, T_1\, U_0(t_1), \qquad (4)$$

$$U_0(t) = e^{-i\mathcal{H}_0 t} , \qquad (5)$$

$$T_i = e^{-iV_i} \; . \qquad (6)$$

It has been assumed that there are exactly n pulses in time t. Of course, n is a random variable and must be averaged over in the final expression for the line shape. The transition operators T_i have a significance of their own: If the state of the system immediately prior to a pulse is ψ the pulse causes the system to jump to the state $(T\psi)$. Taking the V_i in Eq. (1) to be Hermitian implies that the transitions induced by them between states $|a\rangle$ and $|b\rangle$ are equally probable in either direction. This does occur at infinite temperature, but at a finite temperature the ratio of transition probabilities is given by a Boltzmann factor. It is thus necessary to allow, in general, non-Hermitian terms in the Hamiltonian to provide detailed balance at finite temperatures. These terms are required because of the nature of the model. We are replacing the effects of a "heat bath" by a single term in the Hamiltonian, so that the irreversibility must be introduced explicitly.

The time dependence of the operator A is given by

$$A(t) = U^\dagger(t) A\, U(t) \; , \qquad (7)$$

where the appearance of the adjoint, *not* the inverse, of U is the only noteworthy feature. In the calculation of line shapes in Ref. 18, use was made of the Liouville operator to write $e^{C} B\, e^{-C} = e^{C^\times} B$, where $C^\times B \equiv [C, B]$. The definition of the Liouville operator must be generalized slightly for non-Hermitian operators. Essentially, Zwanzig[21] defines the Liouville operator such that the time dependence of an operator is given by

$$B(t)=e^{it\mathcal{H}^{\times}}B \tag{8}$$

for time-independent Hamiltonians. For Eq. (8) to hold for non-Hermitain Hamiltonians, the Liouville operator must be given by the relation

$$C^{\times}B\equiv C^{\dagger}B-BC, \tag{9}$$

which reduces to the usual commutator when C is Hermitian. From Eq. (9), we may easily derive, following the discussion in the Appendix of Ref. 18, the relation

$$e^{iC^{\dagger}}B\,e^{-iC}=e^{iC^{\times}}B. \tag{10}$$

Using Eqs. (4)–(6) and (10) we may rewrite Eq. (7),

$$\begin{aligned}A(t)&=\mathcal{U}(t)A\\&=\mathcal{U}_0(t_1)\mathcal{T}_1\mathcal{U}_0(t_2-t_1)\cdots\mathcal{T}_n\mathcal{U}_0(t-t_n)A,\end{aligned} \tag{11}$$

where the superoperators $\mathcal{U}_0$ and $\mathcal{T}$ are defined by

$$\mathcal{U}_0A=U_0^{\dagger}A\,U_0, \tag{12}$$

$$\mathcal{T}A=T^{\dagger}A\,T, \tag{13}$$

for *any* operator A. From Eqs. (5), (6), and (10), we see that $\mathcal{U}_0$ and $\mathcal{T}$ are also given by

$$\mathcal{U}_0(t)=e^{it\mathcal{H}_0^{\times}}\ , \tag{14}$$

$$\mathcal{T}_i=e^{iV_i^{\times}}\ . \tag{15}$$

Using Eq. (11) we may rewrite Eq. (2)

$$F(p)=\langle A^{\dagger}\int_0^{\infty}dt\,e^{-pt}(\mathcal{U}(t))_{\mathrm{av}}A\rangle\ , \tag{16}$$

and our task is to evaluate the matrix elements of the transform

$$\mathcal{U}(p)=\int_0^{\infty}dt\,e^{-pt}\,(\mathcal{U}(t))_{\mathrm{av}}\ . \tag{17}$$

The average which must now be performed consists of two separate parts: one over the instants of time at which the pulse occurs, and the other over the type of pulse (e.g., the value of $\vec{h}_i$ in the example cited above). We assume that these two averages are independent and further that the types of successive pulses are uncorrelated (e.g., $\vec{h}_i$ is independent of $\vec{h}_{i-1}$). These assumptions can be made somewhat less restrictive (e.g., $\vec{h}_i$ can be dependent on t_i-t_{i-1}, the time from the previous pulse) without much greater difficulty, but we do not consider this situation here. We thus have

$$(\mathcal{U}(t))_{\mathrm{av}}=(\mathcal{U}_0(t_1)\,\mathcal{T}_{\mathrm{av}}\mathcal{U}_0(t_2-t_1)\,\mathcal{T}_{\mathrm{av}}\cdots\mathcal{T}_{\mathrm{av}}\mathcal{U}_0(t-t_n))_{\mathrm{av}}\,, \tag{18}$$

where we have performed the average over the type of pulse

$$\mathcal{T}_{\mathrm{av}}=(e^{iV_i^{\times}})_{\mathrm{av}}\,, \tag{19}$$

and the remaining average on the right-hand side of Eq. (18) is over the instants t_i. From this we deduce

$$(\mathcal{U}(t))_{\mathrm{av}}=\sum_{n=0}^{\infty}P_n(t)\int_0^t dt_n\int_0^{t_n}dt_{n-1}\cdots\int_0^{t_2}dt_1\,W_n(t_1,\cdots,t_n;\,t)\,\mathcal{U}_0(t_1)\mathcal{T}_{\mathrm{av}}\cdots\mathcal{T}_{\mathrm{av}}\mathcal{U}_0(t-t_n), \tag{20}$$

where $P_n(t)$ is the probability that exactly n pulses occur in time t. For random occurrences of the pulses, this is given by the Poisson distribution

$$P_n(t)=[(\lambda t)^n/n!\,]e^{-\lambda t}, \tag{21}$$

where λ^{-1} is the mean time between pulses; λ is the mean frequency of the pulses. Also $W_n(t_1,\cdots,t_n;t)\times dt_1\cdots dt_n$ is the probability that, *given* that n pulses occur in time t, these occur at t_1 in $dt_1,\cdots,t_n$ in dt_n, respectively. Since the points are randomly distributed, $W_n=n!\,t^{-n}$. Substituting these in Eq. (20) yields

$$(\mathcal{U}(t))_{\mathrm{av}}=\sum_{n=0}^{\infty}\int_0^t dt_n\cdots\int_0^{t_2}dt_1\,e^{(i\mathcal{H}_0^{\times}-\lambda)t_1}(\lambda\mathcal{T}_{\mathrm{av}})e^{(i\mathcal{H}_0^{\times}-\lambda)(t_2-t_1)}(\lambda\mathcal{T}_{\mathrm{av}})\cdots e^{(i\mathcal{H}_0^{\times}-\lambda)(t-t_n)}. \tag{22}$$

For $\mathcal{U}(p)$ in Eq. (17), we require the Laplace transform of Eq. (22). The Laplace transform of the convolution in Eq. (22) is just the product of Laplace transforms, so that

$$\begin{aligned}\mathcal{U}(p)&=j\sum_{n=0}^{\infty}\frac{1}{p+\lambda-i\mathcal{H}_0^{\times}}(\lambda\mathcal{T}_{\mathrm{av}})\frac{1}{p+\lambda-i\mathcal{H}_0^{\times}}(\lambda\mathcal{T}_{\mathrm{av}})\cdots(\lambda\mathcal{T}_{\mathrm{av}})\frac{1}{p+\lambda-i\mathcal{H}_0^{\times}}\\&=\frac{1}{p+\lambda-i\mathcal{H}_0^{\times}}\sum_{n=0}^{\infty}\left(\lambda\mathcal{T}_{\mathrm{av}}\frac{1}{p+\lambda-i\mathcal{H}_0^{\times}}\right)^n=\frac{1}{p+\lambda-i\mathcal{H}_0^{\times}}\,\frac{1}{1-\lambda\mathcal{T}_{\mathrm{av}}(p+\lambda-i\mathcal{H}_0^{\times})^{-1}}\end{aligned} \tag{23}$$

or, finally,

$$\mathcal{U}(p)=(p-\mathcal{W}-i\mathcal{H}_0^{\times})^{-1}\ , \tag{24}$$

where all the relaxation effects are contained in the superoperator $\mathcal{W}$:

$$\mathcal{W} = \lambda(\mathcal{T}_{\text{av}} - 1). \tag{25}$$

Substituting Eqs. (24) and (17) into Eq. (16), we obtain the line-shape function

$$F(p) = \langle A^\dagger (p - \mathcal{W} - i\mathcal{H}_0^\times)^{-1} A \rangle , \tag{26}$$

or in matrix elements,

$$F(p) = \sum_{\substack{\mu,\nu \\ \mu',\nu'}} p_\nu \langle \nu | A^\dagger | \mu \rangle \, (\mu\nu | \mathcal{U}(p) | \mu'\nu') \langle \mu' | A | \nu' \rangle , \tag{27}$$

where p_ν is the Boltzmann factor for the initial state $|\nu\rangle$. The matrix elements of A are essentially Clebsch-Gordan coefficients. The matrix elements of $\mathcal{U}(p)$ are calculated by inverting the matrix in Eq. (24). This matrix has dimensions $(2S+1)^2 \times (2I_1+1)(2I_0+1)$, where S is the (effective) electronic spin; I_1 and I_0 are the spins of the excited and ground nuclear levels. The matrix elements of $\mathcal{H}_0^\times$ are given by[18]

$$(\mu\nu | \mathcal{H}_0^\times | \mu'\nu') = \delta_{\nu\nu'} \langle \mu | \mathcal{H}_0 | \mu' \rangle - \delta_{\mu\mu'} \langle \nu' | \mathcal{H}_0 | \nu \rangle . \tag{28}$$

Note that $\mathcal{H}_0$ is Hermitian, otherwise $\mathcal{H}_0^\dagger$ would appear in the first term on the right. From Eq. (13) the matrix elements of $\mathcal{T}$ are given by

$$(\mu\, \nu | \mathcal{T} | \mu'\nu') = \langle \mu' | T | \mu \rangle^* \langle \nu' | T | \nu \rangle . \tag{29}$$

In practice, Eqs. (6) and (29) will prove to be more useful for calculating the matrix elements of $\mathcal{T}$ than Eqs. (9) and (15). The average $\mathcal{T}_{\text{av}}$ is obtained by averaging Eq. (29) over the types of hits V_i.

The remaining problem is to determine the appropriate form for V_i. In an *ab initio* calculation, one expects $\mathcal{W}$ to follow from first principles, but in practice this evaluation is very difficult. In our stochastic theory, on the other hand, we must specify either V or T as input information. Our point of view is that we may as well assume a form for the transition operator T as for the potential V, and in Secs. III and IV we discuss the permissible forms of these operators.

III. EXAMPLES

We will consider two simple examples to illustrate the main features of the theory presented in Sec. II. In particular, we will point out how the results differ for hyperfine interactions which are diagonal with respect to the electronic states and for those which are not. In these examples only two electronic states with equal populations will be considered. The more general case will be outlined in a subsequent section.

a. Relaxation operators. We will use a spin-Hamiltonian formalism to describe the electronic portion of the interactions. The two electronic states will be denoted $|+\rangle$ and $|-\rangle$ and are eigenfunctions of the electronic portion of $\mathcal{H}_0$, which is given by

$$\mathcal{H}_e = \alpha S_z . \tag{30}$$

The splitting α produced by $\mathcal{H}_e$ can be a Zeeman splitting, a crystal-field splitting, or no splitting at all ($\alpha = 0$).

For a pulse of the form

$$V_i = \vec{h}_i \cdot \vec{S} , \tag{31}$$

the transition operator is given by

$$\begin{aligned} T &= e^{-i\vec{h}\cdot\vec{S}} \\ &= \cos(\tfrac{1}{2}h) + 2i \sin(\tfrac{1}{2}h)\, \vec{u}\cdot\vec{S} , \end{aligned} \tag{32}$$

where $h^2 = \vec{h}\cdot\vec{h}$ and $\vec{u} = \vec{h}/h$. By restricting $\vec{h}$ so that $h = \pi$ and $h_z = 0$, a particularly simple form of the transition operator may be obtained:

$$T = i(e^{-i\theta} S_+ + e^{i\theta} S_-), \tag{33}$$

where $\cos\theta = h_x/h$ and $\sin\theta = h_y/h$. This form of the transition operator produces relaxation processes equivalent to those considered in previous stochastic treatments: Each pulse causes electrons in the $|+\rangle$ state, for example, to "flip" to the $|-\rangle$ state with a phase change of θ, which we will assume to take on random uncorrelated values at each instant t_i. It may also be seen that T causes the transition rate for + to − transitions to be the same as for − to + transitions, which is necessary to maintain equal populations in both electronic states. Since every pulse causes an electronic transition in this model, the pulse rate λ is also the relaxation rate, i.e., the probability per unit time that the transition + to − occurs, *given* that the electrons are in the + state, and vice versa.

The nonzero matrix elements of $\mathcal{T}$ may be readily obtained using Eq. (29):

$$(+\,+ | \mathcal{T} | -\,-) = (-\,- | \mathcal{T} | +\,+) = 1, \tag{34a}$$

$$(+\,- | \mathcal{T} | -\,+) = (-\,+ | \mathcal{T} | +\,-)^* = e^{-2i\theta} . \tag{34b}$$

Upon averaging over θ the matrix elements of Eq. (34b) vanish, leaving the two matrix elements of Eq. (34a) as the only nonzero matrix elements of $\mathcal{T}_{\text{av}}$. The matrix elements of $\mathcal{W} = \lambda(\mathcal{T}_{\text{av}} - 1)$ are given in Table I.

As a more general case, we assume that $\vec{h}$ is isotropic in three dimensions and put no restrictions on its magnitude. The matrix elements of $\mathcal{T}_{\text{av}}$ may be calculated by using Eqs. (29) and (32) and averaging over the magnitude and direction of the field $\vec{h}$. Since the field direction is random, we take $(u_j)_{\text{av}} = 0$, and $(u_j u_k)_{\text{av}} = \frac{1}{3}\delta_{jk}$, and we define $x = (\sin^2(h/2))_{\text{av}}$ and $1 - x = (\cos^2(h/2))_{\text{av}}$. The matrix elements of $\mathcal{T}_{\text{av}}$ are then given by

$$\begin{aligned} (\mu\nu | \mathcal{T}_{\text{av}} | \mu'\nu') = {} & (1-x)\,\delta_{\mu\mu'}\,\delta_{\nu\nu'} \\ & + \tfrac{4}{3} x \textstyle\sum_j \langle \mu | S_j | \mu' \rangle \langle \nu' | S_j | \nu \rangle . \end{aligned} \tag{34c}$$

TABLE I. Matrix of $(\mu\nu|\mathcal{W}|\mu'\nu')$ for $T=i(e^{-i\theta}S_{+}+e^{i\theta}S_{-})$.

$\mu\nu \diagdown \mu'\nu'$	$++$	$--$	$+-$	$-+$
$++$	$-\lambda$	λ	0	0
$--$	λ	$-\lambda$	0	0
$+-$	0	0	$-\lambda$	0
$-+$	0	0	0	$-\lambda$

The resulting matrix of $\mathcal{W}=\lambda(\mathcal{T}_{\text{av}}-1)$ is shown in Table II. Note that the relaxation rate, $W=\frac{2}{3}x\lambda$, is determined by the product of λ, the pulse rate, and x, the average of $\sin^2(h/2)$. The factor $\frac{2}{3}$ enters because the pulses with fields along the z axis cause no transitions. Since the pulse causes a precession of the spin around $\vec{h}$ by an angle equal to h, one pulse does not always produce a complete transition from + to −. The factor x measures the average effectiveness of the pulses in causing such transitions.

Because of the simple form of Eq. (33) and the consequent physical insight into the relaxation process, we shall use the first model of relaxation in the remainder of this section. Since the matrices in Tables I and II are so similar, there would be no significant difference in the results if the second model were used.

b. "Diagonal" hyperfine interactions. As the first example, we consider the simple hyperfine interaction aI_zS_z. For our purposes, this is representative of all "diagonal" hyperfine interactions, by which we mean that the hyperfine interactions are diagonal with respect to the electronic states. More complex forms, which include nonaxially symmetric field gradients, for example, but which are still diagonal with respect to the electronic states, differ from this example mainly in that it is necessary to invert a larger matrix.

Combining the hyperfine Hamiltonian and the electronic Hamiltonian, Eq. (30), $\mathcal{H}_0$ is given by

$$\mathcal{H}_0=\alpha S_z+aI_zS_z\,. \tag{35}$$

The matrix elements of $\mathcal{H}_0^{\times}$ may be easily calculated from Eq. (28). The matrix elements of $p-\mathcal{W}-i\mathcal{H}_0^{\times}$ form a large matrix, in general. In the case with which we are dealing, however, neither $\mathcal{H}_0$ nor V_i mixes states of different m_I. Consequently, the large matrix breaks up into a series of smaller 4×4 matrices, each of which may be inverted separately. One of these matrices is given in Table III. For convenience the notation $\beta_0=\frac{1}{2}a_0m_0$, $\beta_1=\frac{1}{2}a_1m_1$ is used. The subscripts 0 and 1 refer to the ground and excited states of the nucleus. These states have different g factors, hence the different values of a.

TABLE II. Matrix of $(\mu\nu|\mathcal{W}|\mu'\nu')$ for isotropic $\vec{h}$.

$\mu\nu \diagdown \mu'\nu'$	$++$	$--$	$+-$	$-+$
$++$	$-W$	W	0	0
$--$	W	$-W$	0	0
$+-$	0	0	$-2W$	0
$-+$	0	0	0	$-2W$

TABLE III. Matrix of $(\mu m_0,\ \nu m_1|p-\mathcal{W}-i\mathcal{H}_0^{\times}|\mu' m_0,\ \nu' m_1)$ for $T=i(e^{-i\theta}S_{+}+e^{i\theta}S_{-})$, $\mathcal{H}_0=\alpha S_z+aI_zS_z$.

$\mu\nu \diagdown \mu'\nu'$	$++$	$--$	$+-$	$-+$
$++$	$p+\lambda-i\beta_0+i\beta_1$	$-\lambda$	0	0
$--$	$-\lambda$	$p+\lambda+i\beta_0-i\beta_1$	0	0
$+-$	0	0	$p+\lambda-i\alpha-i\beta_0-i\beta_1$	0
$-+$	0	0	0	$p+\lambda+i\alpha+i\beta_0+i\beta_1$

The matrix of Table III breaks up further into 2×2 matrices. Since the matrix elements of A in Eq. (27) are diagonal with respect to the electronic states, only the upper-left 2×2 matrix of Table III enters into the line shape. It is interesting to note that if Blume's[22] treatment were applied to this example, only the upper-left 2×2 matrix of Table III would appear. The remainder of the matrix, which is important for "nondiagonal" hyperfine interactions, does not appear. The matrix elements of $\mathcal{T}$ in Eq. (34b) that vanished when averaged over θ would have appeared in the lower right-hand corner of Table I. In this example, and generally for "diagonal" hyperfine interactions, these matrix elements do not affect the important matrix elements of $\mathcal{U}(p)$. Consequently, the value of θ is irrevelant in this example and we could have taken $\theta=0$. As will be seen in the next example, however, this is not true for "nondiagonal" hyperfine interactions.

Inverting the matrix in Table III (which is trivial for the 2×2 matrix of concern) the following line-shape function is obtained:

$$F(p)=\sum_{m_0,m_1}|\langle m_0|A|m_1\rangle|^2\,\frac{p+2\lambda}{p^2+2p\lambda+(\beta_0-\beta_1)^2}\quad. \tag{36}$$

Upon substituting $p=\frac{1}{2}\Gamma-i\omega$, the line shape will be given by the real part of Eq. (36). Not surprisingly, this is the same result as obtained by Anderson[11] (with $\Gamma=0$) for a similar case.

To emphasize the equivalance of Anderson's approach and ours in the case of "diagonal" hyperfine interactions, we will examine the time dependence of the wave function in more detail. For an initial wave function $\psi(0)=|+,m\rangle$, the wave function immediately prior to the first pulse at t_1 becomes $\exp[-i(\frac{1}{2}\alpha+\beta)t_1]\,|+,m\rangle$, with $\beta=\frac{1}{2}am$. Immediately after the pulse, the wave function is

$\exp[-i(\frac{1}{2}\alpha+\beta)t_1+i\theta_1]|-,m\rangle$, etc. In particular, $\psi(t)$ is either $|+,m\rangle$ or $|-,m\rangle$ (multiplied by a phase factor), and never a mixture of the two. After n pulses, the wave function will be given by

$$\psi(t)=e^{i\phi(t)}|\pm,m\rangle, \qquad (37)$$

with

$$\phi(t)=-(\tfrac{1}{2}\alpha+\beta)\int_0^t f(t')\,dt'-\sum_{j=1}^{n}(-1)^j\theta_j, \qquad (38)$$

where $f(t')=(-1)^j$ when $t_j<t'<t_{j+1}$. In Eqs. (37) and (38) a resemblance to Anderson's model begins to appear: In computing $\langle +,m_0|A(t)|+,m_1\rangle$, the terms involving α and θ_j in Eq. (38) drop out leaving

$$\langle +,m_0|A(t)|+,m_1\rangle$$
$$=\langle m_0|A|m_1\rangle\exp[i(\beta_0-\beta_1)\textstyle\int_0^t f(t')\,dt'], \qquad (39)$$

which is the same result as one obtains by having a fluctuating magnetic field proportional to $f(t)$ acting on the nuclear spin.[23]

c. "Nondiagonal" hyperfine interactions. In Sec. III *b* we considered an example which served to bring out the similarities between our treatment and previous stochastic-model treatments. In this section we consider an example where the hyperfine interaction is not diagonal with respect to the electronic states. For reasons discussed earlier, these off-diagnoal matrix elements are generally ignored in previous treatments of the stochastic model.

For the hyperfine interaction in this example we use aI_zS_x, so that $\mathcal{H}_0$ becomes

$$\mathcal{H}_0=\alpha S_z+aI_zS_x\ . \qquad (40)$$

The same results would be obtained with the hyperfine interactions aI_xS_x, aI_yS_y, etc.; however, for simplicity of notation, aI_zS_x was chosen. When $a\ll\alpha$, this Hamiltonian produces the pseudoquadrupole interaction.[24] The matrix elements of $p-\mathcal{W}-i\mathcal{H}_0^\times$ may be calculated following the same procedure as in the last example. For the same reason, the large matrix again breaks up into 4×4 matrices, one of which is shown in Table IV. This matrix can be inverted exactly, though the procedure is somewhat tedious. The resulting expression for $F(p)$ contains a 4th order polynomial in the denominator which can not be factored. As a result, this approach yields little information on the line shape. Instead, we have inverted the matrix numerically and plotted the resulting spectra. Figure 1 shows a few spectra. These particular spectra are very similar to spectra obtained in the "diagonal" case with the same values of λ and Γ, but with a adjusted to give the same splitting for $\lambda=0$. This similarity, however, does not occur in more complicated cases. We will postpone a detailed discussion of these spectra until a future paper.

TABLE IV. Matrix of $(\mu m_0,\ \nu m_1|p-\mathcal{W}-i\mathcal{H}_0^\times|\mu' m_0,\ \nu' m_1)$ for $T=i(e^{-i\theta}S_+ + e^{i\theta}S_-)$, $\mathcal{H}_0=\alpha S_z+aI_zS_x$.

$\mu\nu$ \ $\mu'\nu'$	$++$	$--$	$+-$	$-+$
$++$	$p+\lambda$	$-\lambda$	$i\beta_1$	$-i\beta_0$
$--$	$-\lambda$	$p+\lambda$	$-i\beta_0$	$i\beta_1$
$+-$	$i\beta_1$	$-i\beta_0$	$p+\lambda-i\alpha$	0
$-+$	$-i\beta_0$	$i\beta_1$	0	$p+\lambda+i\alpha$

In the "nondiagonal" case, the motion of the wave function is not nearly so easy to follow. If one starts with an eigenfunction of $\mathcal{H}_e$ at $t=0$, then $U(t)$ promptly mixes in other states. If, on the other hand, one starts with eigenfunctions of $\mathcal{H}_0$ this problem is overcome, but the transition operator T generally produces new wave functions which are neither eigenfuntions of $\mathcal{H}_0$ nor of $\mathcal{H}_e$.

IV. ELECTRONIC RELAXATION: GENERAL CASE

In Sec. III*a*, a specific example of relaxation was considered which contained only two electronic states and was restricted to equal populations of the two states. In this section we consider the general case of N electronic states with populations not necessarily equal. In Sec. III*a*, the form of V_i was chosen *so that* a particular form of the transition operator T_i was obtained. For this reason we shall henceforth deal directly with the transition operators and make no further references to the potential V_i. Indeed, we could have started directly with Eq. (4) as a mathematical description of the stochastic model. The result of Sec. II would then

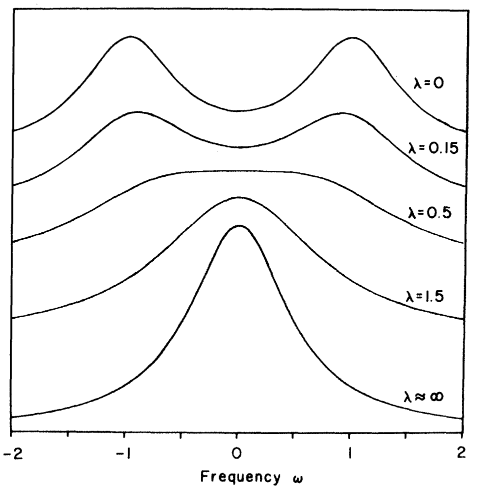

FIG. 1. Partial spectra for different relaxation rates λ in the "nondiagonal" case. The values of α, β_0, β_1, and Γ were chosen to correspond approximately to the $m_1=\frac{3}{2}\rightarrow m_0=\frac{1}{2}$ portion of the Mössbauer spectrum of Tm^{169} in $\mathrm{TmCl_3\cdot 6H_2O}$ (see Ref. 24). These values are $\alpha=300$, $\beta_0=5$, $\beta_1=18$, $\Gamma=1.0$.

follow with only minor changes in notation to eliminate references to V_i.

a. Relaxation operator. The particular model we present here has the following properties: (i) Transitions are induced between the electronic states without affecting the nuclear wave functions. That is, the transition operator acts only on the electronic portion of the wave function. (ii) The model is specifically designed to handle different transition rates between the electronic states. There is no restriction that the probability for the transition $a \to b$ must equal the probability for $b \to a$. Subsequently, however, "detailed balance" will be required in these transitions to preserve thermal equilibrium. It might also be noted that related forms of the transition operator T can be constructed to describe other forms of relaxation, such as nuclear relaxation.

The time-independent Hamiltonian $\mathcal{H}_0$ may be divided into three parts:

$$\mathcal{H}_0 = \mathcal{H}_e + \mathcal{H}_{en} + \mathcal{H}_n \ . \tag{41}$$

The electronic term $\mathcal{H}_e$ contains interactions involving only electronic operators such as crystal-field and Zeeman interactions. The nuclear term $\mathcal{H}_n$ likewise contains only nuclear operators. The remaining term $\mathcal{H}_{en}$ contains the interactions between the two systems, the hyperfine interactions. Since we will be concerned with both electronic and nuclear states, we will adopt the convention that Latin indices will be used for nuclear states, Greek indices for electronic states. In particular, the eigenfunctions of $\mathcal{H}_n$ and $\mathcal{H}_e$ will be used:

$$\mathcal{H}_n | m \rangle = E_m | m \rangle , \tag{42}$$

which will usually be eigenfunctions of I and I_z; and

$$\mathcal{H}_e | \mu \rangle = E_\mu | \mu \rangle \ . \tag{43}$$

Product states of the form $|m\rangle |\mu\rangle = |m, \mu\rangle$ are eigenfunctions of $\mathcal{H}_e + \mathcal{H}_n$ (but not necessarily of $\mathcal{H}_0$) and constitute a complete set of states for the electron-nucleus system.

Using these eigenfunctions, we define the electronic operators $P_{\mu\nu}$ by

$$P_{\mu\nu} = \textstyle\sum_m | m, \nu\rangle \langle m, \mu | \tag{44a}$$

or, simply,

$$P_{\mu\nu} = | \nu\rangle \langle \mu | \ . \tag{44b}$$

This projects the electronic state $|\mu\rangle$ into $|\nu\rangle$ without affecting the nuclear state. From these operators, we define the transition operator[25] $T_{\mu\nu}$ which produces the particular transition $\mu \to \nu$:

$$T_{\mu\nu}(\theta) = 1 - P_{\mu\mu} + e^{i\theta} P_{\mu\nu} . \tag{45}$$

As can be seen, $T_{\mu\nu}$ acting on $|\mu', m\rangle$ does nothing unless $\mu' = \mu$, in which case $T_{\mu\nu}$ causes the transition $|\mu, m\rangle \to e^{i\theta} |\nu, m\rangle$. Using these $T_{\mu\nu}$, we define the transition operator T as

$$T(\theta, \mu, \nu) = T_{\mu\nu}(\theta), \tag{46}$$

wherein we now regard μ and ν, as well as θ, to be stochastic variables. The probability for a given pair $\mu\nu$ to occur will be denoted $w_{\mu\nu}$. That is, during a given "hit," $w_{\mu\nu}$ is the probability that the transition $\mu \to \nu$ takes place, provided that the initial state is $|\mu\rangle$. Since hits occur at the rate λ, we see that $W_{\mu\nu} = \lambda w_{\mu\nu}$ is the transition rate for the transition $\mu \to \nu$ given that the initial state is $|\mu\rangle$.

From the above discussion it can be seen that the average transition operator $\mathcal{T}_{\text{av}}$ is

$$\mathcal{T}_{\text{av}} = {\sum_{\mu\nu}}' w_{\mu\nu} (\mathcal{T}_{\mu\nu})_{\text{av}} \ , \tag{47}$$

where the prime on the summation indicates that the terms with $\mu = \nu$ are to be omitted, and where $(\mathcal{T}_{\mu\nu})_{\text{av}}$ denotes an average over θ, but not over μ, ν. The previously undefined $T_{\mu\mu}$ and $W_{\mu\mu}$ may now be defined as

$$T_{\mu\mu} = 1, \tag{48}$$

$$W_{\mu\mu} = - \sum_{\nu(\neq\mu)} W_{\mu\nu} \ . \tag{49}$$

With this notation the superoperator $\mathcal{W}$ defined in Eq. (25) becomes

$$\mathcal{W} = \sum_{\mu,\nu} W_{\mu\nu} (\mathcal{T}_{\mu\nu})_{\text{av}} , \tag{50}$$

where we have made use of the relation

$$\sum_\mu W_{\mu\mu} = - \lambda {\sum_{\mu,\nu}}' w_{\mu\nu} = - \lambda \ . \tag{51}$$

The matrix elements of $\mathcal{W}$ are then given by

$$(\mu m, \nu n | \mathcal{W} | \mu' m', \nu' n') = [\delta_{\mu\nu} \delta_{\mu'\nu'} W_{\mu\mu'} + \delta_{\mu\mu'} \delta_{\nu\nu'} (1 - \delta_{\mu\nu})(W_{\mu\mu} + W_{\nu\nu})] \delta_{mm'} \delta_{nn'} \ . \tag{52}$$

As discussed in Sec. III, when the hyperfine Hamiltonian is diagonal in the electronic states, the only relevant matrix elements are those for which $\mu = \nu$ and $\mu' = \nu'$. These matrix elements are simply

$$(\mu m, \mu n | \mathcal{W} | \mu' m', \mu' n') = W_{\mu\mu'} \delta_{mm'} \delta_{nn'} \ . \tag{53}$$

In this section we have presented a particular model for the transition operator and obtained the necessary matrix elements. The particular transition operator described here is not unique; in fact, the simple transition operator in Sec. III is somewhat different. However, if the reasonable assumption is made that the hyperfine interactions do not affect the relaxation processes, then all models of the transition operator for a given set of relaxation rates should give the same result when the hyperfine interactions are diagonal with respect to the electronic states (i.e., when they don't alter the electronic wave functions). Thus, Eq. (53) should hold for all such models. Similarly, matrix elements of the form $(\mu\,\mu|\mathcal{W}|\mu'\mu'')$ or $(\mu'\mu''|\mathcal{W}|\mu\,\mu)$ with $\mu'\neq\mu''$ should be zero so that the matrix can be broken up into two parts, as discussed in Sec. III.

b. Restrictions on relaxation operators. In this section we discuss the requirements which the transition operators must meet in order to be physically realistic. The first of these is that probability must be conserved, by which we mean that the total probability of finding the electrons must remain constant. In Sec. III, the transitions were produced by Hermitian potentials, which, of course, conserve probability. In Sec. IV*a*, we presented a general model starting directly with transition operators, rather than potentials. Strict conservation of probability requires that we use Hermitian potentials. These, however, can only be used when the rates for the transitions $a\rightarrow b$ and $b\rightarrow a$ are equal. For finite temperatures these rates are not generally equal; indeed, they are related by the Boltzmann factor, as required by detailed balance.

For the transition operators, probability conservation may be expressed as the requirement

$$\langle\psi|\psi\rangle=\langle T\psi|T\psi\rangle=\langle\psi|T^\dagger T|\psi\rangle\ . \tag{54}$$

At first glance the $T_{\mu\nu}$ of Eq. (45) would appear to conserve probability: $T_{\mu\nu}$ acting on an eigenfunction of $\mathcal{H}_e$ gives back an eigenfunction of $\mathcal{H}_e$, so that as long as ψ is restricted to be an eigenfunction of $\mathcal{H}_e$, Eq. (54) will hold for the $T_{\mu\nu}$. In the case of "diagonal" hyperfine interactions (those which do not mix the states of $\mathcal{H}_e$) one is concerned only with eigenfunctions of $\mathcal{H}_e$, so that probability is conserved. When the hyperfine interactions mix the electronic states, however, $T_{\mu\nu}$ no longer satisfies Eq. (54). For an arbitrary wave function ψ, Eq. (54) requires

$$T^\dagger T=1. \tag{55}$$

These apparent difficulties are overcome by requiring only an *average* conservation of probability, wherein Eqs. (54) and (55) hold when an average over the random variables is made:

$$(T^\dagger T)_{\text{av}}=\ \mathcal{T}_{\text{av}}\cdot 1=1\ , \tag{56}$$

or, in matrix element form,

$$\sum_{\mu'}(\mu\,\nu|\ \mathcal{T}_{\text{av}}|\mu'\mu')=\delta_{\mu\nu}\,. \tag{57}$$

The corresponding relation for $\mathcal{W}$ is

$$\sum_{\mu'}(\mu\,\nu|\mathcal{W}|\mu'\mu')=0\ . \tag{58}$$

From Eqs. (49) and (52), it may be seen that our model conserves probability on the average. In fact, the same is true of each of the $\mathcal{T}_{\mu\nu}$ when averaged over θ.

The other requirement is that on the average the transitions must preserve thermal equilibrium. Following Landau and Lifshitz,[26] for example, the density matrices, ρ and ρ', before and after a particular transition are related by

$$\rho'=T\rho T^\dagger\ . \tag{59}$$

Averaging over the stochastic variables, Eq. (59) becomes, in matrix element form,

$$\rho'_{\nu'\mu'}=\sum_{\mu,\nu}\rho_{\nu\mu}(\mu\,\nu|\mathcal{T}_{\text{av}}|\mu'\nu'). \tag{60}$$

Thermal equilibrium requires that $\rho'=\rho$ in Eq. (60). For $\mathcal{W}=\lambda(\mathcal{T}_{\text{av}}-1)$ this condition becomes

$$\sum_{\mu,\nu}\rho_{\nu\mu}(\mu\,\nu|\mathcal{W}|\mu'\nu')=0\ \ . \tag{61}$$

In our general model of relaxation we have essentially neglected nuclear alignment so that the density matrix is diagonal for the electronic states, $\rho_{\nu\mu}=p_\mu\,\delta_{\mu\nu}$. Using the matrix elements of Eq. (52), we see that the model preserves equilibrium if detailed balance is required,

$$p_\nu\,W_{\nu\mu}=p_\mu\,W_{\mu\nu}\,. \tag{62}$$

In the model of relaxation operators proposed in Sec. IV*a*, the transition rates $W_{\mu\nu}$ were built into the model from the beginning. In other models, such as the one with isotropic $\vec{h}$ discussed in Sec. III*a*, it is necessary to determine the transition rates after the model is built. Using Eq. (60) we may obtain the transition rates resulting from any model of relaxation operators: Let us suppose that the system is in the state $|1\rangle$ immediately before a transition. Then ρ in Eq. (60) is given by $\rho_{11}=1$, all other $\rho_{\nu\mu}=0$. Immediately after an "average" transition the density matrix is given by $\rho'_{\nu'\mu'}=(11|\mathcal{T}_{\text{av}}|\mu'\nu')$. For reasons discussed earlier, the matrix elements with $\mu'\neq\nu'$ should vanish. The transition rate is then obtained by multiplying by λ, the pulse rate. Using $\mathcal{W}=\lambda(\mathcal{T}_{\text{av}}-1)$ we obtain the result that the rate $W_{\mu\nu}$ for the transition $|\mu\rangle$ to $|\nu\rangle$ is

$$W_{\mu\nu}=(\mu\,\mu|\mathcal{W}|\nu\nu)\ . \tag{63}$$

By similar arguments, it can be shown that $-(\mu\mu|\mathcal{W}|\,\mu\mu)$ is the lifetime of the state $|\mu\rangle$. By requiring that Eqs. (58), (61), and (63) are satisfied, we are assured of having a physically realistic model for the relaxation operators.

V. CONCLUSION

The treatment of line shapes given in this paper extends previous results to situations in which the effects of surroudings on an emitter can not be approximated by time-varying external fields. The results obtained here are formally similar to those found in *ab initio* calculations of line shape. In the latter treatments a number of approximations must be made whose physical content is obscure. The stochastic theory thus gives some insight into the nature of these approximations. In our central result, Eq. (24), a relaxation superoperator $\mathcal{W}$ appears. This superoperator must, in a stochastic treatment, be treated as input information, to be specified as part of the physical circumstances of the problem. In an *ab initio* calculation this superoperator is in principle determined by the Hamiltonian, but in practice[8] the matrix elements are specified.

In a future paper we will discuss the application of our formalism to a number of specific cases in Mössbauer spectra. It is clear, however, that the theory is of utility in analyzing perturbed angular-correlation spectra and line shapes in other branches of spectroscopy as well.

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[1] M. Blume, Phys. Rev. Letters 14, 96 (1965).

[2] F. van der Woude and A. J. Dekker, Phys. Status Solidi 9, 775 (1965).

[3] H. Wegener, Z. Physik 186, 498 (1965).

[4] H. H. Wickman, M. P. Klein, and D. A. Shirley, Phys. Rev. 152, 345 (1966).

[5] M. Blume and J. A. Tjon, Phys. Rev. 165, 446 (1968); J. A. Tjon and M. Blume, *ibid.* 165, 456 (1968).

[6] A. M. Afanas'ev and Yu. Kagan, Zh. Eksperim. i Teor. Fiz 45, 1660 (1963) [Soviet Phys. JETP 18, 1139 (1964)].

[7] E. Bradford and W. Marshall, Proc. Phys. Soc. (London) 87, 731 (1966).

[8] H. Gabriel, J. Bosse, and K. Rander, Phys. Status Solidi 27, 301 (1968).

[9] L. L. Hirst, J. Phys. Chem. Solids 31, 655 (1970).

[10] H. Schwegler (unpublished).

[11] P. W. Anderson, J. Phys. Soc. Japan 9, 316 (1954).

[12] R. Kubo, in *Fluctuation, Relaxation and Resonance in Magnetic Systems*, edited by D. ter Haar (Oliver and Boyd, Edinburgh, Scotland, 1962), p. 23.

[13] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. P., London, England, 1961).

[14] A. Abragam and R. V. Pound, Phys. Rev. 92, 943 (1953).

[15] R. M. Steffen and H. Frauenfelder, in *Perturbed Angular Correlations* (North-Holland, Amsterdam, 1964).

[16] M. Blume, in *Hyperfine Structure and Nuclear Radiations* (North-Holland, Amsterdam, 1968), p. 911.

[17] A preliminary report on this work was given earlier by M. J. Clauser and M. Blume, Bull. Am. Phys. Soc. 15, 260 (1970).

[18] M. Blume, Phys. Rev. 174, 351 (1968).

[19] M. C. Wang and G. Uhlenbeck, Rev. Mod. Phys. 17, 323 (1945).

[20] R. L. Stratonovich, *Topics in the Theory of Random Noise* (Gordon and Breach, New York, 1963), Vol. I, p. 143.

[21] R. Zwanzig, J. Chem. Phys. 33, 1338 (1960); Physica 30, 1109 (1964).

[22] In particular, compare Table I of Ref. 18 with our Table II. By specializing both examples to treat the same case, the similarities of both treatments may be seen.

[23] Cf. Eq. (16) of Ref. 11.

[24] M. J. Clauser and R. L. Mössbauer, Phys. Rev. 178, 559 (1969).

[25] We emphasize that $T_{\mu\nu}$ denotes an operator, *not* the matrix element $\langle \mu | T | \nu \rangle$.

[26] L. D. Landau and E. Lifshitz, *Statistical Physics* (Pergamon, New York, 1958), p.20.

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Mössbauer Effect of Sn^{119} in Alpha-Brass and Related Alloy Systems*†

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The Mössbauer effect of Sn^{119} has been measured in alloys of the α-brass type: Cu-Sn, Cu-Sn-Zn, and Cu-Sn-Al. The isomer shift of the tin resonance is a function of the electron-to-atom ratio of the alloy, and is insensitive to the valence of the solute. The change in isomer shift with electron-to-atom ratio is rather small, but shows effects similar to those observed by soft-x-ray spectroscopy in α-brass, and by positron annihilation in α-copper-aluminum alloys.

I. INTRODUCTION

For many years, considerable effort has been expended to understand better the changes in the electronic densities of states upon alloying the noble metals with polyvalent metals. Conflicting experimental results, and disagreement between experiment and theory, have left the answer to the question still in doubt. The experimental work to date for the whole range of the α phase, rather than for only very dilute alloys, has been largely low-temperature specific-heat studies, and optical-absorption measurements,[1-7] with a limited amount of work using soft-x-ray spectroscopy[8] and positron annihilation.[9] Unfortunately, many of the