ing splitting at $T=0$ using the results of Fig. 6 and by taking into account intermolecular broadening [Eq. (8)], it was found that $\delta\nu(T=0)$ decreases by $(2.5\pm1.0)\%$, which is slightly larger than that predicted from Eqs. (12) and (7), namely, 1.4% over the orthoconcentration range mentioned above.

VI. CONCLUSION

The rotational ordering in the cubic phase, as investigated by NMR, seems qualitatively understood, but the high value of the critical orthoconcentration deserves further theoretical research. The study of the rotational angular momentum $\langle J_Z^2\rangle$ in the cubic phase near the ordering region may be complicated by the coexistence of both hcp and cubic phases over an extended temperature range. In solid D_2, it has been shown[12] that the cubic phase can be stabilized up to higher temperatures after repeated thermal cycling through the crystalline transition. Hence a study of NMR in the cubic phase of deuterium may be promising and may avoid the difficulty of phase coexistence and also of the large ortho-para conversion one encounters in solid H_2. Such a study will be undertaken in this laboratory in the near future.

Several phenomena in H_2 ortho-para solutions are yet to be understood. One of them is that the NMR doublet, expected at intermediate orthoconcentrations at temperatures where the orientation of the $J=1$ molecules is almost complete, has not been observed. More experiments are in progress in a different cryostat to study the line shape at $c\approx0.55$ at temperatures below 0.4°K with the hope of observing this doublet.

We also hope that the information obtained so far will stimulate more theoretical research on the rotational ordering of ortho-para solutions.

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Spin-Lattice Linewidths for EPR in Multilevel Systems

L. L. Hirst
Physik-Department, Technische Hochschule München, München, Germany

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The magnetic relaxation of an isolated moment via contact coupling to conduction-electron spins is considered for the case where the splitting scheme of the moment shows an effective-spin doublet plus other levels. Relaxation transitions proceeding via these other levels are considered, and it is shown that they produce significant deviations from the proportional-to-temperature linewidth obtained by considering only direct transitions within the doublet. Some results for phonon processes are also given.

I. INTRODUCTION

In treating paramagnetic resonance transitions among a few low-lying levels of an isolated magnetic ion, it is often convenient to consider these levels as being described by an "effective spin," while the remaining levels can be for some purposes ignored. However, matrix elements of the dynamic spin-lattice Hamiltonian connecting the effective spin levels to the other levels correspond to processes in which "effective spins" are not conserved in number but are destroyed and recreated. It is clear that such processes can contribute to the relaxation of the effective spin system and cannot, in general, be neglected. A well-known example is the so-called "two-step" phonon-induced longitudinal relaxation of rare-earth ions.[1,2]

In the present paper, we consider relaxation by conduction-electron spin flip of crystal-field-split moments in dilute rare-earth alloys, which have recently become of considerable interest for electron-paramagnetic-resonance (EPR) experiments.[3,4] We will show that in such systems the other-level transitions can lead to significant deviations from the proportional-to-temperature linewidth which is conventionally considered to be the "earmark" of relaxation via conduction-electron spins.[5]

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[12]

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[4] C. R. Burr and R. Orbach, Phys. Rev. Letters **19**, 1133 (1967).

[5] A bottleneck in conduction-electron spin relaxation can also alter the temperature dependence of the linewidth [see, for example, A. J. Heeger, A. C. Gossard, and J. H. Wernick, J. Appl. Phys. **38**, 1251 (1967)]. These effects need not be considered here since the g value of a crystal-field doublet is normally quite different from two.

Since it is the linewidth which is measured in practice in the alloy systems, we are primarily interested in calculating the transverse Bloch relaxation time T_2. For this purpose we employ the Redfield formalism,[6] which is essentially a generalization of second-order time-dependent perturbation theory in which the rates of change of off-diagonal elements of the density matrix are obtained, and in which relaxation contributions via various channels are systematically kept track of. Use of this formalism eliminates a great deal of bookkeeping labor in a calculation of the present kind, and permits the formula for T_2 (and for T_1 as well) to be written almost by inspection for any reasonably simple spin-lattice interaction. The calculation of T_2 in Sec. II will be done for the specific case of dilute rare-earth alloys, but the generalization to other spin-lattice interactions is obvious and will be briefly alluded to in Sec. IV.

II. DERIVATION OF RELAXATION TIME

We assume an exchange coupling

$$\sum -2J_{s-f}(\Lambda-1)\mathbf{J}\cdot\mathbf{S}\delta(\mathbf{R}_J-\mathbf{r}_s)$$

to the conduction electrons, initially supposed to be a free noninteracting electron gas in thermal equilibrium. Here Λ is the Landé factor and $\mathbf{J}$ is the total angular momentum of the corresponding free ion. The magnetic properties of the localized moments can be described by a $(2J+1)\times(2J+1)$ density matrix ρ, whose motion is given in terms of a relaxation matrix $R_{\alpha\alpha'\beta\beta'}$ involving the spectral density of the spin-lattice forces.[6] We suppose an effective spin doublet, with a and b denoting the two levels between which resonance is observed. We assume that no other pair of levels has the same energy separation E_b-E_a; such degeneracy is expected only by accident, and it would complicate the analysis without introducing qualitatively new effects. The dynamic magnetic response near the resonance frequency may then be written as $-\sum_{i,j}\mu_B\Lambda J_{ij}\rho_{ji}$, where the summations are taken over only a and b instead of all $2J+1$ levels, which just corresponds to the usual truncation of unwanted satellite lines. With this nondegeneracy assumption, the Redfield equations give a simple damped exponential for ρ_{ab}, and consequently the transverse magnetization satisfies the transverse Bloch equation with

$$\begin{aligned}1/T_2&=-R_{baba}\\&=\sum_q\Big[-J_{bb}{}^{(q)}J_{aa}{}^{(q)}2j(0)+\sum_r J_{ar}{}^{(q)}J_{ra}{}^{(q)}j(r-a)\\&\qquad+\sum_r J_{br}{}^{(q)}J_{rb}{}^{(q)}j(r-b)\Big].\qquad(1)\end{aligned}$$

Here the q sum is over x, y, z; the r sum is over the $2J+1$ levels; and $j(\alpha-\beta)$ is the spectral density of conduction-electron spin flips at frequency $(E_\alpha-E_\beta)/\hbar$, which is evaluated as

$$j(\omega)=\tfrac{1}{2}\pi[2(\Lambda-1)J_{s-f}N_E{}^{(1)}]^2\omega/(e^{\omega/kT}-1)\,,\qquad(2)$$

where $N_E{}^{(1)}$ is the conduction-electron density of states at the fermi surface for one spin orientation.

Following Moriya,[7] one may consider additional effects arising from exchange interactions within the conduction-electron system. A solvable model is obtained by using an interaction of δ-function form. The result is simply an enhancement factor, $K(\alpha)/(1-\alpha)^2$ in Moriya's notation, which multiplies the spectral density $j(\omega)$ and is independent of frequency and temperature provided these are small compared to the Fermi energy, as will be the case in practice. Discussion and a tabulation of $K(\alpha)$ are given in Ref. 7.

III. DISCUSSION FOR EPR IN DILUTE ALLOYS

If we first consider only the terms a and b of the r sum of Eq. (1), we obtain

$$\begin{aligned}1/T_2=\tfrac{1}{2}\pi\{2[(\Lambda-1)/\Lambda]J_{s-f}N_E{}^{(1)}\}^2\{g_z{}^2kT\\+\tfrac{1}{4}\delta\coth[\delta/2kT](g_x{}^2+g_y{}^2)\}K(\alpha)/(1-\alpha)^2.\end{aligned}$$

This is just the usual Heitler-Teller-Overhauser[8] result for a spin doublet, but generalized to take into account the finite splitting $\delta=E_b-E_a=g_z\mu_BH$ as well as possible g anisotropy (we have taken H along a principal axis of the g tensor for simplicity). The finite-splitting correction has the result that whereas the quasistatic broadening represented by the term in $j(0)$ in Eq. (1) is proportional to T at all temperatures T, the dynamic broadening represented by $j(a-b)$ approaches a finite low-T limit ascribable to zero-point motion.[9] The contributions in Eq. (1) from the r sum for $r\neq a,b$ represent the transitions via the other crystal-field levels; as is to be expected from general principles, each r has a negligible effect so long as $E_r-E_b\gg kT$, gets switched on exponentially with increasing temperature, and finally gives a contribution proportional to T for $kT\gg|E_r-E_b|$. If $E_b-E_r\gg kT$ (when a and b are not the lowest levels of the system), a constant linewidth contribution results. In the limit kT large compared to all level spacings we obtain

$$\begin{aligned}1/T_2=\tfrac{1}{2}\pi\{2[(\Lambda-1)/\Lambda]J_{s-f}N_E{}^{(1)}\}^2\\\times[\tfrac{1}{2}g_z{}^2+2\Lambda^2J(J+1)][K(\alpha)/(1-\alpha)^2]kT.\end{aligned}$$

Increasing the temperature will have strong effects on the intensities of the various lines in addition to its effect on their widths, which will make it impossible in practice to observe the high-temperature limit;

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[6] A. G. Redfield, IBM J. Res. Develop. **1**, 19 (1957); see, also, C. P. Slichter, *Principles of Magnetic Resonance,* (Harper & Row, Publishers Inc., New York, 1963).

[7] T. Moriya, J. Phys. Soc. Japan **18**, 516 (1963). See also Ref. 4.

[8] W. Heitler and E. Teller, Proc. Roy. Soc. (London) **A155**, 637 (1963); J. Korringa, Physica **16**, 601 (1950); A. Overhauser, Phys. Rev. **89**, 689 (1953).

[9] This result has been independently obtained by R. Orbach and H. J. Spencer, Phys. Letters **26A**, 457 (1968). Analogous results for phonon-relaxed ions have given in Ref. 2, and for nuclear relaxation by W. D. Brewer, D. A. Shirley, and J. E. Templeton, Phys. Letters **27A**, 81 (1968).

nevertheless significant deviations from the effective-spin-only linewidth should be observable when there exists a crystal-field level within 20°K of a ground doublet.[10] This is of practical importance since a principal aim of paramagnetic resonance experiments with dilute rare-earth alloys has been to deduce values of $s-f$ exchange coupling from the temperature dependence of the linewidth. In the case of Er*Ag*, Er*Au*, and Yb*Au*, analysis of susceptibility measurements shows that the remaining crystal-field levels lie too high to give a linewidth contribution,[3] but for other systems, such as Er*Mg*, the level scheme has not yet been established.[4] Low-lying levels have been found in other systems where EPR is absent.[3]

IV. FURTHER APPLICATIONS

Although up to the present the experimental emphasis in studies of the phonon-dominated relaxation of rare-earth ions in insulators has been on longitudinal relaxation, linewidth studies are also a potentially useful measure of phonon interactions at temperatures above the helium range. Accordingly, we remark that the $1/T_2$ contribution from single-phonon other-level transitions can be written immediately with the present approach as

$$\frac{1}{T_2}=-R_{baba}=\sum_{j,\alpha}\frac{3\omega_{j\alpha}{}^3}{4\pi\hbar(e^{\omega_{j\alpha}/kT}-1)\rho v^5}\sum_{m,n}|\langle j|v_n{}^m|\alpha\rangle|^2,$$

where $\omega_{j\alpha}$ denotes $(E_j-E_\alpha)/\hbar$, $v_n{}^m$ are operator equivalents for the dynamic crystal-field couplings, the α sum is over a and b, and the j sum is over levels excluding a and b. (The terms for $j=a,b$ give the direct-transition contribution.) The first factor represents the spectral density for single-phonon processes in the Debye model, and it is understood that all terms with $|\hbar\omega_{j\alpha}|>k\theta_D$ are excluded from the sums. This result, like all results of the present paper, holds equally well if a and b are not the lowest levels of the system. In the limit usually considered, $E_j-E_a\gg kT\gg|E_b-E_a|$, it reduces to the standard result[1] for $1/T_1$.

In fact, the equality of contributions to $1/T_1$ and $1/T_2$ from other-level processes in dilute systems is quite general, except that T_2 is always well-defined while T_1 is sometimes not. (We still assume the spacing E_b-E_a to be unique.) To see this, we consider briefly the derivation of T_1 from the diagonal elements of the Redfield equations, or rather their equivalents, the rate equations. These can be written

$$\frac{dn_\alpha}{dt}=\sum_\beta(-W_{\alpha\beta}n_\alpha+W_{\beta\alpha}n_\beta),$$

where n_α is the population of level α minus its thermal equilibrium value and $W_{\alpha\beta}=R_{\beta\beta\alpha\alpha}$ are the lattice-induced transition rates. Using $\sum n_\alpha=0$ and defining $n\equiv n_a-n_b$, we eliminate n_a and n_b to obtain

$$\frac{dn}{dt}=-[W_{ab}+W_{ba}+\tfrac{1}{2}\sum_j(W_{aj}+W_{bj})]n+\sum_j\{[W_{ab}$$
$$-W_{ba}+W_{ja}-W_{jb}+\tfrac{1}{2}\sum_{j'}(W_{aj'}-W_{bj'})]n_j\},$$

where the j sums exclude levels a and b. There are $2J-1$ further equations and, in general, the population time dependence involves $2J$ modes with different characteristic times, so that a well-defined T_1 for the effective spin doublet does not exist. However, n will have the well-defined relaxation rate $1/T_1=W_{ab}-W_{ba}+\frac{1}{2}\sum_j(W_{aj}+W_{bj})$ whenever the coefficients of n_j in the above equation approach zero. In particular, this will be true for $E_b-E_a\ll kT$ if a and b are a Kramers doublet of the usual sort, excluding accidental degeneracy of levels of different symmetry class or Zeeman-induced crossover degeneracy. From the definition of the R matrix,[6] which will not be written out in full, it is easily verified that the contributions to $1/T_1$ from processes via the levels $J\neq a,b$ equal their contributions to $1/T_2=-R_{baba}$. Note that isotropy of the system is not necessary.

For ordinary Heitler-Teller-Overhauser relaxation, provided that $|E_b-E_a|\ll kT$ and g is isotropic, one has the well-known relation $1/T_2=1/T_2{}^*+1/2T_1=1/T_1$, where $1/T_2{}^*$ represents the quasistatic broadening corresponding to the spectral density at zero frequency. In the case of broadening from transitions via other levels, the spectral density at zero frequency is not involved and there can be no quasistatic contribution, yet we still find $1/T_2=1/T_1$. This can be interpreted in the following heuristic way: When a spin-lattice process works directly between members of a doublet, each "flip", considered as transverse relaxation, randomizes the transverse magnetization to zero; considered as longitudinal relaxation, it reverses the magnetization and has doubled effect, so $1/T_1\approx 2W_{ba}$, where $W_{ba}\approx W_{ab}$ is the flip probability, whereas the dynamic "flip" contribution to $1/T_2$ is $W_{ba}=1/(2T_1)$. For indirect relaxation via another level r, each transition $b\rightarrow r$ may be considered to fully relax the transverse magnetization; considered as longitudinal relaxation, it produces on the average only one unit change in magnetization, since there is now a 50% probability the spin will fall back into level b rather than a; hence,

$$1/T_1\approx\sum_r W_{br}\approx 1/T_2.$$

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[10] Although absolute estimates of relaxation rates from phonon processes are notoriously inaccurate, we believe that they should not be important below about 40°K in these alloys. Thus the only question is whether the other-level processes can come into play before relaxation via conduction-electron-spin mechanism itself renders the resonance unobservable. This typically occurs at 20°K with good apparatus sensitivity (Ref. 3).